www.schema-ocean.eu

Grant Agreement no: 614002

SCHeMA: INTEGRATED IN SITU CHEMICAL MAPPING PROBE

Collaborative project
FP7-OCEAN.2013-2: Innovative multifunctional sensors for in situ monitoring of marine environment and related maritime activities

Final Publishable Summary Report

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1 Executive summary

SCHeMA has successfully developed an array of miniaturized sensors 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 sensors were assembled into miniature low power consumption probes based on advanced green and enOcean technology.

A Network Controller, dedicated wired/wireless communication interfaces, and web-based front-end system were also developed. These devices enable plug-and-play integration of a specific suite of sensing probes as well as data open access in compliance with Global Earth Observation System of Systems Common Infrastructure (GCI) recommendations and the international Open Geospatial Consortium - Sensor Web Enablement (OGC-SWE) standards.

Interfacing of the SCHeMA submersible devices and a commercially available multiparameter probe provides a fully integrated autonomous marine water quality observatory system with capability for high-resolution, simultaneous monitoring of: the bioavailable fraction of a range of trace metals (arsenite, mercury, cadmium, lead, copper, zinc); nutrients (nitrate, nitrite); species relevant to the carbon cycle (carbonate, calcium, pH); toxin producing algae; and master variables (temperature, pH, dissolved oxygen, conductivity, salinity, turbidity, chlorophyll *a*, PAR, phycocyanin, phycoerythrin).

The SCHeMA submersible individual sensing modules and autonomous marine water quality observatory system were successfully field evaluated, validated and applied in Atlantic and Mediterranean coastal areas (six field campaigns of one week and one three-month field campaign). Their capabilities, when operating in real conditions, were demonstrated to potential end-users as part of several field demonstrations.

The field application campaigns of the SCHeMA system in European coastal key areas provide a unique set of data and new insights into various biogeochemical processes observed for the first time at such high spatial and temporal resolution. These original results will be disseminated to the scientific communities via publications in peer reviewed scientific journals. Overall, the complete integration of the rich SCHeMA data bank will help to (i) improve sampling and measurement strategies for both environmental research and water quality monitoring, (ii) better understand aquatic ecosystem functioning, (iii) predict the impact of aquatic organism's exposure and (iv) ultimately, give clues for sustainable management based on new scientific knowledge.

Dissemination activities to public and the scientific community as well as to potential end-users and stakeholders include to date: 43 published peer reviewed papers; 40 oral presentations and 44 posters presented at 53 different regional, national and international conferences/meetings; participation in 9 business exhibitions and 7 meetings with end-users; organization of two conference sessions on the development of innovative sensors for in situ monitoring of aquatic systems as part of the international conferences ASLO 2015 (Aquatic Science Meeting) and IEBS 2015 (International Estuarine and Biogeochemistry Symposium); organization, in collaboration with several Ocean of Tomorrow projects, of two Workshops and Round-Tables on "What can the Ocean of Tomorrow projects do for you?" (Oceanology International 2016 Conference and Exhibition), and "Sensor and System Innovations for the Oceans of Tomorrow" (IEEE OCEAN 2017 Conference and Exhibition); a one-week Summer School at the Plentzia Marine Station (Spain) in June 2016; the publicly accessible SCHeMA Website (www-schema-ocean.eu) providing access to the informational factsheets, brochures and videos, the Web data information portal, copies of public Deliverables and peer-reviewed published scientific papers (special Clause 39), when they will be available.

2 SCHeMA project context and objectives

SCHeMA (www.schema-ocean.eu) is a multi-disciplinary collaborative project aiming to develop a network of submersible chemical probes that is flexible, modular, web-accessible, and refines the state of the art by incorporating different sensors to map a range of chemical and biological hazardous compounds in marine ecosystems (Fig. 1).

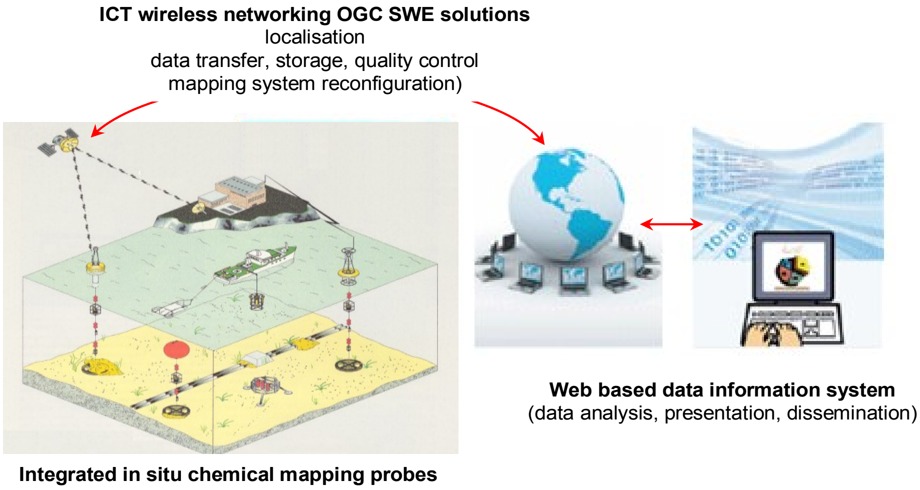

Figure1: *Illustration of the SCHeMA vision and overall objective.*

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. Marine phytoplankton provides 50% of the oxygen on earth and plays a key role in the carbon cycle, being one of the links in the chain that contributes to the maintenance of life on Earth. The marine ecosystems are also vital to the livelihoods and food security of billions of people around the world, and to the economic prosperity of most countries. Today, the European 'blue' economy represents roughly 5.4 million jobs and generates a gross added value of almost € 500 billion a year[1]. At the global level, the World's economy output is estimated at US$ 3 trillion per year. As land-based resources become more scarce, the ocean resources have become more attractive than ever. The exploitation of marine sectors is expected to expand drastically in the coming years. Forecast for most of these sectors predict doubling or quadrupling in size by 2030, and others are forecast to increase by ten times their current size or more.[1] However, no economy can sustain its prosperity if the natural resource upon which this prosperity depends is systematically being degraded. Today, a number of marine ecosystems are underperforming due to the severe environmental stress from land- and marine-based human activities.

Marine environments are highly vulnerable and influenced by a wide diversity of anthropogenic and natural substances and organisms that may have adverse effects on the ecosystem equilibrium, on living resources and, ultimately, on human health. The majority of the pollution impact on coastal environment comes from land-based sources, but also some naturally present compounds generated in the marine environment (e.g. biotoxins, viruses) are highly relevant to coastal sustainable development. Identification of relevant types of hazards at the appropriate temporal and spatial scale is crucial to detect their sources and origin, to understand the processes governing their magnitude and

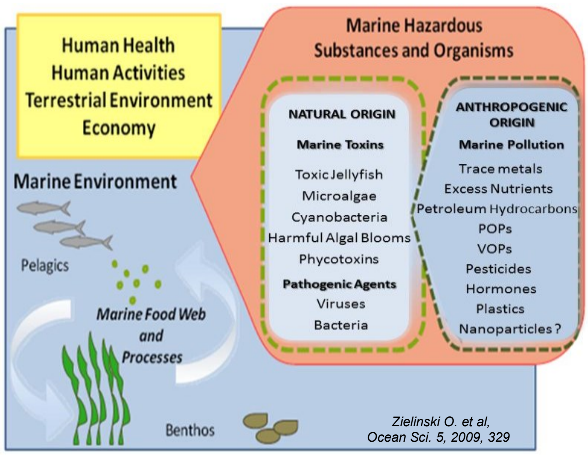

Figure 2: *Marine hazards of anthropogenic and natural origin and schematic of marine and terrestrial systems threatened by these harmful substances/organisms.*

distribution, and to ultimately evaluate and manage their risks and consequences preventing economic losses.

Most monitoring approaches are still based on costly field campaign sampling followed by analysis of the collected samples after return to the laboratory. This approach can only harvest data for a limited time-space window, resulting in the serious issue of insufficient data resolution. The need for greater resolution is motivated by the growing concerns about the health of the oceans and their capacity to continue to provide resources, goods and services as well as associated risks to the human health. There is also an increasing demand for real-time monitoring of the environmental status of marine water quality and the provision of early warning systems. Real-time detection of marine chemical and biological contaminants is of utmost importance for the sustainable management of the exploitation of the oceans resources.

Recent approaches therefore involve the use of submersible chemical sensor probes enabling real-time in situ monitoring of marine status and chemical and biological hazardous compounds. They are deployed from various facilities as part of a number of international, European and national ocean monitoring programs. Such autonomous sensing systems allow 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. Thus, reducing the cost for data acquisition is now a key priority for ocean management and for funding agencies in order to implement current European legislations and international initiatives like European Marine Strategy Framework Directive (MSFD), Global Ocean Observing System (GOOS) and the Global Earth Observation System of System (GEOSS).

In this context, current research and developments focus on more robust, easily usable, cost effective multifunctional sensing tools that provide reliable in-situ measurements of key parameters. These efforts address a broad range of issues including design and production of cost-effective sensors suitable for large-scale production, taking advantage of "new generation" technologies such as within the fields of miniaturization, communication, positioning systems, disposable technologies, and IT tools, software, energy storage and usage. It also turns out that sensing probes should be more compact, autonomous and multifunctional and deployable from several types of platforms like free floating devices or, buoys, platforms, or ships of opportunities including fishing vessels. Sensor probes by themselves are pointless if they cannot be installed on hosts capable of transmitting the information, or if the data they produce are not responding to the needs of society. Ease of installation and maintenance, data flow issues, storage, transmission, standardization and interoperability are therefore key features to their integration as part of an end-to-end system.

SCHeMA, funded as part of the Ocean of Tomorrow European initiative, aimed at contributing to enhance the capability of the Ocean observation system networks. Toward this aim, the SCHeMA's specific objectives were:

- ➢ Development of an array of novel chemical sensors for in-situ detection of the bioavailable fraction taking advantage of various innovative analytical solutions
- ➢ Incorporation of these novel sensors into miniature, low power consumption, multichannel probes based on Eco-Design-ISO/IEC standards and EnOcean technology as well as energy harvesting devices.
- ➢ Development of a Network Controller and dedicated wired/wireless communication interfaces and web-based front-end system compatible with EU standard requirements (OGC-SWE, INSPIRE, sensorML, SEIS) and programs (EMODnet, Copernicus Marine).

- Evaluation, optimization, validation and demonstration of the SCHeMA sensing tools and integrated system via short- and long-term field applications in contrasting Atlantic and Mediterranean coastal areas.

Target chemical and biological compounds are a range of trace metals, namely inorganic mercury (Hg) and arsenic (As), cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn); species relevant to the carbon cycle; nutrients; volatile organic compounds; potential harmful algae producing biotoxins. All of them may represent a severe threat to the normal functioning of the marine ecosystems and may have feedback (synergic) interaction as briefly discussed below.

Trace elements are ubiquitous and diverse components of the Earth's geochemistry, and play 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 CO_2 may also 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. All these changes may have significant impact on water quality, on solution and particle chemistry and on the dynamics of sediment as sinks/sources of chemical pollutants.

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, and methylation of Hg(II)). Increase in UV irradiation may increase photoreduction of natural inorganic colloids (e.g. Mn and Fe (oxy)-hydroxides) and alter the structure and reactivity of dissolved organic matter/organic compounds, thus decreasing the metal binding capacity and increasing metal bioavailability. 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 will provide rich data base enabling a more complete picture on their behavior and fate as well as a better prediction of their synergic impact on water quality, marine organisms and ultimately on society and economy. Such knowledge will ultimately support implementation of European Maritime Policies and development of knowledge-based protective policies for sustainable management.

3 SCHeMA main scientific and technical achievements

SCHeMA successfully developed an open and modular sensing solution for wireless, in situ, high resolution mapping of a range of anthropogenic and natural chemical compounds that may adversely affect marine ecosystems, living resources and human health. This has been achieved via the development of:

- electrochemical probes based on: i) solid-state ion-selective sensors for simultaneous measurements of species relevant to the carbon cycle (H^+, carbonate and Calcium); ii) solid state ion-selective membrane sensors, on-line desalination module and passibe acidification module allowing detection of nutrients (nitrate, nitrite);
- a compact multichannel voltammetric probe incorporating antifouling gel integrated microselectrode arrays (GIME) for simultaneous measurements of Hg(II), As(III), Cd(II), Pb(II), Cu(II), Zn(II);
- a miniaturized fully integrated optochemical multichannel probe for early detection and reliable identification of harmful algae species;
- an integrated optochemical mid-infrared sensor for the selective detection of a range of dissolved volatile organic constituents (VOCs);
- a network controller unit, based on Linux operating system, allowing the interfacing of the SCHeMA submersible chemical probes as well as other commercially available probes (e.g. CTD and multiparameter probes). The Network control unit is completed with a wireless WAN data transceiver (GPRS, UMTS) and a GPS module;
- a web-based system interface for accessing, interacting and configuring the SCHeMA network, controller and probes, according to the international OGC-SWE standards;
- a web interface for the management and access of data compatible with standard requirements such as EU Fisheries Data Collection Framework, the Marine Strategy Framework Directive, the INSPIRE directive, the GMES and GOOS/GEOSS initiatives.

The individual sensing probes and integrated system were optimized throughout their development via short field tests and inter-comparisons with data obtained from analysis of collected samples using established laboratory techniques. Field tests in selected coastal areas providing a huge panel of contrasting and challenging conditions (e.g. salinity gradient, high turbidity, strong current, primary production, industrial discharges, dredging) enabled to i) evaluate the sensor performance, robustness, stability, and reliability; ii) define their suitability for different applications and commercial production; and iii) demonstrate their monitoring capability and features to end-users and policy decision makers.

The results gathered during field application of the SCHeMA system at relevant selected coastal observation sites (protected marine areas, seafood production areas) provided new insights into high spatial and temporal resolutions data of various biogeochemical processes observed for the first time. The obtained results will help to (i) improve sampling and measurement strategies in both research and monitoring, (ii) better understand aquatic ecosystem functioning, (iii) predict the impact of aquatic organism’s exposure and (iv) ultimately give clues for sustainable management based on new scientific knowledge.

The sections below briefly summarize the SCHeMA state of the art developments and their analytical performances determined from field evaluation and cross-validation by measurements of collected samples using traditional laboratory techniques. The potentials of these innovative sensing devices as revealed by the results obtained from their field deployment in contrasting Atlantic and Mediterranean coastal areas are illustrated by selected examples.

3.1 SCHeMA state of the art development

3.1.1 Trace Metal Sensing Module: TMSM

The growing necessity to continuously monitor the level of trace metals reflects the critical roles they play in ecosystem functions. 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) (Fig.3).[2] Only some specific metal species are potentially available for bio-uptake (Fig.3).

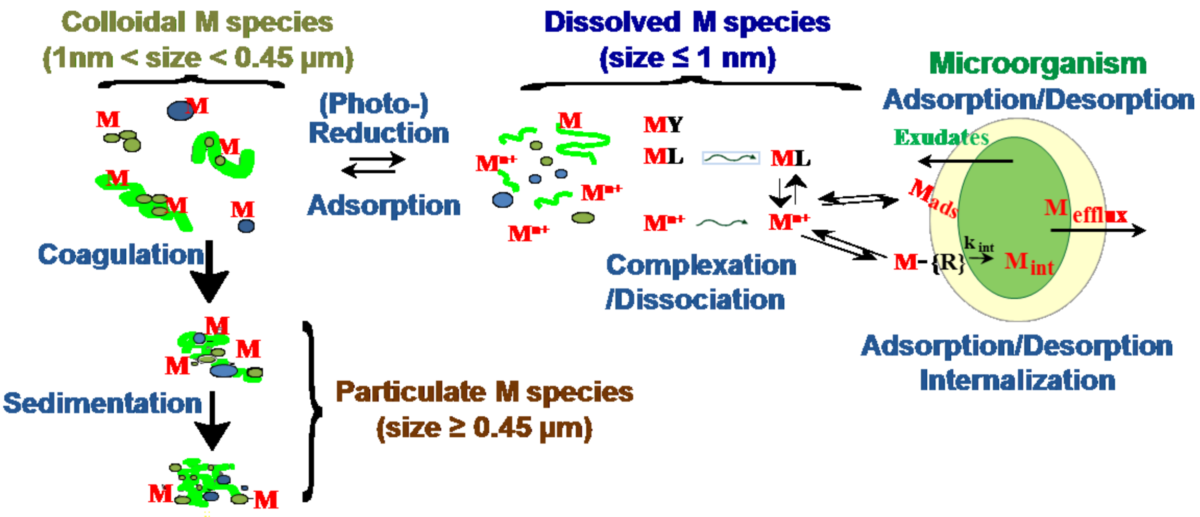

Figure 3: Schematic representation of the bio-geochemical processes regulating metal cycling in the aquatic systems[2].Once they enter the ecosystem, they are involved in bio-geochemical processes and distributed under various physical-chemical forms, including: particulate (> 0.45 µm), colloidal (1 nm – 0.45 µm) and dissolved metal species (≤ 1 nm). The latter includes the so-called dynamic metal species, defined as the sum of the free (hydrated)-metal ions (M^{n+}) and small labile and mobile inorganic and organic complexes (ML), that are potentially available for bio-uptake. Inorganic and organic colloidal/particulate materials play a key role in coagulation, sedimentation, and adsorption processes that influence trace metal residence time and transport from the water column to the sediments.

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[3] allowing direct, simultaneous measurements of the bioavailable fraction a range of trace metals (cadmium, lead, copper, zinc, arsenic, mercury) with sensitivity at the sub-nanomolar (ng/L) level. This is achieved using antifouling Gel-Integrated MicroElectrode arrays (GIME) interrogated by anodic stripping voltammetry (ASV) consisting in a reduction and pre-concentration step followed by the stripping and recording of the pre-concentrated metals.

GIME are based on newly designed on-chip 190 interconnected iridium microdisk arrays electrochemically plated with appropriate transducing elements and covered by an antifouling membrane[4]. When a GIME sensor is interrogated using ASV, the metal flux (or current) at the GIME during the electrochemical pre-concentration step selectively represents the so-called dynamic metal species, defined as the sum of free metal ions and small (< 4 nm) labile complexes (Fig. 2) and corresponding to the maximum concentration of metals potentially available for bio-uptake [2,5,6].

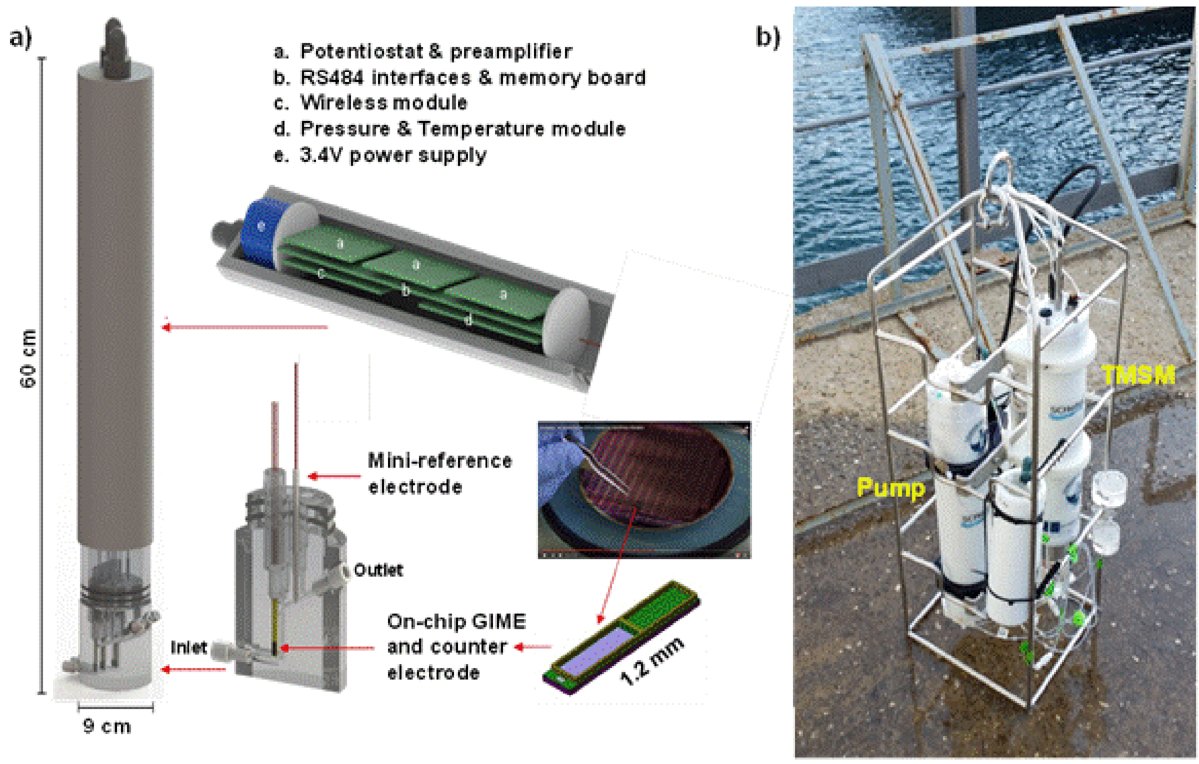

Figure 4: *a) Details of the key components of the TMSM. b) The TMSM individual probe ready for deployment.*

The entire system comprises an electronic housing, a three-channel flow-through cell and an external multi-channel pump (Fig. 4). 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.

3.1.2 Species relevant to the Carbon Cycle Sensing Module: CSM

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.

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[6] for pH, carbonate and calcium together with a reference electrode (Fig. 5a-c)[7]. 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 (Fig. 5d).

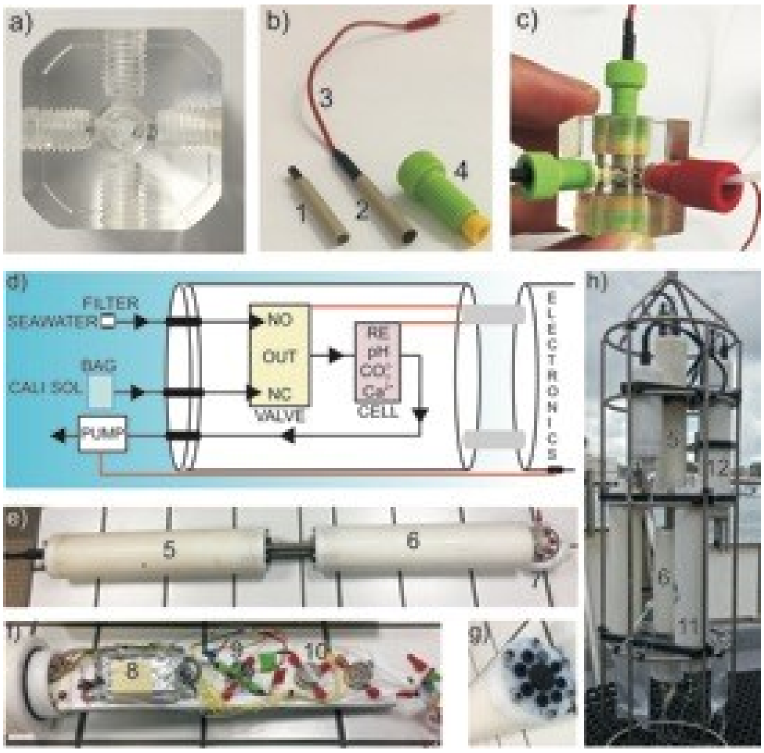

Figure 5. *(a) Flow cell. (b) Electrode set-up. (c) Detection cell. (d) Fluidics design. (e) View from outside of the CSM probe. (f) View from inside of the CSM probe. (g) Cap to close the submersible housing allowing the coupling between internal and external connections. (h) SCHeMA probe. 1: miniaturized 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 (Fig. 5d). The detection cell is placed together with the algae module into a water- and pressure-proof cylindrical housing (Fig. 5e-g), 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 into the titanium cage together with the rest of the SCHeMA probes (Fig. 5h).

3.1.3 Nutrients Sensors Module: NSM

The importance of the reliable long-term monitoring of nutrients in seawater lies in their crucial role in primary production and in their use as indicators of anthropogenic activities that disturb aquatic ecosystems. Currently established approaches for nutrient detection involve sample extraction using power intensive pumps, followed by analysis using expensive centralized laboratory instrumentation. Such 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. 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 hydroxide, prior to 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. 6). Thus, the desalination module reduces the amount of chloride in seawater down to millimolar levels and the acidification module subsequently lowers 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 one compensating any electrode drift.

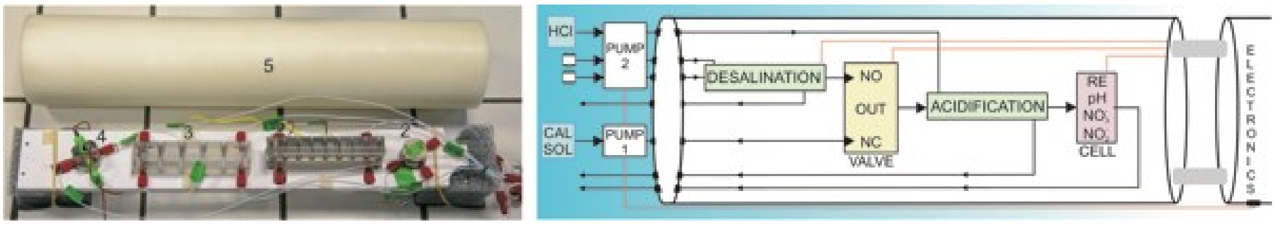

Figure 6: *NSM image and fluidics design. 1: desalination unit, 2: valve, 3: acidification unit, 4: potentiometric flow cell, 5: submersible housing.*

3.1.4 Miniaturized, multi-channel Algae Sensing Module: ASM

Harmful algal groups, which can produce several biotoxins, are of particular interest since they can kill fish, marine mammals and birds when they bloom. Further, algal blooms can cause green, brown or even red colorations of the surface water wherefore these harmful algal blooms are also known under the synonym red tides.[11] After accumulation among the food web, biotoxins can also lead to human disorders such as gastrointestinal, neurological and cardiovascular disturbances. Furthermore, cyanobacteria, formerly known as blue-green algae, constitute another phytoplankton group of interest. Cyanotoxins produced by this group of phytoplankton, can also lead to gastrointestinal disorders, liver disease, heart failure or even death after accumulation over the food chain.[12] In addition to health effects, harmful algal blooms constitute also a threat to the fish industry as well as to the tourism sector by having tremendous economic impacts.[13] Due to algal contamination, food products in the shell fish industry or even the shell fish itself gets poisoned and have to be disposed. The tourism sector suffers heavy losses since local authorities have to close beaches until the nature of the algae is determined. Moreover, the occurrence and intensity of (harmful) algal bloom has been increased over the last few years.[14] Therefore, in-situ detection and reliable identification of harmful algae species at an early stage are of steadily growing importance.

Phytoplankton absorbs light at very specific wavelengths and re-emits part of the absorbed energy as fluorescent light at longer wavelengths. Fluorescence can therefore be used as a 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 fluorimeters compare the fluorescence emitted upon excitation at two different wavelengths aiming at separating 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 coloured 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.

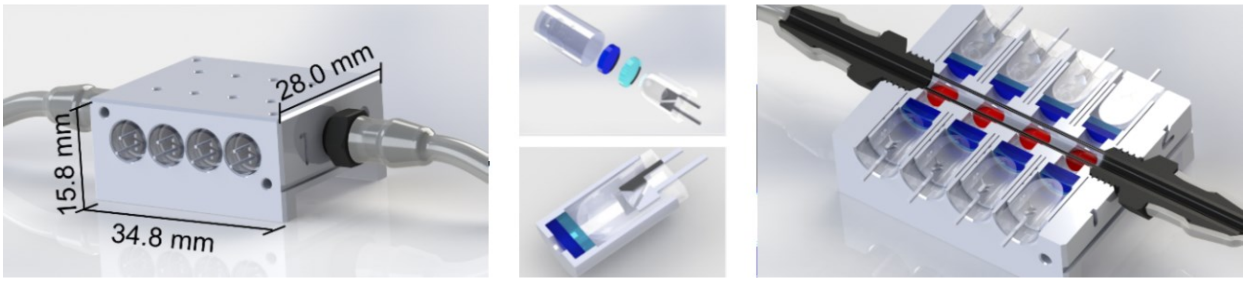

Figure 7: *Rendered picture of the algae detection module (left and right) and the modular LED modules used as excitation sources (middle). The picture on the right illustrates the arrangement of optical and electronic components. Photodetectors are aligned with 90° angle to the excitation source and covered with emission filters to minimize cross-talk between excitation and emission channels.*

In the detection module (Fig. 7), 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 centre. 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 are 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. 8).

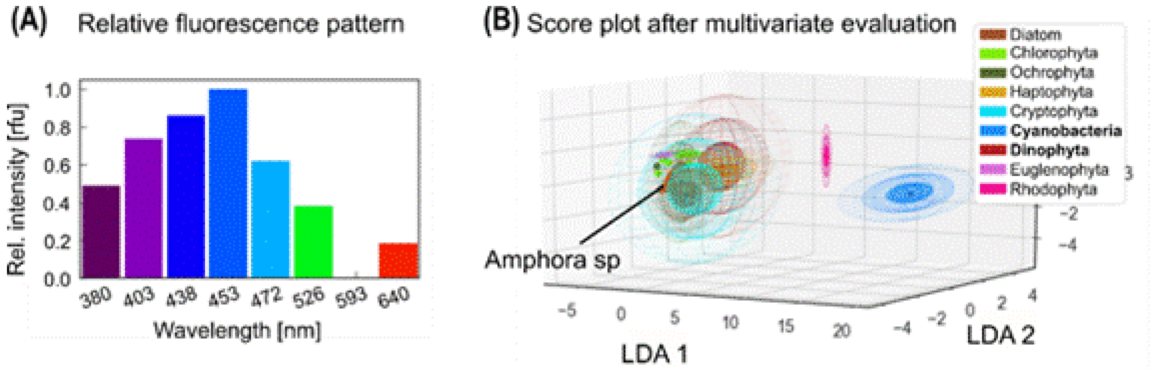

Figure 8: *(A) Relative fluorescence intensity upon excitation at different excitation wavelengths for amphora sp, a diatom sample. (B) Resulting score plot after applying the multivariate pattern recognition algorithm aiming at the comparison of the unknown sample to a set of reference data.*

To ensure the inter-comparability of the measurement results and for long-term stability reasons, another focus was the development of internal referencing strategies. Signal responses are highly dependent on various instrument parameters, e.g. spectral characteristics of the excitation sources and of the 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 during the project allowing now the direct comparison within the multi-channel detector system and between different measurement instruments.

In addition to this, work has also focused on developing a software interface for external and detailed data evaluation of individual cell events by the user itself. The software combines the acquired knowledge of standardization procedures and data evaluation methodologies using a multivariate pattern recognition algorithm. This facilitates now 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.

3.1.5 **Dissolved organic constituent sensing module: VOCs-SM**

Monitoring of hazardous pollutants such as volatile organic compounds (VOCs) of contaminated coastal areas, harbor areas, and industrial sites close to the marine environment is imperative for ensuring water quality since they are toxic, mutagenic, and carcinogenic, and pose a potential risk to humans, animals, and the marine ecosystem.

Conventionally, VOCs are detected *via* chromatographic methods. Since these methods are limited to laboratory use, real-time monitoring is not possible. Furthermore, such methods are time- and cost-extensive compared to sensing based on IR spectroscopy.

UULM, as part of the SCHeMA project, has developed a portable infrared fiber-optic evanescent wave/field spectroscopy (IR-FEWS) sensor enabling direct and real-time monitoring of VOCs in aqueous matrices (i.e., seawater) on-ship, on-shore, on-buoy, or for land-based sensing (Fig. 9). Each organic compound shows characteristic absorption peaks in the "fingerprint region" of the mid-IR spectral range enabling differentiation of the analytes. The silver halide (AgX) fiber sensing element (i.e., transducer) acting as an internal total reflection waveguide was located inside a µ-flow cell build by microechnology. The AgX waveguide has a flattened section actually transducing the absorption signatures of VOCs enriched from aqueous solution into a 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. Various coating materials were tested, especially, non-woven fiber mat provided by SCHeMA partner NanoMyP, were investigated besides the commonly used ethylene/propylene co-polymer (E/P-co polymer). However, the investigated membranes were highly hydrophobic resulting in no or only weak enrichment of analytes into the coating layer. Compared to the highly hydrophobic polymers from NanoMyP, E/P-co polymer shows enhanced enrichment properties resulting in increased absorption peaks. Therefore, E/P-co polymer was selected as most suitable coating membrane and is still used.

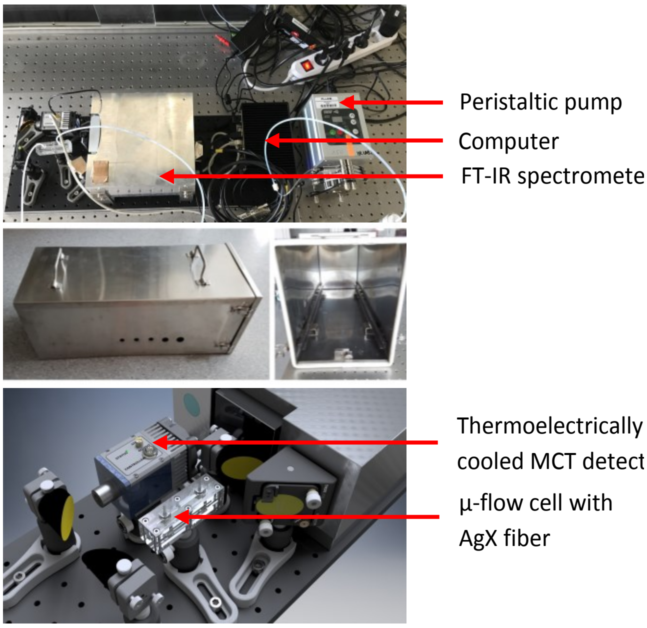

Figure 9: *(Top) IR-FEWS sensor system, (center) system housing, (bottom) rendered image of the developed optical sensor concept.*

For enabling field testing, a transportation box made from stainless steel was manufactured. The portable IR-FEWS sensor system was tested under real-world environmental conditions during a one-week field measurement campaign in Arcachon, France (May 12th to 20th 2017). Data evaluation can easily be performed with univariate methods (i.e., integration of the respective absorption feature). Up to ten analytes, spiked at various concentrations in freshly collected samples from different area, were successfully simultaneously detected with recovery close to 100%. Changes in salinity, turbidity, pH, and temperature during the field measurement campaign have been confirmed of little to no influence on the sensor performance providing a robust, accurate, and reliable detection of hazardous pollutants. However, the achieved detection limits are not within the concentration range (ppt, i.e., pg/L) in which VOCs are present in seawater. In the event of an oil tanker accident or tearing in a pipeline, the portable IR-FEWS sensor system of UULM can serve as a useful environmental threshold alarm system. The sensor system is easy to handle and only minor maintenance is required such as exchange of AgX fiber and PTFE tubes during extended application periods (approx. 6-12 monts).

3.1.6 SCHeMA integrated autonomous marine water quality observatory system

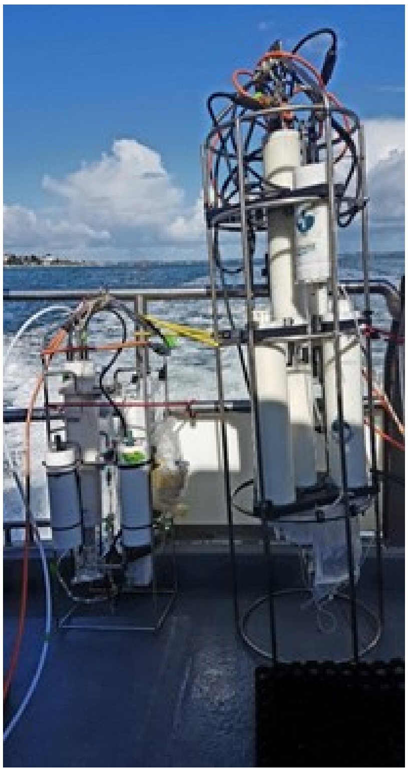

Figure 10: *(Left) TMSM and (right) Integrated system incorporating one TMSM, CSM, ASM and CTD.*

The SCHeMA's individual submersible sensing modules can be promptly prepared and deployed from multiple platforms. They can also be deployed simultaneously when connected to a Network Controller thus providing a fully integrated autonomous marine water quality observatory system (Fig. 10). The integrated system is a chain of devices, hardware and software modules, and communication interfaces that cover the entire process, from sensing module measurements to web application for data distribution and sharing.

The TMSM, CSM, NSM and ASM innovative sensors, micro-fluidics elements and hardware are incorporated in very compact submersible packages provided with advanced OGC-SWE interfaces. The CSM and ASM share the same electronics and are installed together in one submersible fluidic module. Advanced green technologies were adopted in any single element being part of the submersible probes, to reduce the power consumption and the environment impact as much as possible. The SCHeMA submersible chemical sensor probes can be promptly prepared and deployed from multiple platforms. The complementary acquisition of the master bio-physicochemical parameters (Temperature, Conductivity, Salinity, Pressure, pH, Dissolved Oxygen, Chlorophyll *a*, Turbidity, PAR, Phycocyanin and/or Phycoerytrin) is carried out by coupling an off-the-shelf IDRONAUT OCEAN SEVEN 316*Plus* CTD to the SCHeMA submersible probes. The Network Controller was specifically designed and developed in the frame of the project. This unit enables the plug-and-play interfacing of selected or all sensing modules, thus providing flexibility and modularity of the sensor network. The Network Controller is built on an open HW/SW platform based on LINUX operating system and a custom hardware, specifically developed in the frame of the project. The Network Controller was developed using up-to-date technologies, which guarantee the maximum performance allowing the interfacing of the SCHeMA submersible chemical probes as well as other commercially available probes (e.g. CTD and multiparameter probes). The network control unit is completed with a wireless WAN data transceiver (GPRS, UMTS) and an interface compliant with EU standards (OGC SWE, SensorML, INSPIRE) and compatible with EU infrastructures (e.g., EMODnet, SEIS).

An ad-hoc ICT wireless networking solution allows remote control of data transfer, system reconfiguration (Sensor Panning Service – SPS) and errors management (Sensor Alert Service – SAS) according to the OGC standard. The land station provides a web-based system interface for accessing sensor information and measured sensor observation. This system is implemented as a SOS (Sensor Observation Service) system thus providing standard interoperability and access to measured sensor observations – through Observation and Measurements (O&M) standard – as well as sensor descriptions – encoded in Sensor Model Language (SensorML). A more detailed description of the web-based observation and information systems are reported in the section 3.1.7 below.

3.1.7 **Web-based observation data information system**

Access to marine data is of crucial importance for marine research and a key issue for various studies, from climate change prediction to off shore engineering. Sharing observed data benefits everyone: changes in one country's waters affect those of its neighbors and national data alone are not sufficient to improve our knowledge on the sea as a European and global system connected by shifting winds, seasonal currents etc. In this context, the SCHeMA data portal infrastructure provides a series of interface features allowing users to discover and access all the data and metadata registered by the SCHeMA integrated mapping probes in a standard way compliant with major European Directives and recommendations for data interoperability.

3.1.7.1 SCHeMA Infrastructure Architecture.

The SCHeMA system is a complex chain of devices, hardware and software modules, and communication interfaces (Fig. 11). Where pertinent and possible, the protocols were designed to operate both in wired and wireless data transmission contexts. It is composed of four main modules:

- SCHeMA M2M Interface: web service interface that implements the OGC-SOS standard (v.1.0) that enables
  - Data producers (the SCHeMA submersible probes) to register themselves to the system and to send its collected observation, and
  - Data consumers (users, client applications) to discover and retrieve data and metadata on SCHeMA probes and observations.
- Web Interface: user front-end to access from the web all the information stored in the SCHeMA system.
- Notification Manager: application that manages the alarms notification to the users.
- Database: the RDBMS where the data are stored. It is based on Microsoft SQL Server 2012 R2.

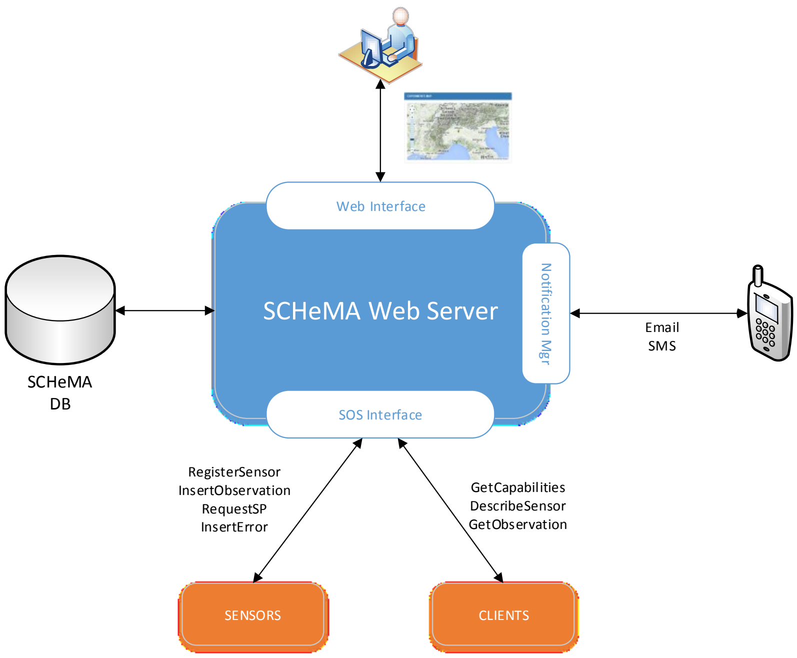

***Figure 11**: SCHeMA Architecture*

The SCHeMA M2M interface is modeled implementing the Sensor Observing System (SOS) standards in order to provide easy access and full interoperability with other systems and sensors (Fig. 12). A Network Controller is the transducer of the information sent by the in situ integrated mapping probes to a Land

Station that hosts and makes available all the data (web user and machine to machine) for interoperability and accessibility. The Land Station provides the user (i.e. the SWE client) with the registries (catalogue) with metadata for the different types of sensors and the kind of data they are capable of providing.

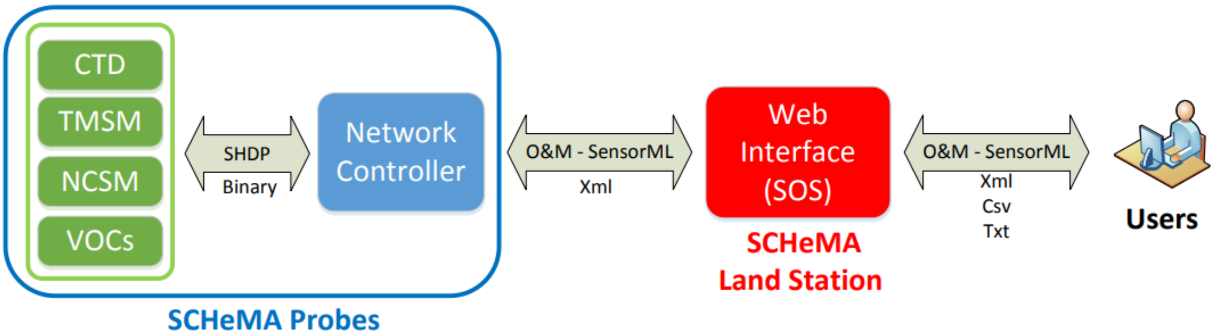

***Figure 12**: SCHeMA SOS architecture*

The SOS v1.0, used in the SCHeMA project, implement two operational profiles: Transactional Profile Operations for the communication between the probes and the Land Station and Core Profile operations for data and metadata data access

3.1.7.2 Transactional profile implementation.

For the implementation of the producer-SOS service interaction, the SCHeMA project adopted the OGC conceptual and logical architecture and develop additional proprietary methods to facilitate maintenance and fast design-development updates during tests and field tests. The SCHeMA system is developing four different sensor modules that are managed by the network controller (NC):

- IDRONAUT multiparameter probe - measuring Pressure, Temperature, Conductivity, Salinity, Dissolved Oxygen, pH, Eh, Turbidity and Chlorophyll(a)
- TMSM – Trace Metal Sensing Module– measuring Zn(II), Cd, Pb, Cu, As(III) and Hg(II)
- CSM – Carbone species Sensing Module– measuring pH, CO2, carbonate, calcium
- NSM – Nutrient Sensing Module – measuring nitrate and nitrite; this module also enables the measurements of chloride
- ASM – Algae Sensing Module – for identification of various algal species; this module is integrated in the CSM.

In order to make the SCHeMA SOS able to manage any configuration/combination of the described modules, each sensor, plus the network controller itself, is considered as a data producer and it has to send a *RegisterSensor* request. The *insertObservation* is designed to handle more observational data within the same interaction (via the <dataArray/> section) while transmitting the least amount of data package (for saving power and let the system to operate longer in the field): the heading metadata are reduced as much as possible.

In addition to the two standard methods of the transactional profile, two custom methods for alarms management and sensor planning were designed and implemented.

- *InsertError*: information sent by the probe about system failures and problems or system status info (e.g. low battery level)
- *RequestSP*: a simple custom Sensor Planning operation. Each sensor asks the land station if there is some change in the configuration that should be uploaded onto the probe (such as acquisition interval, repetition number, acquisition protocol).

3.1.7.3 Core profile implementation.

The SOS Core profile interface implemented in the SCHeMA system provides a way for external software applications to access programmatically all the data and metadata registered in the database using three different methods:

- *GetCapabilities*: returns a service description with information about the interface (offered operations and endpoints) as well as the available sensor data, such as the period for which sensor data is available, sensors that produce the measured values, or phenomena that are observed.
- *DescribeSensor*: metadata on the registered probes and sensors. The sensor description can contain information about the sensor in general, the identifier and classification, position and observed phenomena.
- *GetObservations*: allows pull-based querying of observed values, including their metadata stored in the SCHeMA database

All these methods support HTTP/GET and HTTP/POST request types. To encode observations, the Observations & Measurements (*O&M*) standard is used. To encode sensor descriptions, the Sensor Model Language (*SensorML*) is used.

3.1.7.4 SCHeMA Web Data Portal.

The SCHeMA web user interface (WUI) is the SCHeMA system front-end and it 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. Some of the features are restricted to SCHeMA users and the SCHeMA WUI is running a specific module to manage user authentication and user rights.

The web interface was developed in ASP.net 4.5, C# and BootStrap framework (http://getbootstrap.com), data interaction is provided by the Entity Framework 6.1 (http://msdn.microsoft.com/it-it/data/ef), while plots are displayed by using methods from the HighCharts library http://www.highcharts.com.

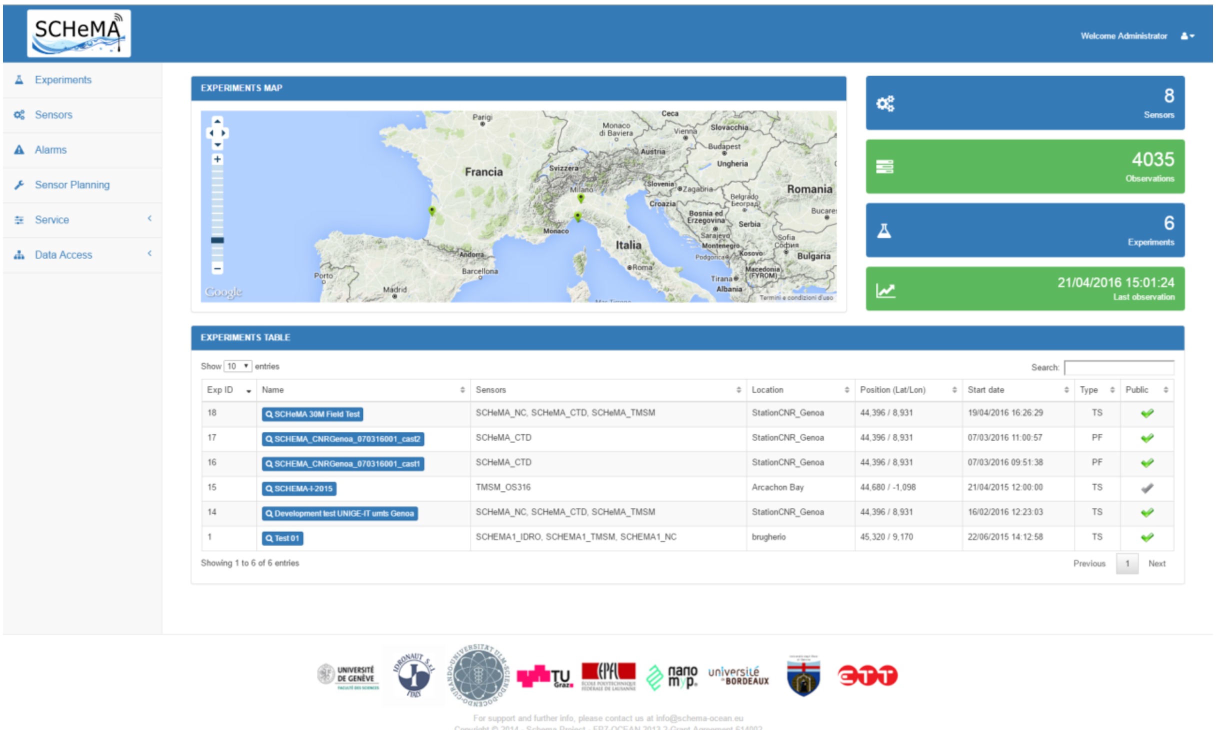

***Figure 13**: The SCHeMA web data portal*

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

3.1.7.5 Usage Monitoring.

Different indicators have been studied to provide an understanding of the readiness and service performance of the infrastructure providing access to data. The main results from the survey can summarized in the following points:

- The SCHeMA Consortium partners are to date the principal data portal users. The data portal provides a detailed view of the raw data coming from the field tests. Most of these data concern the probe data acquired during the development stage, and therefore they are not yet relevant to the main public or non-research users. This is evident from the indicators that correlate the data access and web portal views with the countries of the requests.
- The SOS features for data harvesting according to the OGC standard published online have attracted different research players that are interested in marine data interoperability, namely:
    - the ***EMODnet Physics Consortium*** (www.emodnet-physics.eu), responsible for most of the access to the SOS interface,
    - the ***Borderless Geospatial Web project*** (https://bolegweb.geof.unizg.hr/site) providing of a search facility on resources delivered by OGC-services available all over on the Internet,
    - the ***SeaDataCloud* Consortium** (www.seadatanet.org) who is networking the National Oceanographic Data Centers and develops and promotes common standards and metadada across Europe.
- The SCHeMA data portal provides different methods to access data by means of both the user interface (the web data portal) and the M2M interoperability interface (the SOS interface). The studied indicators demonstrate that all the data and metadata stored in the SCHeMA database are accessible through several channels, and that the users access the data by means of different channels according to their needs.

3.2 Field evaluation, validation and application

Preliminary field tests of the SCHeMA submersible probes (TMSM, CSM, NSM, ASM), deployed individually or as part of the SCHeMA integrated autonomous marine water quality observatory system, were performed during the following field campaigns: SCHeMA-I-2015: Arcachon Bay; SCHeMA-II-2016: Genoa Harbour; and SCHeMA-III-2016: Plentzia Marine Station (PiE). These first short-term SCHeMA field campaigns allowed testing the various sensing probe components and, step by step, identifying analytical and technical limitations and/or problems. This in turn allowed for continuous optimization of the protocols for the sensors preparation and the electrochemical or optical measurements; fluidic systems; hardware and firmware of the sensing modules; and the interfaces for wired and wireless bidirectional communication with the NC and the Web data portal until the end of the year 2016.

In the year 2017, three other short-term and one long-term field tests were held in the Genoa Harbor, the Arcachon Bay, and the Gironde Estuary:

- SCHeMA-IV-2017: Genoa Harbour long-term field tests (18 January to 10 April 2017)
- Genoa Harbour & coastal area (3 to 6 April 2017)
- SCHeMA-V-2017: Arcachon Bay (15-19 May 2017)
- SCHeMA-VI-2017: Gironde Estuary (16-23 June 2017)

The Genoa Harbor was selected since this site is highly influenced by human activity inputs. Industrial effluents have been the major cause of water pollution in the Genoa Harbor for many years, before the main heavy industries adjacent to the harbor have been closed during the 1990s. Today, the discharges from the sewage treatment plants and from the creeks have led to a general elevation of especially trace metals, nutrients, organic matter in the harbor waters. Furthermore, the UNIGE-IT could benefit from valuable facilities in the Genoa Harbor being the CNR platform allowing sensor deployment, calibration, and sample conservation. This sampling site was therefore the place for long term stability test (facilitated by the UNIGE-IT team proximity for sensor maintenance). Spatial cartography of contaminants and other parameters inside and outside the Genoa Harbor was carried out on-board R/V MASO.

The Arcachon Bay was selected for the second time for field application of the sensors. Since the stepwise ban of organotin compounds in antifouling paints, the Arcachon Bay water and shellfish suffer other contamination issues related in particular to trace metals and especially Cu pollution (Cu replacing TBT in the antifouling paints composition). Furthermore, abnormal proliferation of toxic green algae frequently leads to the cessation of oyster production due to human health risk related to consumption. This sampling site is therefore a suitable place for an integrated environmental study of different targeted pollutants, providing information with high socio-economics impacts. Also the UBx could benefit from the Marine Station facilities for sensor calibrations ex-situ measurements, and sample conservation as well as from a National Research Vessel (Planula IV; INSU) for spatial cartography in the bay.

Finally, the Gironde Estuary is characterized by a high turbidity gradient. In fact, Ocean water fluxes at the estuary mouth are 30–40 times higher than fluvial inputs, and the asymmetrical progression of the tidal wave toward the upstream estuary induces a pronounced maximum turbidity zone (MTZ), where concentrations of suspended particulate matter (SPM) exceed 1 g/L in surface water (Sottolichio and Castaing 1999). Other specificities of this study site include urban wastewater inputs by the Bordeaux Agglomeration (~1 million inhabitant equivalents) and related oxygenation problems in the MTZ during low discharge conditions. It is therefore a suitable sampling site for last stage development sensor deployment, using a National Research Vessel (Thalia, Ifremer).

Samples were collected in parallels to the in situ (or on-board) measurements during each field campaign and analyzed after return to the laboratory using a panel of selected traditional techniques. The year 2017 SCHeMA field campaigns provided also opportunity to evaluate on-board or in an on-shore laboratory the performances of yet non-submersible devices, namely: Au-GIME sensor and methodology for direct detection of total inorganic arsenic (As(III) + As(V)) and determination of arsenate (As(V) by subtraction of As(III) from total inorganic As; the VOCs portable sensing module.

3.2.1 Performances of the SCHeMA sensors and sensing probes

Reliability of the SCHeMA submersible sensing probes was demonstrated by intercomparison of the results from in situ monitoring with those obtained from laborarory analyses of collected samples. The performance of the SCHeMA chemical probes revealed by the field data gathered in contrasting conditions (i.e.: highly dynamic tidal areas, complete salinity gradient, low to high turbidity) were in-line with the analytical specifications determined from their characterization in the laboratory (Table 1), validating their capability for direct measurements in complex media.

The potentialities of the SCHeMA individual sensing probes as efficient tools for environmental studies and water quality control (Table 1, last column) were assessed by intercomparison of the performances achieved (Table 1) with the target chemical concentration ranges in open sea and coastal area and, when available, the EU (or EU members) standards for environmental and water quality.

Table 1: *Current analytical performances of the SCHeMA sensors and sensing probes.*
(UM: Unit of measure. LOD: Limit of detection).

SCHeMA unit	Parameter	Sensor type/ UM	Sensor LOD		Instrumental (Linear) Response Range	Max. depth / m	Applications
TMSM	Cadmium dynamic	190 GIME / ng/L (nM)	2 (0.02) *Preconc.: 10 min*	0.6 (0.005) *Preconc.: 30min*	a) 2-11000 (0.02-100) b) 0.6-5000 (0.005-50) *Preconc.: a) 10 and b) 30min*	300	Env. monitoring (heavily to unpolluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
	Lead dynamic	190 GIME / ng/L (nM)	4 (0.02) *Preconc.: 10min*	1 (0.005) *Preconc.: 30min*	a) 4-21000 (0.02-100) b) 1-11000 (0.005-50) *Preconc.: a) 10 and b) 30min*	300	Env. monitoring (heavily to unpolluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
	Copper dynamic	190 GIME / ng/L (nM)	15 (0.25) *Preconc. 10min*	6.3 (0.1) *Preconc.: 30min*	a) 15-6500 (0.25-100) b) 6.3-3000 (0.1-50) *Preconc.: a) 10 and b) 30min*	300	Env. monitoring (heavily to unpolluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
	Zinc dynamic	190 GIME / ng/L (nM)	25 (0.40) *Preconc.: 10min*	1.5 (0.015) *Preconc.: 30min*	a) 25-6500 (0.40-50) b) 1.5-3000 (0.015-50) *Preconc.: a) 10 and b) 30min*	300	Env. monitoring (heavily to unpolluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
	Inorganic arsenic (III) dynamic	190 AuNP-GIME / ng/L /nM)	35 (0.50) *Preconc.: 10min*	15 (0.2) *Preconc. 30min*	a) 35-4000 (0.5-50) b) 15-500 (0.2-15) *Preconc.: a) 10 and b) 30min*	300	Env. monitoring (heavily to unpolluted area) / Sentinel/Alarm system for: Water quality control / Accidental emissions and discharges
	Inorganic As(V) + As(III) dynamic	single Au-GIME / ng/L (nM)	100 (1.5) *Preconc.: 10min*	35 (0.5) *Preconc. 30min*	a) 100-4000 (1.5-50) b) 35-500 (0.5-15) *Preconc.: a) 10 and b) 30min*	surface	Env. monitoring (heavily to unpolluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
	Inorganic mercury (II) dynamic	190 AuNP-GIME / ng/L /nM)	8 (0.04) *Preconc.: 10min*	2 (0.015) *Preconc.: 30min*	a) 8-10000 (0.04-100) b) 2-4000 (0.015-20) *Preconc.: a) 10 and b) 30min*	300	Env. monitoring (heavily to slightly polluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
CSM	Sea water pH	Solid state ISE / -	3		3-9	30	Sentinel for ocean acidification
	Carbonate	Solid-state ISE / mg/L (mM)	0.6 (0.01)		0.6-6000 (0.01-100)	30	
	Calcium	Solid-state ISE / mg/L (mM)	0.4 (0.01)		0.4- 4000 (0.01-100)	30	
NSM	Nitrate	Solid state ISE / µg/L (µM)	56 (0.9)		56-62000 (0.9-10000)	30	Env. monitoring (heavily to slightly polluted area) / Sentinel/Alarm system for: Water quality control (EQS,WQS) / Accidental emissions and discharges
	Nitrite	Solid state ISE / µg/L (µM)	28 (0.6)		28-46000 (0.6-10000)	30	Env. monitoring (heavily polluted area) / Alarm system: Accidental emissions/discharges
ASM	*Algae / Cyanobacteria*	Optical / -	10 cells/L		10 cells/L - 5.24E+9 cells/L	30	Sentinel for harmful algal groups/bloom
VOCs-SM	Benzene	Optical / µg/L	18140			surface	Alarm system: Accidental emissions/discharges
	Xylene isomers	Optical / µg/L	420			surface	Alarm system: Accidental emissions/discharges
	Toluene	Optical / µg/L	7500			surface	Alarm system: Accidental emissions/discharges
	trichloroethylene	Optical / µg/L	2800			surface	Alarm system: Accidental emissions/discharges
	1,3-dichlorobenzene	Optical / µg/L	925			surface	Alarm system: Accidental emissions/discharges
	Tetrachloroethylene	Optical / µg/L	472			surface	Alarm system: Accidental emissions/discharges
	1,2,4-Trichlorobenzene	Optical / µg/L	808			surface	Alarm system: Accidental emissions/discharges
	p-cymene	Optical / µg/L	1079			surface	Alarm system: Accidental emissions/discharges

This evaluation has revealed that:

- The TMSM fulfils the performance requirements for direct detection of the target trace metals in a concentration range covering the open sea (environmental background level concentration) to highly polluted coastal areas by adjusting the pre-concentration time. The only exception is Hg(II) that presently is expected to be detected only in slightly to heavily polluted areas. The TMSM has therefore great potential for environmental studies as well as for water quality and pollution control (surveillance). This system is probe to become a valuable tool for more efficient and reliable environmental studies on the influence of the bio-physicochemical conditions on trace metal speciation and especially on the proportion of the metal-fraction available for bio-uptake. This is of primary concern for trace metals that act either as toxicants (Hg(II), Cd(II), Pb(II), As(III), As(V)) or essential micronutrients or toxicants (Cu(II), Zn(II)), depending on their concentrations, species and/or the nature of the organisms. The TMSM has also the potentiality to serve as a real-time i) sentinel for the tracing of diffuse or well-localized trace metal sources at extremely low levels; ii) alarm system when the target analyte concentrations are close or above the EQS or WQS.

- The CSM fulfils the performance requirements for accurate measurement of the carbonate system in both open seawater and coastal/surface waters and therefore has promising capability to serve as a sentinel for ocean acidification and for studying carbonate precipitation/dissolution processes that may be triggered by changes in the physical conditions of the media.

- The NSM has demonstrated potential to serve as a sentinel for the tracking of anthropogenic diffuse and punctual sources of nitrate and nitrite at relatively low concentrations in coastal area and to act as an alarm system when the nitrate concentration is close or above the EU-WQS.
- The ASM fulfils the performance requirements to identify and quantify, down to 10cells/L, toxin-producing cyanobacteria and dinoflagellates from among other algae in an algal assemblage of mixed composition; and therefore has promising capability to serve as an efficient real-time sentinel and alarm system for harmful algae groups at the very beginning of their bloom. Furthermore, the ASM allows monitoring spatial and temporal changes in relative algal composition. Identification of the algae is achieved due to a data base established from a comprehensive study of various algae species (76 algae species, 9 algae phyla) performed during the project and a new in-house software.
- The portable VOC-SM developed is attractive due to its capability of simultaneous detection of a range of VOCs. However, the remaining challenges are further improvement of the achievable limit of detections towards the environmental limits recommended by the European Union. Currently, the VOC-SM installed in industrial areas may serve as a real-time alarm system in case of accidental emissions or release.

3.2.2 Key outcomes of SCHeMA submersible probe field deployments

Selected results, resulting from the deployment of the individual probes and integrated system during the SCHeMA year 2017 field campaigns, are reported below to demonstrate their capability and potential.

The Carbon species Sensing Module (CSM) has demonstrated appropriate and validated operation during three weeks continuously measuring in the Genoa Harbour (Italy). The environmental application of the system has been demonstrated in the Mediterranean Sea and the Atlantic Ocean. The CSM allowed to detect small variations in pH as well as carbonate and calcium.

As a result, interesting trends have been observed, such as day/night cycles and temperature-dependence of carbonate and calcium levels in Genoa Harbour (Italy) (Fig. 14). In the Arcachon Bay, variations of carbonate and calcium levels were related to the tidal cycles as expected. Minimal concentrations coincide with high tide conditions, while the maximum values occur at low tides as a consequence of the greater carbonate species load in freshwater (Fig. 14). Carbonate and calcium levels were slightly lower during the daylight hours, possibly due to the incorporation in algae. The carbonate-to-calcium ratio was in agreement with the speciation.

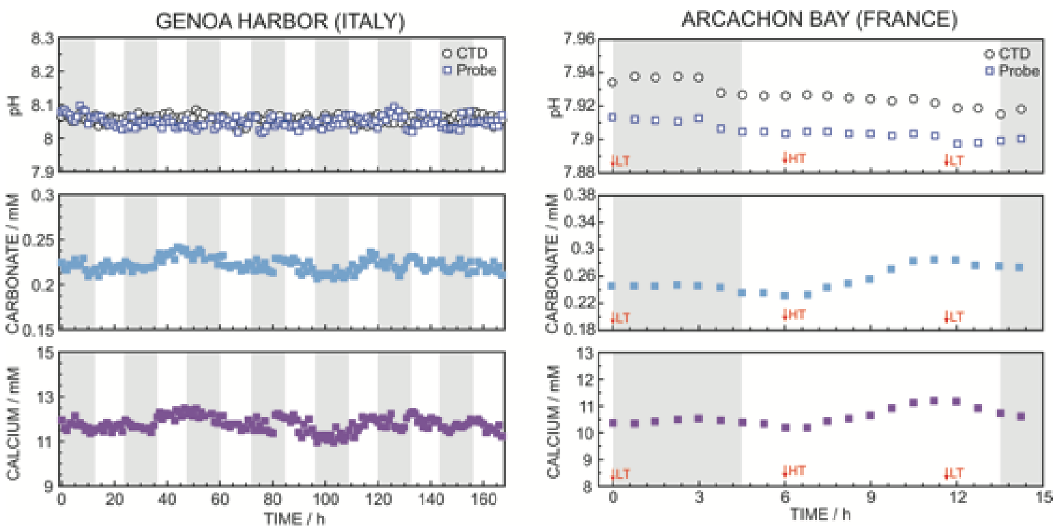

Figure 14: *In situ temporal variation of pH, carbonate and calcium during a deployment in Genoa Harbour (from April 3th, 2017 at 07:00 to April 10th, 2017 at 12:00) and in Arcachon Bay (from May 17th, 2017 at 17:00 to May 18th, 2017 at 09:00). Light hours are indicated with grey squares. HT=high tide and LT=low tide.*

The Nutrient Sensing Module (NSM). Chloride, nitrate and nitrite submersible probes were tested in the Arcachon Bay. For this purpose, the seawater flows through the desalination module (cyclic voltammetry is run first under stop mode to detect the chloride, then the desalination takes place), then through the acidification and finally through the potentiometric cell containing nitrate, nitrite and pH electrode. Note that the pH electrode is used to confirm the pH after the desalination + acidification in order to check the right functioning of the system.

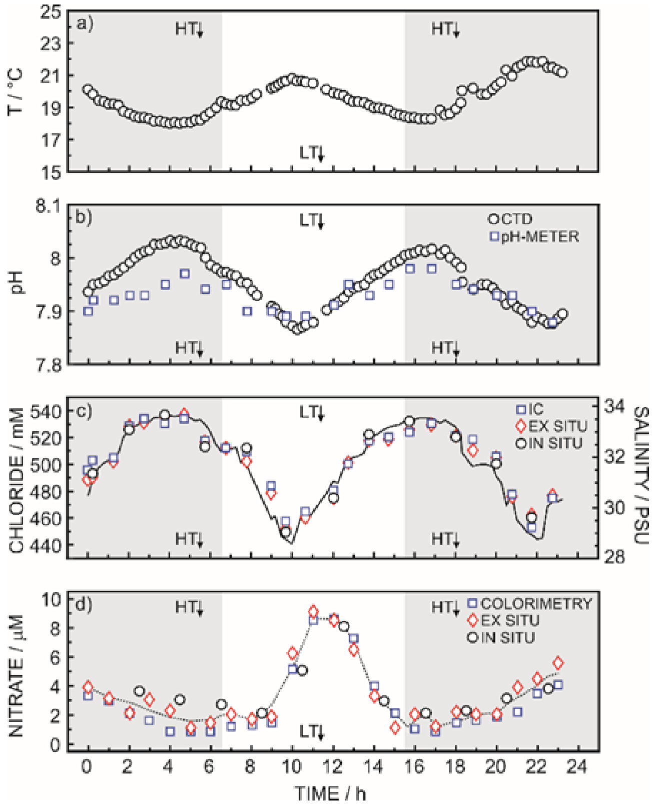

Figure 15*: In situ profiles obtained for (a) temperature (CTD), (b) pH (CTD and pH meter), (c) salinity (CTD) and chloride (in situ, ex situ and using ion chromatography), (d) nitrate (in situ, ex situ and using colorimetry) during a 24-h deployment in the Arcachon bay (from May 15th, 2017 at 15:00 to May 16th, 2017 at 15:00). Depth of deployment = 2.3 m in average. The local time for high and low tides (HT and LT) are determined according to the tidal record at Jetée d'Eyrac (44°40'N 1°10'W) and considering the temporal evolution of the seawater level in the Arcachon basin. Light hours are indicated with gray squares.*

A clear salinity-chlorinity correlation, which level is tidal dictated, was observed (Fig. 15). Thus, chloride measurements could be used to predict salinity and vice versa. Nitrite concentrations were below the limit of detection of the potentiometric sensor. Regarding the temporal profile observed for nitrate (Fig. 15), the registered levels were also clearly tidal-dependent and maximum concentrations were reached at low tide as a consequence of the higher nitrate loading in effluents and underground freshwater discharges in the bay. Thus, the bell shape of this temporal profile is due to the "tidal flushing" effect in the lagoon and the developed submersible probe may therefore serve as a tool to study the role of the Atlantic ocean as a (partial) sink of nutrient effluents in the lagoon as well as to follow eutrophication gradients in the water column through in situ data in real time.

Trace Metal Sensing Module (TMSM). The TMSM was deployed for three months from the CNR platform in 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 typical life time of the GIMEs used was one month. During each one-month operational deployment, up to 350 simultaneous measurements of the four metals were successfully achieved. Temporal and spatial profiles of all the target trace metals were monitored in the Arcachon Bay and the Gironde Estuary hosting major coastal protected areas and economic activities (seafood production areas) (see examples in Fig. 16).

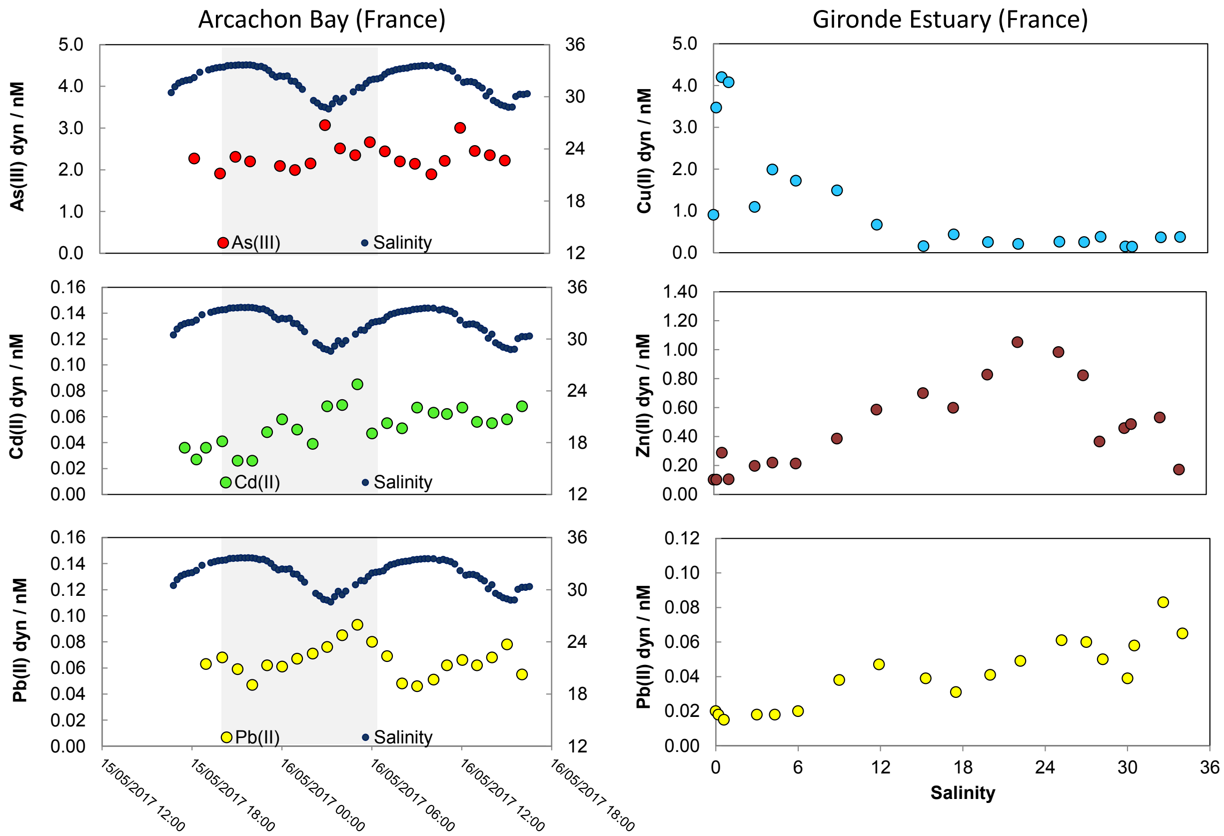

Figure 16: *In situ recorded temporal As(III), Cd(II) and Pb(II) bioavailable concentrations and longitudinal profiles of Cu(II), Zn(II) and Pb(II) bioavailable concentrations monitored during a TMSM deployment in respectively the Arcachon Bay (May 2017) and the Gironde Estuary (June 2017).*

Temporal profiles did not show tidal dependencies. Despite this, the results of both sites revealed that, in dynamic tidal coastal areas, the bioavailable fraction of the targeted trace metals may double within few hours (e.g. Fig. 16). The dynamic fraction of Cu was found significantly higher in the Arcachon Bay compared to the Gironde Estuary mouth; while the dynamic concentrations of Cd(II), and in most cases Zn(II), were higher in the Gironde Estuary mouth. The other dynamic metal species were found to be relatively similar in concentration, whatever the Atlantic Coast site. This is interesting knowing that since the stepwise ban of organotin compounds in antifouling paints, the Arcachon Bay water and shellfish suffer other contamination issues related in particular to trace metals and especially Cu pollution (Cu replacing TBT in the antifouling paints composition). The Lot–Garonne–Gironde fluvial–estuarine system is affected by multi-metal pollution, especially Cd and Zn, originating from a common main point source being a former Zn-ore mining/metallurgic industry on the Riou-Mort River near Decazeville. These results clearly suggest that the TMSM may serve as efficient tools to trace contaminant sources at extremely low levels and study their spatial spreading even in highly dynamic environments.

The results obtained in the Gironde Estuary revealed that the dynamic fraction of the target trace metals is highly variable, showing different trends depending on their complexation properties, and changing by up to one order of magnitude along the salinity / turbidity gradients (e.g. Fig. 16).

Algae sensing module. Different environmental interesting processes were observed applying the algae detection module in seawater. For instance, in the Gironde Estuary which is a complex and dynamic environment and during the 24 hour measurements, phytoplankton assemblages varied at hourly time intervals together with other environmental features (Fig. 17). Algae detection module observations were compared to results from microscopic observations. Diatoms and Ochrophytes constitute the major phytoplankton groups found in the surface water (Fig.17). This finding is confirmed by the inverted microscope analyses, although the percentages are far higher if using this last method, in part because it does not take into account Cyanobacteria or other small algae. The amount of dinoflagellates was high throughout the whole measurement cycle. When considering the microscopic counts dinoflagellates showed high abundance (>10,000 cells/L) and high relative contribution (>25%) only in one sample (mainly constituted by armored dinoflagellates), conversely in the other the relative contribution remains below 10%. Thus, even considering the limitation of the detection at the inverted microscope that leads to underestimation of naked flagellates, the detection module overestimates this taxon, especially in the samples corresponding to the highest turbidity levels. Cyanobacteria were detected at few specific times.

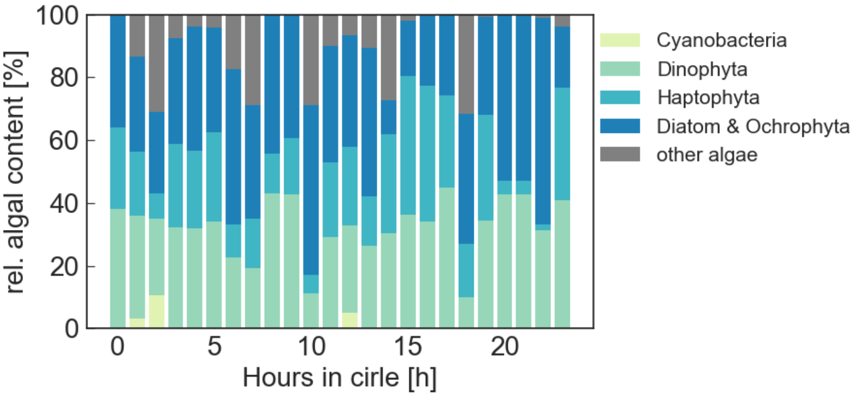

Figure 17: *Relative algal composition and its variation over 24 hours at the Gironde estuary close to Royan harbor.*

Overall, the field application campaigns of the SCHeMA system in European coastal key areas were successful. All the results proved the efficiencies of the individual probes and of the integrated system in providing high resolution in situ relevant data. The rich data provided new insights into high spatial and temporal resolutions data of various biogeochemical processes observed for the first time. Interestingly, real environment results obtained by the trace metal sensors strengthen the importance and the need for such in situ continuous monitoring. In situ sensors have proven to be sentinels of contaminant levels in the dynamic fractions being the potentially bio-available fraction. This result emphasizes the importance of considering this kind of measurements in the Water Framework Directives. Other interesting results were observed when applying the algae detection module especially in the Arcachon Bay, together with sensors measuring nutrients and species relevant to the carbon cycle, showing diurnal/tidal cycles at high temporal resolution. The complete integration of this rich data bank will be the base for different scientific publications that are already published or in preparation for publication in peer-reviewed international scientific journals. Overall, the field application campaigns of the SCHeMA system in European coastal key areas were successful, providing new insights into high spatial and temporal resolutions data of various biogeochemical processes observed for the first time.

3.3 **Field demonstrations to invited stakeholders and potential end-users.**

Demonstration of SCHeMA sensor data flow and web based discovery, access and interoperability features were carried out taking advantage of commercial exhibitions where Idronaut and ETT participated. ETT also demonstrated and shared information about the SCHeMA web sensor portal infrastructure at the occasion of meetings organized in collaboration with, especially, other Ocean of Tomorrow projects on the request of the EU Commission. In parallel, the functioning of the Network Controller and the web-based data flow were shown during the demonstration activities coupled with the Field Tests in Genoa Harbour (January to April 2017) and in Arcachon (May 2017). Moreover, the data-portal on the SCHeMA web site was active since April 2016, making the raw data acquired during the Field Tests immediately available to the public: all metadata and data are OGC standards and INSPIRE directive compliant, and the data have been published and shared through OGC-SOS services. The SCHeMA web-based infrastructure was thus a key part of the SCHeMA project demonstration, helping the users to have access to information and data and to download them from other systems, achieving a real interoperability goal.

The demonstrations of the SCHeMA individual sensing probes and the integrated system were organized several times during short and long-term field applications in the coastal Atlantic Ocean and the Ligurian Sea. More than 60 persons from different institutions and SMEs working in various sectors have participated. The last demonstration activity was performed during the SCHeMA-V-2017: Arcachon Bay field campaign held in May 2017. Potential end-users were invited, on two different days, to participate to the SCHeMA field monitoring on-board of the R/V Planula IV in order to let them discover the functioning of the individual sensing probes and integrated system operating in real use-case field, providing a real use-case experience. The SCHeMA TMSM, CSM, NSM and ASM were mapping simultaneously a range of trace metals, nutrients, species related to the carbon cycles and algae coupled to master variables using Idronaut multiparameter probes. The Network Controller was active providing real-time data visualisation of integrated modules via the connection to the Web data information system.

The invited participants were stakeholders in the water management field, environment protection policy makers and collaborating local marine research groups (including Master and PhD students), selected on the basis of their involvement in National or European environmental monitoring and marine environmental protection programs to fulfill requirements of EU Directives and Strategies. The choice of the SCHeMA components and prototypes to be demonstrated each time was made taking into account the "Technology Readiness Level" concept and the suggestions by the partners involved in the various sensor and sensing module developments.

The demonstration days coupled with the Field Tests and applications intended to 1) demonstrate the capability and potentiality, under real field condition, of the individual sensor probes and SCHeMA integrated systems that were successfully evaluated and validated during the short-term field applications; and 2) create and consolidate long-term interactions with the potential end-users by informing them regularly about the near future improvements/optimization and industrialization activities. This last action is supported by the dissemination of the Video-brochure, the web site up-dates and the SCHeMA mobile APP. Maintaining contacts with end-users even after the end of the project would be very useful, especially for those sensors and modules that are still not fully optimized, but may fulfill end-users' requirements in a next future.

Overall, the collected feedbacks were fully positive. Demonstration activities were valued for clarity. The project and its outcomes stimulated interest in its innovative aspect, interdisciplinary developments, and its applications showing that the use of sensors and integrated mapping systems is in line with on-going scientific environmental programs and water quality monitoring activities.

The SCHeMA partners intend to further simplify the procedures of setting and calibrating the probes and to control the overall weight of the integrated system to facilitate the operation and the maintenance operation especially in view of deployment from moored facilities.

Most of the participants were interested in at least one of the sensors/sensing modules; the Network Controller and the web data-portal infrastructure. Moreover, the interactions during the field tests and the demonstration events with end-users, institutions and SMEs involved in the water quality monitoring and studies of environmental processes provided valuable opportunities to discuss perspectives of future joint observation activities.

4 Impact

4.1 Increase in the temporal and geographic coverage from in situ marine sensors.

The oceans are crucial role for the prosperity and future of civilization; providing natural resources, food, recreation, a route for global transport of goods and services and they 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 in marine systems. To understand, predict, protect and manage ocean processes and resources requires a step change in the available data addressing this environment.

The field application campaigns of the SCHeMA system in European coastal key areas have produced high resolution (spatial and temporal) data providing new insights into various biogeochemical processes observed for the first time. They have also shown that these new systems are robust and reliable tools having the potential to serve as (i) sentinels for the tracing of diffuse or well-localized sources of hazardous chemical and biological compounds as well as (ii) alarm system when the target analyte concentrations are close or above the EQS or WQS.

Therefore, SCHeMA is an integrated autonomous marine water quality observatory system providing versatile tools to enhance in situ ocean observing system capabilities in terms of:

- the number of hazardous chemical compounds that can be quantified simultaneously;
- temporal resolution and spatial dimension to rapidly localize problems, to alert authorities in charge of remedial action at appropriate time scale.

The simultaneous data acquisition of a large number of parameters as provided by the SCHeMA system is a prerequisite to:

- promote new discoveries leading to better understanding of the synergic interaction between the target analytes and their impact on water quality, marine organisms, society and economy;
- propose Environmental Quality Standards based on scientific knowledge (e.g. EQS for trace metals based on bioavailable concentration instead of total dissolved concentration);
- define strategies to set up efficient water quality monitoring programs for estuaries and coastal zones;
- support implementation of European Marine Policies and development of knowledge-based protective policies for sustainable management.

4.2 Support to Marine Strategy Framework Directive and Regional Sea Conventions

In 2008, the European Union has established the Marine Strategy Framework Directive (MSFD) with a goal to protect the marine environment in Europe. The MSFD uses a set of 11 descriptors which, together, summarize the way in which the whole system functions (Table 2). Some of these descriptors can be said to represent the most important ecosystem features of concern (D1 – Biological diversity, D2 – Non-indigenous species (NIS), D3 – Commercial fish and shellfish, D4 – Food webs, D6 –Sea floor integrity, D7 – Hydrological conditions) either in terms of favorable or threatened features, forming different sectors of the ecosystem-based approach. Another part of the descriptors represents human drivers, pressures on the ecosystems and their resulting alterations (D3 – Fishery, D5 – Eutrophication, D8 – Contaminants, D10 – Litter, D11 – Energy and noise).

Table 2: *Qualitative descriptors for determining good environmental status in the MSFD (Directive 2008/56/EC).*

MSFD descriptor	Short name
Biological diversity	D1
Non-indigenous species	D2
Commercially exploited fish and shellfish	D3
Marine food webs	D4
Human-induced eutrophication	D5
Sea floor integrity	D6
Hydrographical conditions	D7
Concentrations of contaminants	D8
Contaminants in fish and other seafood	D9
Marine litter	D10
Energy, including underwater noise	D11

The developed SCHeMA sensing probes address a number of variables relevant to several descriptors (Table 3). Among these variables are a range of dissolved trace metals (D8) for which the SCHeMA TMSM is presently the only available system allowing their real-time in situ detection. Trace elements are ubiquitous and diverse components of the earth's biogeochemistry, playing critical roles in ecosystem functioning. 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. Fe, Cu, Zn), depending on their concentrations and the nature of the organisms exposed. Due to their intrinsic properties of toxicity, persistence, and/or tendency to bio-accumulate, trace metals may have a long-term impact on the biomass composition, activity and health, even a long time after a significant decrease in their release. Therefore, as the nutrients (D5), they also contribute to the achievement of D1 and D4.

Table 3: *Variables relevant to several descriptors of the MSFD and the monitoring programmes of the HELCOM, OSPAR and Black Sea Regional Sea Conventions addressed by SCHeMA*

SCHeMA unit	SCHeMA Parameter	MSFD 2008/56/EC Summarized Descriptors	Sea Conventions		
			HELCOM	OSPAR	BlackSea
TMSM	Cadmium dynamic fraction	8	x	x	x
	Lead dynamic fraction	8	x	x	x
	Copper dynamic fraction	4,8	x	x	x
	Zinc dynamic fraction	4,8	x	x	x
	Inorganic arsenic (III) dynamic fraction	8	x	x	x
	Inorganic arsenic (V) dynamic fraction	8	x	x	x
	Inorganic mercury (II) dynamic fraction	8	x	x	x
CSM	Sea water pH	7	x	x	x
	Carbonate	4	x	x	x
	Calcium	4	x	x	x
NSM	Nitrate concentration	4,5,7	x	x	x
	Nitrite concentration	4,5,7	x	x	x
ASM	Algae (Phytoplankton) / Cyanobacteria	1,4,5,7			
VOCs-SM	VOCs	2, 8			x
Multiparameter probe	T	7			
	pH	7			
	Dissolved oxygen	4, 5, 7			
	Conductivity/Salinity	7			
	Turbidity	7			
	Chlorophyll a	4,5,7			
	Phycocyanin	4,5,7			
	Phycoerythrin	4,5,7			

The SCHeMA integrated autonomous marine water quality observatory system - interfacing the TMSM, CSM, NSM and ASM together with a multiparameter probe - provides capabilities for simultaneous, in situ, high-resolution monitoring of a significant number of parameters relevant to the descriptors D1, D4, D5, D7 and D8. It appears therefore to be a very promising near-future tool to support studying, and ultimately better understanding, the synergic interaction between the variables relevant to these descriptors.

The integration of the data of chemical monitoring programmes, and combination of data from chemical and biological effects to define consistent sets of EQS taking account mixture effects, are an active part of Science within the Regional Sea Conventions (i.e. OSPAR, HELCOM, Black Sea, Barcelona Conventions). Therefore, the sensing probes suitable for in-situ and high-resolution acquisition of a range of chemical and biological parameters (Table 3) in marine environments (estuaries, coastal and open ocean) as well as the ICT wireless networking solution and the Web data information system developed as part of SCHeMA contribute to the availability of technological solutions to address key aspects of these Conventions.

4.3 New tools for environmental monitoring programs

The SCHeMA submersible sensing modules (TMSM, CSM, NSM and ASM) - thanks to their technical specifications (low-power consumption, miniature multichannel sensing devices, wireless interfaces) and analytical performances (selectivity, sensitivity, multielement analysis, high-resolution data acquisition), together with the comprehensive ICT solution based on international standards developed - provide attractive new tools to address the objectives of a large number of on-going environmental monitoring programs and projects as illustrated in Table 4. The aim of this table is not to be exhaustive as there are many further initiatives (e.g. other H2020 projects) that are not listed. The Table 4 intends to show the relevance of the developed devices and tools to representatives of major European monitoring programs and projects.

Some surveillance programs mainly focus on some specific parameters, therefore the individual modules themselves are already valuable devices. Some other initiatives are looking at integrated datasets and for those the integrated system is more pertinent.

Attractive advantages of the SCHeMA proposed solution are thereby:

- the flexibility and modularity of the system that, in modules or as integrated system, can contribute to studying ocean processes by providing high quality data for key parameters;
- each of the developed SCHeMA submersible probes has the capability to monitor simultaneously several parameters relevant to specific groups of chemical and biological indicators while being compact; most of the commercially available tools are restricted to the measurement of one parameter per probe.

***Table 4:** Variables relevant to several descriptors of the MSFD and monitoring programmes of the HELCOM, OSPAR and Black Sea Regional Sea Conventions addressed by SCHeMA*

SCHeMA unit	SCHeMA Parameter	Observation and monitoring programs						Research Infrastructures and projects					Interoperability	
		EMODnet Physics	EMODnet Chemistry	EMODnet DIngestion	Copernicus Marine	GOOS	SOCAT	SeaDataCloud	JERICO Next	AtlantOS	Odyssea	EMSO	GEOSS	OGC SWE
TMSM	Cadmium dynamic fraction		x	x					x		x			
	Lead dynamic fraction		x	x					x		x			
	Copper dynamic fraction		x	x					x		x			
	Zinc dynamic fraction		x	x					x		x			
	Inorganic arsenic (III) dynamic fraction		x	x					x		x			
	Inorganic arsenic (V) dynamic fraction		x	x					x		x			
	Inorganic mercury (II) dynamic fraction		x	x					x		x			
CSM	Sea water pH	x	x	x	x		x	x	x		x			
	Carbonate		x	x	x	x	x	x	x		x			
	Calcium		x	x	x			x	x		x			
NSM	Nitrate concentration		x	x	x	x		x	x		x			
	Nitrite concentration		x	x	x	x		x	x		x			
ASM	Algae (Phytoplnakton) / Cyanobacteria		x	x		x		x	x		x	x		
Multiparameter probe	T	x	x	x	x	x	x	x	x	x	x			
	pH	x	x	x	x	x	x	x	x	x	x	x		
	Dissolved oxygen		x	x	x		x	x	x	x	x	x		
	Conductivity/Salinity	x	x	x	x	x	x	x	x	x	x	x		
	Turbidity	x	x	x	x		x	x	x	x	x	x		
	Chlorophyll a		x	x	x	x	x	x	x		x	x		
	Phycocyanin		x	x	x	x	x	x	x		x	x		
	Phycoerythrin		x	x	x	x	x	x	x		x	x		
Network controller		x		x		x			x					
Data information system		x		x		x		x					x	x

4.4 Data access and Interoperability

The SCHeMA project, through the partners responsible of the ICT infrastructure, is participating in an international network of competence on Sensor Observation Services to study interoperability issues within the Sensor Web framework and working towards the creation of a SWE Marine profile. The core group of the network is formed by representatives of the FP7 Ocean of Tomorrow Projects.

So far, the result of this collaboration is a document describing the data recommendations for different aspects covered by the OoT projects in terms of standardization of marine data and interoperability. The document covers the following themes:

- Standards implemented by the OoT projects with joint recommendations and lessons learned
- Standards that emerged during the OoT project with recommendations
- Research priorities beyond the end of the OoT projects

These success stories exemplify the impacts that the OoT projects 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 operational 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 (e.g. limitation of communication bandwidths for Iridium satellite services) in the flow of information from sensors to users. Ultimately, the ability to have interoperable data enhances the comparison of observations of diverse character and disciplines, 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 OGC Standards implemented by SCHeMA 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.
- *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

The implemented W3C standards were:

- WC3 compliant web portal and web data portal
- *Resource Description Framework* (RDF) - Standard model for data interchange on the Web.

Table 5 shows the implementation of these standards by the OoT projects and the SCHeMA contribution to their adoption, adaptation, update and implementation.

Table 5: Summary of the standards implemented by the OoT projects

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

SCHeMA, in collaboration with the other OOT projects, also significantly contributed to the standardization of metadata and data on the web. These are key activities and they will continue after the end of the project.

4.5 Competitiveness of Europe within the Marine sensing sector

SCHeMA has promoted 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 developments and validation of the SCHeMA sensors, sensing probes and integrated system. Thanks to their collaboration, the OoT projects have made a significant contribution to data standardisation that is expected to advance not only European programs in ocean observations, but also Europe's role as a global leader in data interoperability and improved data access. Idronaut and ETT, SCHeMA SME partners, have foreseen the commercialisation of several SCHeMA R&D solutions (see section 4.3).

4.6 Main dissemination activities

To target a wide public audience and as many as possible potential end-users, the website (www.schema-ocean.eu) was continuously enriched with copies of Informational Factsheets about the project, the individual sensing probes, the web interface and the data portal. These factsheets have also been distributed by the partners who joined workshops, conferences, exhibitions and 'Demonstration to end-users' activities. The "News and Events" and "Field Tests" sections provided information about the field and Demonstration activities calendar and kept the public informed about ongoing project activities with brief summary and selected photos. In the Dissemination section, pages about scientific publications and public Deliverables were regularly updated and pages about Demonstration days were added. Four videos of 5 to 7 minutes were issued from shootings performed during the Summer School and a field campaign. Two of them present the objectives of the project, the preparation of the sensors and sensing probes, the integrated SCHeMA system, as well as an example of the field deployment and application of individual probes and the integrated system in the Arcachon Bay. The third video presents the web data portal and instructs the users on how to access to the data files and plots as well as to all information available. The last video give an overview on the activities performed during the SCHeMA Summer School. These videos were posted in the Dissemination section (www.schema-ocean.eu/dissemination/video) and on YouTube. Six short videos were also issued from this material and assembled in the SCHeMA video brochure disseminated to the potential end-users identified. They were also posted in the Dissemination section (www.schema-ocean.eu/dissemination/video) and on YouTube. Links to the other FP7-OCEAN 2103 running projects were available from the early beginning of the project through the website (http://www.schema-ocean.eu/links) and cross references for SCHEMA are available in those project websites.

The outcomes of the activities that have been carried out all over the duration of the SCHeMA project were continuously disseminated to:

The international scientific community: 43 peer reviewed papers have been published (3 are under revision and 4 are in preparation). Copies of the peer-reviewed published scientific papers will be made available via the project web site publicly accessible domain, following the rules of the special Clause 39 "Open Access". A link enables accessing the available publications through the publisher (http://www.schema-ocean.eu/Scientific-Publications). The SCHeMA partners took part in 53 different regional, national or international conferences/meetings through 32 oral contributions, 44 poster presentations, 6 invited contributions and 2 keynote lectures. In this frame, the PCs of the four FP7-Ocean-2013.2 projects organized jointly a Session on "Next generation of in situ sensors for aquatic systems" as part of the ASLO 2015 Conference (Granada-Spain, 26 February 2015). UBX and UNIGE organized a Special Session on "New sensor developments for monitoring aquatic systems" as part of the International Estuarine Biogeochemistry Symposium (Bordeaux-France, 07-10 June 2015, http://www.schema-ocean.eu/news-e-events).

The end-users: SCHeMA partners participated in 7 business exhibitions and organized 4 conference sessions. Informal factsheets and videos are available on the SCHeMA web site (http://www.schema-ocean.eu/Project-Factsheets; http://www.schema-ocean.eu/Dissemination/Video). A video-brochure was designed for dissemination to potential end-users invited to the demonstration activities organized during the SCHeMA Field Tests. The development of a "SCHeMA APP" for mobile communication systems has been initiated. SCHeMA SMEs have disseminated the project information from the early beginning of the project by participating to OCEANOLOGY 2014 (a short description of the project is available on the Idronaut web site www.idronaut.it), OCEAN BUSINESS 2015 (13-17 April 2015, Southampton - UK) and OCEANOLOGY 2016 (15-17 March 2016, London Excel - UK). During the OCEAN BUSINESS 2017 exhibition (04-07 April 2017, Southampton - UK), a poster presenting the SCHeMA project and the electronic prototype of the Multi-channel Trace Metals Submersible TMSM was displayed at the IDRONAUT stand. During these events, hundreds of fact-sheets were distributed to visitors, thus promoting and disseminating the information about the SCHeMA project. SCHeMA partners and several other Ocean of Tomorrow projects: SenseOcean, NeXOS, COMMON SENSE, BRAVOO, EnviGuard, MariaBox, SEA-on-a-CHIP and SMS, were present at Oceanology International 2016 with a stand showcasing the latest developments from all projects. The PCs of these OoT projects organized jointly 2 workshops and Round-Tables, namely: ***"What can the Ocean of Tomorrow projects do for you?"*** at OI 2016 (Oceanology International Conference and Exhibition); and ***"Sensor and System Innovations for the Oceans of Tomorrow"*** at IEEE OCEANS 2017 (IEEE Oceanic Engineering Society (OES) and the Marine Technology Society (MTS) Conference and Exhibition) held 21-22 June 2017 at Aberdeen-UK.

The general public: 5 press releases; 1 web news, 1 brochure, 4 factsheets, 5 videos were used. To target a wider public audience the website was continuously enriched with a set of field campaign information, photos , reusable illustrations and videos, which are all available on the project website (www.schema-ocean.eu/dissemination/video). To target a wider audience, the videos were also posted on YouTube.

The students and early stage researchers (PhD and postdoctoral fellows): 16 early stage researchers (PhDs and PostDocs) have contributed to the successful developments and validation of the SCHeMA sensors, sensing probes and integrated system. Integration of sensor-based methods and applications were introduced through teaching in the frame of the: (i) Oceanography Master, Bordeaux France; (ii) ERASMUS MUNDUS MASTER MER (Marine Environment and Resources (Universities of Bilbao, Bordeaux, Southampton, Liège); Advanced analytical chemistry courses for Master students (University of Geneva). A Summer School has been organized from the 14th to the 16th of June 2016 in Bilbao (Spain), where 18 ESR and 18 master students have participated. A video has been produced and posted on the website (http://www.schema-ocean.eu/Summer-School-Copy and YouTube). The SCHeMA early stage researchers (ESR) along with students who participated in the Summer School have edited a report, which has been published as a conference report in Chimia, a peer-reviewed journal.

4.7 Exploitation of results

The maturity levels of the SCHeMA components and prototypes were evaluated using the "Technology Readiness Level (TRL)" concept. A first evaluation was made at month 36 to choose the prototypes ready for the year 2017 field campaigns and on-field demonstration to end-users. A re-evaluation was made at month 48 after the field evaluation and application in Atlantic and Mediterranean coastal areas during the year 2017 (Table 6). The components that are the most promising for short-term commercialization were identified (Table 6, last column).

***Table 6:** TRL ratings of the SCHeMA components and prototypes at month 36 and 48 and SCHeMA units ready for short-term commercialization.*

	SCHeMA unit	Parameter	Technology Readiness Level		Commercialization
			36M	48M	
TMSM sensors	GIME	Cadmium dynamic fraction	TRL8	TRL8	Yes
		Lead dynamic fraction	TRL8	TRL8	
		Copper dynamic fraction	TRL8	TRL8	
		Zinc dynamic fraction	TRL8	TRL8	
	AuNP-GIME	Inorganic arsenic (III) dynamic fraction	TRL3/TRL4	TRL6/7	Yes
		Inorganic arsenic (V) dynamic fraction	TRL1	TRL4	No
		Inorganic mercury (II) dynamic fraction	TRL3/TRL4	TRL6	Yes
CSM / NSM sensors	Solid-state ISE	Sea water pH	TRL6	TRL6/7	No
		Carbonate activity in water	TRL6	TRL6/7	
		Calcium activity in water	TRL6	TRL6/7	
	Solid-state ISE	Nitrate concentration	TRL5	TRL6/7	No
		Nitrite concentration	TRL5	TRL5	
		Phosphate concentration	TRL1	TRL1	
ASM detector	LED	Algae / Cyanobacteria	TRL6	TRL7	No
		STX	TRL3	TRL3	
VOC	IR-FEWS sensor system	VOCs*	TRL4	TRL4	No
SCHeMA other components	TMSM HW/SW mechanic	Trace metal submersible probe	TRL8	TRL8	Yes
	CSM HW/SW mechanic	Carbon species submersible probe	TRL7	TRL8	No
	NSM HW/SW mechanic	Nutrient species submersible probe	TRL5	TRL7/8	No
	ASM - HW/SW mechanic	Algae sensing module	TRL6	TRL7	No
	FACM	Single/double submersible peristaltic pump	TRL8	TRL9	Yes
	NC	Network controller	TRL8	TRL7/8	Yes
	Web system interface	Web-based system and user interfaces	TRL8	TRL8	Yes

The forecast on how the various devices could be industrialized and commercialized is discussed in more detail below. These conservative forecasts and opinions have been formulated by Idronaut (SCHeMA SME partner). IDRONAUT has been manufacturing state-of-the-art CTDs and advanced sensors for 35 years, selling them all over the world to scientists in environmental sciences and especially to the marine research community (chemists, geochemists, biologists, oceanographers, limnologists) studying aquatic environments. The present, extremely fluctuant market and average of sales and declarations of interest in this kind of products that IDRONAUT has received in the last few years from their sales network have been taken into account.

At the moment of the release of this document, the most promising project devices for commercialization within short-term are:

- The NC - Network Controller unit.

- The TMSM – Fully integrated three-channel trace metals submersible probe measuring simultaneously the potentially bioavailable Cd(II), Zn(II), Pb(II), Cu(II), As(III) and Hg(II) fractions.
- The FACM - Double and/or single submersible peristaltic pump with integrated battery pack
- Web information

The other project products that we presently judge to need more important R&D investment prior to commercialization are:

- CSM - Submersible probes for in-situ simultaneous detection of species relevant to the carbon cycle (pH, carbonate, calcium).
- NSM - Submersible probes for in-situ simultaneous selective detection of nitrate and nitrite.
- ASM – Fully integrated miniaturized multi-channel optical detection module enabling in-situ early stage detection of phytoplankton species in algal blooms and the real-time identification of their taxonomic affiliation.

4.7.1 NC - Network Controller

IDRONAUT presently produces and sells the BUOY CONTROLLER unit, which is the core of the IDRONAUT BUOY 601 PROFILER system. The BUOY CONTROLLER unit has become obsolete and in the future the SCHeMA Network Controller will replace it.

Before introducing the NC into the market, it is necessary that IDRONAUT provides the R&D investment to rebuild the NC electronics and add the HW/SW interface for the available IDRONAUT BUOY WINCH PROFILER. The motorized winch interface is a unique feature that makes the NC different from the many other "data loggers" presently available on the market and makes it indispensable to guarantee the BUOY PROFILER product continuity.

When the NC is ready for the commercialization, IDRONAUT will collaborate with ETT, which developed the NC OGC/SWE interface and the WEB DATA PORTAL, to offer a complete and up-to-date solution. This collaboration will guarantee the interoperability of the NC with the most important international networks of marine monitoring, such as: EMODnet, GOOS, EuroGOOS, Copernicus Marine Environmental Monitoring Service, and SeaDataNet network of National Oceanographic Data Centers (now running the SeaDataCloud project).

4.7.2 TMSM - Three-channel Trace Metal Sensing probe

IDRONAUT presently produces and sells the GIME-VIP (Voltammetric In Situ Profiler), a single-channel submersible trace metal probe, to detect: Zn, Cu, Pb, and Cd in marine and fresh waters[15]. The VIP was developed in collaboration with UNIGE and IMT as part of a previous EU project (VAMP-MAST III program, contract no. MAS3-CT95-0033). The VIP is the only system commercially available with capacity for in situ trace metal monitoring and profiling, down to 500 m, with sub-nanomolar sensitivity.

The TMSM, based on up-to-date electronic components and highly integrated sensors is of similar size as the VIP albeit providing three independent measuring channels. The novel and highly integrated sensors greatly simplify the preparation and field deployment and provide new detection capability for additional trace metals (As (III), Hg (II) using novel AuNP-GIME).

Reliable mass production of on-chip 190 interconnected Ir-based arrays using simplified deposition/patterning protocols has been demonstrated. The sensitivity of GIME prepared using these novel on-chip devices is twice as high compared to what had been reached previously[3]. The GIME-TMSM can therefore replace advantageously the GIME-VIP.

Concerning the AuNP-GIME for direct detection of As(III) and Hg(II), R&D investment is still required, as the preparation of these sensors is far from being reproducible enough to be performed by non-specialist end-users. Further improvement in term of sensitivity for Hg(II) detection is also required for environmental studies.

We believe that the TMSM, when completed and fully characterized, could induce new interest mainly in the Far East countries like China and India, where the demand for trace metal analysis, especially As(III) and Hg(II), in water is increasing. In Europe, the interest is presently scarce, mainly because of the lack of funds for environmental monitoring. However, we believe that the interest for the TMSM could greatly increase if i) the revised WFD Priority Substance Directive (2013/39/EU) suggesting to monitor the bioavailable concentration of trace metals instead of their total concentration, and ii) the MSFD (2008/56/EC) extending the requirement to monitor and define appropriate EQS not only for the WFD priority substances but for all substances entailing a significant risk to the health of marine environment[22] are properly supported, which is the case for the targeted trace metals.

4.7.3 FACM - Submersible peristaltic pump

The developed submersible double and/or single submersible peristaltic pumps with integrated battery pack are ready for the commercialization. This is rather a new market, where IDRONAUT was not present before. Therefore, it is difficult to estimate the commercial potential of this rather unique and peculiar product. After the end of the project, IDRONAUT will start a dissemination campaign (newsletters via email, advertising on specialized magazines) to their dealers and sales network and will then verify the interest in this kind of product.

4.7.4 CSM and NSM - Nutrient and Carbon species submersible probes

Even though these devices are based on innovative all solid-state ISE and in-line desalinator and acidification modules, they need further R&D investment before commercialization. Indeed, the sensors for nutrients (nitrate and nitrite) and species relevant to the carbon cycle (calcium, carbonate, pH) as well as desalinator and acidification modules are still hand-made laboratory prototypes and the associated required fluidic systems are still too complex. More rugged devices that can be readily assembled and ideally deployed without the requirement of a fluidic housing, limiting deployment at depth > 30 m, are needed.

We believe that when such developments will be completed and the new probes fully characterized, the CSM and NSM could attract significant interest, as the measurement of nutrients and CO_2 are important topics for the scientific community and environmental protection agencies all around the world.

4.7.5 ASM – Miniaturized multi-channel algae sensing module

The algae detection module is at prototype stage and while it has been successfully validated in field and in laboratory it is still far from becoming an industrial product that can be commercialized as it is.

The system is ready for inclusion into submersible housings and can be deployed in surface water down to ~30 m depth.

Products characterizing the algae in water, such as: i) Chelsea V-Lux; ii) Turner designs PhytoFind; iii) Bbe-Moldaenke GMBH Fluoroprobe; etc., currently present on the market, are integrated submersible probes that are sold as standalone probes or OEM components ready for the integration into CTD or/and multi-parameter submersible probes. However, we think that with further R&D investment to produce a more rugged device that can be deployed without the requirement of a fluidic housing the ASM may be competitive due to due to its extremely miniaturized size (Fig. 5), very low-cost components, validated algorithms to correct biological and chemical interferences, and integrated data base. Low-cost alarm systems for the early detection of harmful algal blooms (HABs) having important socio-economic impacts represent a huge potential market as such blooms are occurring with increased regularity worldwide.

4.7.6 Web based system interface

The developed web interface relies on a very innovative and unique information system. It includes several modules, each of them providing key features (e.g. OGC SWE interoperability, interactive data quality check and quality flagging, sensing probes planning services, sensor alarm system etc.) that can be activated or de-activated according to the specific needs of the user. The developed information system is highly flexible and as it interacts with the hardware by means of SOS standard, it can also be connected to interact with any device supporting such an interface. The system was also designed to provide access to multiple users having various right levels on the control of the mapping modules, thereby turning the information system in a highly valuable tool with strong exploitation potential.

Besides being the ICT interface for the SCHeMA system when it is going to be sold, ETT can already propose the SCHeMA web package on the market. Clients can be institutions owning systems that support SOS and interested in having a complete tool to interact with their device and data, as well as owners of devices that are interested in one specific SCHeMA web features (e.g. the Quality Check / Quality Flag, QC/QF).

Moreover, the expertise that ETT gained by developing the SCHeMA ICT wireless networking solution facilitated ETT being invited to participate to meetings and to collaborate in projects adopting OGC standards. These projects are targeting remote sensing and internet data information system solutions for a broad range of monitoring programs (environment, land, buildings, infrastructure for transport, etc.).

5 Website and consortium information and contacts

SCHeMA public website: www.schema-ocean.eu.

SCHeMA Consortium. The consortium comprised 9 partners from 6 countries. It was a multi-sectorial partnership between three SMEs (Idronaut, ETT, nanoMyP), five Universities (UNIGE, UULM, TUGRAZ, UBX, UNIGe-IT) and one Federal Institute of Technology (EPFL). The well-balanced composition of the consortium in terms of contributions from the different sectors is illustrated in Figure 18.

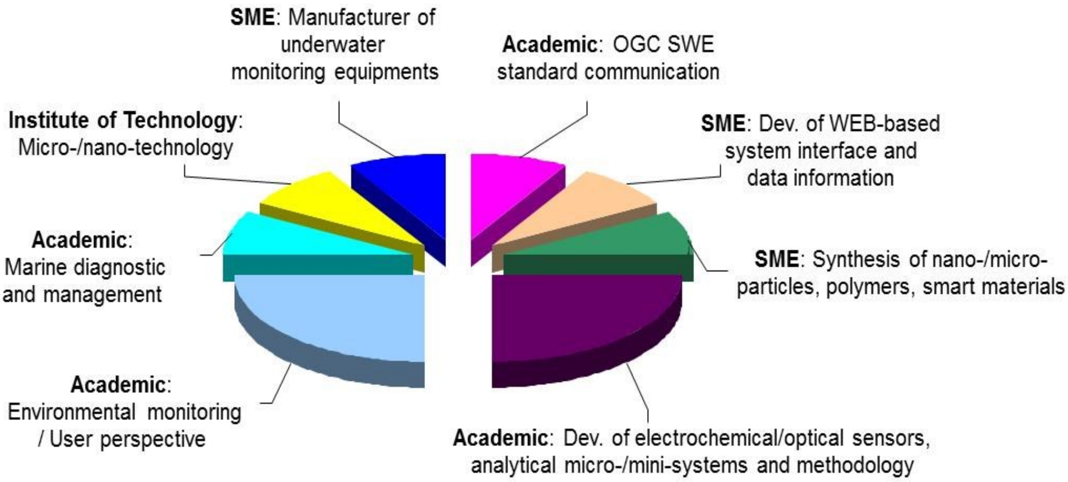

***Figure 18**: Consortium composition and sectors*

The main expertise of the partners can be briefly summarized as follows:

University of Geneva, Switzerland – UNIGE: specialist in the development of innovative electrochemical sensors (bioanalogical sensors, solid state ion-selective membrane sensors), mini-/micro- integrated analytical systems and analytical methodologies; application of these tools for *in situ* measurements of trace metal speciation and metal bioavailability, nutrients, species related to carbon cycles coupled to master bio-physicochemical parameters.

Contact: Mary-Lou Tercier-Waeber (PC), marie-louise.tercier@unige.ch;
Eric Bakker, eric.bakker@unige.ch

Idronaut Srl, Italy - IDRO: specialist in the development of underwater instrumentation in particular regarding analytical measurements, data acquisition and transmission under extreme conditions.

Contact: Fabio Confalonieri, Flavio Graziottin, idronaut@idronaut.it

University of Ulm, Germany – UULM: specialist in the development of mid-infrared spectroscopic sensing methodology and technology for the detection of volatile organic constituents (VOCs) in liquid and gas phase, optochemical sensors and submersible probes, and applications of optochemical sensors for in-situ monitoring of organic hazards.

Contact: Boris Mizaïkoff, boris.mizaikoff@uni-ulm.de

Technische Universitaet Graz, Austria – TUGRAZ: specialist in the development of optical sensing techniques, luminescence and photometric methods, sensor instrumentation, and in the development of new sensors and their applications for environmental analyses.

Contact: Ingo Klimant, klimant@tugraz.at

Ecole Polytechnique Fédérale de Lausanne, Switzerland – EPFL*:* specialist in micro and nanotechnology, in particular in relation to potentiometric, amperometric and voltammetric microsensor fabrication as well as micro-fluidic platforms for on-line preconcentration/regeneration.

Contact: Peter van de Wal, peter.vanderwal@epfl.ch

Nanomateriales y Polimeros S.L., Spain – nanoMyP*:* specialist in the design and synthesis of nano-, micro-particles, polymers, copolymers, smart materials with tailored properties, and the manufacture of polymeric and hybrid nano and micro-materials as well as the development of projects for industry-wide scalability.

Contact: Jorge F. Fernadez Sanchez, jfernandez@nanomyp.com

Université de Bordeaux, France - UBX*:* specialist in environmental observation, biogeochemical cycles of trace elements, geochemical signatures, transport from continent to ocean, speciation, transfer mechanisms, carrier phases, fluxes, (spatial and temporal variability, source identification), bioaccumulation and ecotoxicology of metals in bivalves and fishes.

Contact: Jörg Schäfer, jorg.schafer@u-bordeaux.fr

Università degli Studi di Genova, Italy - UNIGe-IT*:* specialist in research and support for the management and development of monitoring activities, environmental decision making and management of marine coastal and port areas, Web-based data service tool for management integrated environmental information, analysis of trace elements, speciation studies, analysis of micro-pollutants, analysis of chemical species in the marine ecosystem.

Contact: Paolo Povero, povero@unige.it

ETT S.r.l, Italy – ETT*:* specialist in the development of machine-to-machine interface and web data information system implementing standards in order to provide easy access and full interoperability with national and international initiatives and programs.

Contact: Antonio Novellino, antonio.novellino@ettsolutions.com

6 Annex: References

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