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Conference Report

SCHeMA EU Project Summer School Report

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Abstract: This conference report describes the training activities that took place in the frame of the Integrated in **S**itu **Che**mical **MA**pping probe (SCHeMA) summer school organized from the 14th to the 16th of June 2016 in Bilbao (Spain).

Keywords: FP7 Ocean 2013.2 · SCHeMA · Sensors

1. Introduction

SCHeMA is a multi-disciplinary collaborative project funded in the framework of the EU FP7 Ocean 2013.2 program, topic: Innovative multifunctional sensors for *in situ* monitoring of marine environment and related marine activities. SCHeMA aims to provide an open and modular sensing solution for *in situ* high-resolution mapping of a range of anthropogenic and natural chemical compounds coupled to master bio-physicochemical parameters. Key targets are chemicals that may adversely affect marine ecosystems, living resources and ultimately human health, namely a range of trace metals, nutrients, and species related to the carbon cycle, volatile organic compounds, algae species and biotoxins (*www.schema-ocean.eu*). The SCHeMA long-term objective is contributing to enhance ocean observing system capabilities by i) tracking the sources of these compounds, their behaviour and fate as a function of the master bio-geochemical conditions and ii) evaluating their impact on marine water quality trends, thereby allowing one to rapidly localise problems and alert targeted groups. To achieve this goal, a consortium of nine partners has been gathered to develop and field validate robust, innovative, submersible chemical sensing devices that can be readily interfaced and deployed from different facilities to perform continuous monitoring and profiling with adequate spatial and temporal resolution. An *ad-hoc* ICT wireless networking solution allows remote control of the data transfer and system reconfiguration. Gathered data are sent to the SCHeMA web-based data information system for data logging, storage, standardization, evaluation, modelling, and user-friendly accessibility.

An additional central objective of SCHeMA is the training by research of students and early stage researchers (ESR). SCHeMA partners thus organized a summer school, which took place at the PiE Marine Station of Plentzia, in Bilbao (Spain) 14–16 June 2016 (*www.schema-ocean.eu/Summer-School*). This summer school was organized to train the student and ESR attendees in the principle and use of the devices developed by the SCHeMA project partners. The students and ESRs attendants report in here on this summer school at which 56 participants attended: seven external invited speakers, seven SCHeMA principal investigators (PIs), five PiE researchers, eighteen ESR and eighteen master students, as well as a professional photographer.

2. Program

Lectures took place in the morning, followed by the practical workshops in the afternoon. Time was dedicated to informal discussions between participants at the end of each day.

The oral morning sessions included an introductory lecture and seven sessions of one hour covering the main topics addressed as part of the SCHeMA project. The summer school welcomed invited speakers of recognized expertise in each of the topics proposed. The invited speakers gave a general introduction to one of the seven sessions. These 40-minute lectures were then followed by a 20-minute presentation given by the respective SCHeMA partners to make the link between the problematic and the approach undertaken by the SCHeMA consortium. A Round Table, animated by all invited speakers and the SCHeMA PIs, was organised to wrap up the oral sessions.

The afternoon practical workshops were mainly held by the ESR SCHeMA partners. The organization, however, ensured that they could also participate in the practical demonstrations of their SCHeMA fellows.

A summary of the lectures and of the activities performed during the practical workshops is given below. More details on the aspects addressed by the invited speakers can be found in their respective abstract available on the SCHeMA website (*www.schema-ocean.eu/Summer-School*).

2.1 *Introductory lecture*

An introductory lecture was given by ***Mary-Lou Tercier-Waeber*** (SCHeMA Coordinator, UNIGE). In this lecture, an overview of marine diversity, marine resources and impacts of human activities on marine ecosystems equilibrium and productivities was first illustrated using selected examples. The estimated present and future contributions of the oceans and seas to the European and worldwide economy were then presented and used to introduce the concepts of 'Blue Economy', 'Sustainable Blue Economy Growth' and to discuss the associated challenges. Among them, the requirements of more efficient spatial and temporal monitoring of the water quality for a better assessment of environmental stress from land- and marine-based human activities and the definition of appropriate actions to ensure further sustainable management of the marine resources were highlighted. An overview of sensing tools and sensor networks available today was given and their advantages and limitations briefly discussed. SCHeMA objectives could thus be introduced as well as an overview of the SCHeMA research and development activities, expected to contribute to the improvement of monitoring networks. These activities can be divided into seven main topics corresponding to the seven oral sessions proposed in the program.

2.2 *Organics, Volatile Organic Compounds*

Nestor Etxebarria (UPV/EHU, Plentzia Bilbao- Spain) gave his analysis on micro-organic legacy and on emerging pollutants in marine environments. Along this line, a new sensor system developed in the frame of the SCHeMA project by the University of Ulm was introduced. This sensor is able to detect volatile organic compounds in the µg L^{-1} range in marine environments. It is based on waveguide-assisted (silver-halide fibre) evanescent field absorption spectroscopy in the mid-infrared spectral regime. ***Florian Luxenburger*** (SCHeMA PhD student, UULM) specified the detection principles and talked about the challenges encountered at the different development stages. He also pointed out the ongoing improvement activities.

During the practical session, the students got the chance to apply the knowledge they acquired during the morning session by engaging in some practical work. Florian Luxenburger explained the principle of evanescent field spectroscopy in the mid-infrared spectral regime. The students could perform measurements of some volatile organic compounds by using a sensor system similar to the system developed by the University of Ulm in the framework of the SCHeMA project. The obtained IR-spectra were evaluated using dedicated software. Passive samplers and polar organic chemical integrative samplers (POCIS) were described during this practical session by ***Cristiana Mirasole*** (SCHeMA PostDoc, UNIGe-IT) (Fig. 1).

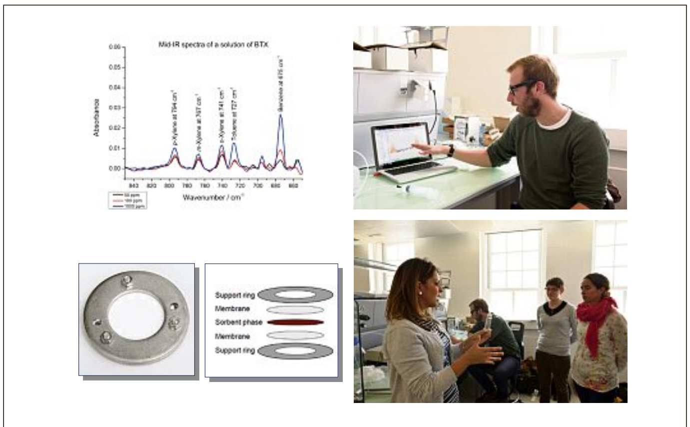

Fig. 1. Top: mid infrared spectroscopy detection of xylene animated by Florian Luxenburger (SCHeMA PhD, UULM). Bottom: scheme of principle of polar organic chemical integrative samplers (POCIS) described by Cristiana Mirasole (SCHeMA PostDoc, UNIGe-IT).

2.3 *Trace Metals*

Jörg Schäfer (SCHeMA PI, UBx) gave an introduction to the world of trace metals playing a central role in the functioning of aquatic systems. Focus was made on their essential or toxic role to living organisms depending on the element, their chemical form and the biological target. The requirement of submersible sensing devices (such as those being developed in the SCHeMA Project) allowing real time, high spatial and temporal monitoring in order to identify anthropogenic and natural sources of trace metals, better understand their environmental distribution and the biogeochemical processes that control their speciation has been stressed.

In this frame, ***Mary-Lou Tercier-Waeber*** presented the current laboratory methodologies for trace metal analysis and gave an overview of field-deployable systems, currently developed to minimize analytical artefacts and allow for more reliable detection of specific fractions of trace metals. Mary-Lou Tercier-Waeber highlighted the potential of microsensors incorporated in submersible probes and interrogated by voltammetry for direct *in situ* detection of the bioavailable fraction of trace metals. Representative examples of applications of such tools, which are developed and miniaturized as part of SCHeMA, have been selected to evidence the extent of their applicability to simultaneous *in situ* detection of a larger range of trace metals.

The practical session was led by ***Miquel Coll Crespi*** (PhD, UNIGE), ***Abra Penezic*** (SCHeMA PostDoc, UNIGE), ***Justyna Lucja Kowal*** (SCHeMA PostDoc, UNIGE), ***Marianna Fighera*** (SCHeMA PhD, EPFL), ***Melina Abdou*** (SCHeMA PhD, UBx), and ***Teba Gil-Diaz*** (PhD, UBs). First the basic principles of trace metal analysis by square wave anodic stripping voltammetry (SWASV) and analytical approaches for its adaptation/miniaturization in view of *in situ* measurements were presented by Abra Penezic, Justyna Lucja Kowal and Miguel Coll Crespi. In short, the technique enables the detection of the bioavailable fraction of trace metals at nanomolar concentrations by applying a negative potential to the electrode for a certain period of time to reduce and pre-concentrate the metal ions present in the sample in the truly dissolved form and as small labile complexes. This step is then followed by an anodic 'stripping' scan in order to oxidize all the pre-concentrated analytes and detect the electrochemical response (peak) proportional in height (peak current) to the analyte concentration and pre-concentration time, and with a specific position (peak potential) for each analyte of interest (Fig. 2). The students could further learn from Marianna Fighera about the fabrication of interconnected micro-disk arrays and three-electrode on-chip sensors using thin film technology and observe them by optical microscopy. The integrated on-chip sensors (Fig. 2) consist of interconnected microdisc arrays (190 to 500 Ir mi-

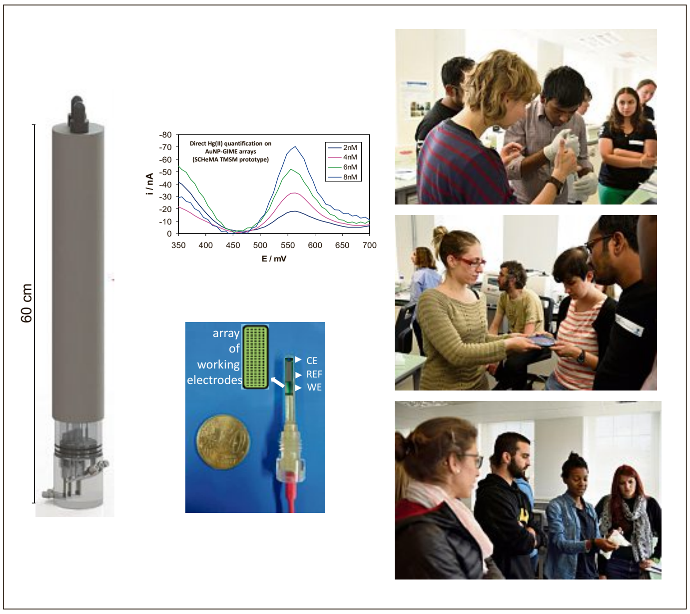

Fig. 2. Left: SCHeMA integrated three channel submersible voltammetric probe and three-electrode on-chip sensor (*i.e.* working, reference and counter electrodes (WE, REF, CE) on a single chip); example of SWASV voltammograms recorded for increasing concentration of mercury after a five minute pre-concentration step. Right, from top to bottom: Abra Penezic (SCHeMA PostDoc, UNIGE) supervising the practical application of SWASV for the direct detection of trace metals at sub-nanomolar concentration; Marianna Fighera (SCHeMA PhD, EPFL) describing the fabrication of on-chip sensors using thin film technology; and Melina Abdou (SCHeMA PhD, UBx) presenting the sample preparation procedures for subsequent detection of trace metals using classical laboratory techniques.

crodiscs of 5 µm diameter) coated electrochemically with gold nanoparticles or mercury micro-hemispheres, a counter electrode and a reference electrode whose testing is currently ongoing. An innovative approach, based on hydrogel coating to protect the sensor surface against fouling and to eliminate the influence of ill-controlled dynamic conditions on voltammetric signals, was also explained.

The students acquired practical skills on this technique by using a prototype potentiostat (an integrated three-channel submersible voltammetric probe) developed as part of SCHeMA for *in situ* detection of a range of trace metals. They used a gold microelectrode for detecting arsenic and mercury in a model electrolyte solution and antifouling gel integrated mercury-plated iridium-based microelectrode arrays for simultaneous monitoring of cadmium, copper and lead in a seawater sample collected from the Plentzia Marine Station mesocosm. To wrap up the practical session, the students were also reminded that, within the SCHeMA project, validation with classical techniques such as GC-ICP-MS or HG-AAS will be used to assess the performance of these prototypes. Such conventional sampling and sample preparation procedures were presented by Melina Abdou and Teba Gil-Diaz.

2.4 *Nutrients, Carbon Cycle*

Luis Angel Fernandez (UPV/EHU, Plentzia Bilbao-Spain) addressed the topic of estuarine acidification within the wider context of ocean acidification whereas ***Eric Bakker*** (SCHeMA PI, UNIGE) presented series of electrochemical strategies for the development of *in situ* ion-sensing platforms for aquatic systems, some of the activities that are part of the SCHeMA project such as the development of potentiometric sensors for pH, calcium, carbonate and pCO_2. It has been emphasized that for appropriate sensitivity for nitrate and nitrite-selective potentiometric sensors, preliminary desalination (chloride reduction down to millimolar levels) and acidification (to *ca.* pH 4.8, to reduce the interference of hydroxide anions) of the seawater is necessary.

The practical session was led by ***Nadezda Pankratova*** (PhD, UNIGE) and ***Maria Cuartero Botia*** (SCHeMA PostDoc, UNIGE). There were two main aims of the practical with the students: i) understanding the fundamental principles of the operation of the potentiometric sensors as well as desalination and acidification approaches; ii) preparation of the sensors and their application in seawater, as well as changing the pH of different samples with the acidification module.

All the fundamental concepts involved in the detection of species relevant to the carbon cycle (pH, CO_3^{2-} and Ca^{2+}) and nutrients (NO_3^- and NO_2^-) were recalled during the practical session. The students were informed about the configuration of the submersible probe used for the SCHeMA field measurements. Two exchangeable units were presented as well as the flow cells for potentiometry, desalination and acidification. The first unit is composed of one potentiometric flow cell with four miniaturized electrodes: three potentiometric sensors (for pH, CO_3^{2-} and Ca^{2+}) and one custom-built miniaturized reference electrode. The second unit comprises sequentially the electrochemical cell for the desalination, the flow cell for the in-line acidification of the desalinated seawater (from pH 8 down to pH 5) and the potentiometric flow cell with three sensors (for NO_3^-, NO_2^- and pH) and the reference electrode. Finally a procedure of potentiometric sensor fabrication was demonstrated using miniaturized glassy carbon electrodes, lipophilic carbon nanotubes (f-CNTs) as ion-to-electron transducers and permselective membranes containing a different ionophore for each ion.

The students prepared miniaturized calcium-selective electrodes, first depositing the f-CNTs by drop casting and then the ion-selective membrane on top (Fig. 3). The electrodes were finally incorporated into the flow cell together with a reference electrode. Since the electrodes need an appropriate conditioning procedure for a correct performance, students observed the operation with pre-conditioned electrodes measuring directly pH, CO_3^{2-} and Ca^{2+} in seawater collected from the PiE marine station mesocosm. In the second part of the practical work, the students assembled all the elements of the acidification cell and used it for acidifying both seawater and freshwater samples (Fig. 3).

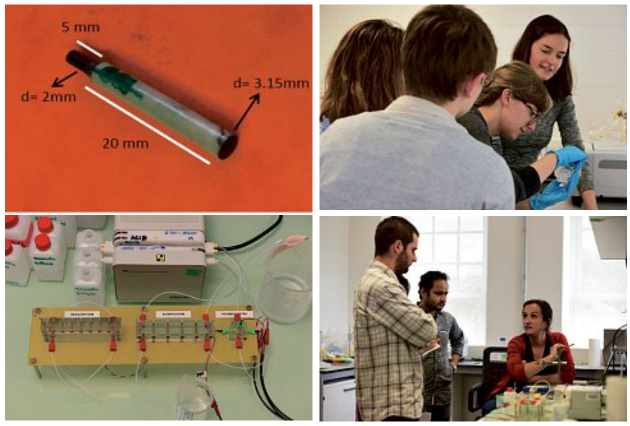

Fig. 3. Top: Preparation of a solid-state ion selective electrode under the supervision of Nadezda Pankratova (PhD, UNIGE); Bottom: Flow-through system for potentiometric detection of nutrients after on-line desalination and acidification described by Maria Cuartero Botia (SCHeMA PostDoc, UNIGE).

2.5 *Algae, Biotoxins*

A general overview of the challenges of toxin-producing algae classes was given by ***Veronique Séchet*** (Ifremer, Nantes-France). ***Ingo Klimant*** (SCHeMA PI, TuGRAZ) presented an approach to deal with harmful algal blooms, *i.e.* detect and identify different algae classes based on their intrinsic fluorescence properties.

During the practical course led by ***Silvia Zieger*** (SCHeMA PhD, TuGRAZ), ***Lukas Troi*** (mechanical engineer, TuGRAZ) and ***Ingo Klimant*** (SCHeMA PI, TuGRAZ), the features of the detection system were demonstrated to the student groups, who discovered the optical and electronics components of the SCHeMA system as well as the characteristics of the instrument. The students could get familiar with the information of the measured time-drive-plot representing the emitted fluorescence signals by algae cells passing through the system over time (Fig. 4).

Three different algae species belonging to three different classes – cyanobacteria, diatom and green algae – were analysed to demonstrate the differences between the emitted fluorescence signals of cyanobacteria and other algae. A histogram from the average measurement signals enabled the visualization of the relative pigment pattern of the cyanobacteria and algae which could be further used to identify an unknown sample depending on the relative pigment pattern.

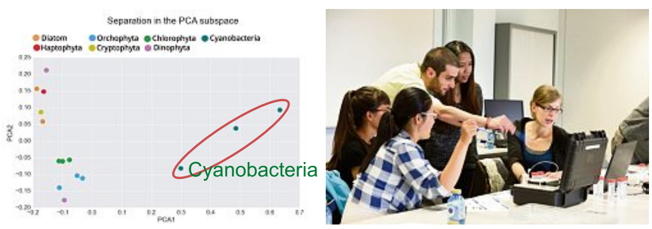

Fig. 4. Practical session on the detection of algae and biotoxins supervised by Silvia Zieger (SCHeMA PhD, TuGRAZ).

2.6 *Microtechnology*

Luis Liz-Marzan (CIC biomaGUNE, San Sebastian-Spain) focused on the peculiar optical properties of nanoparticles, related to localized surface plasmon resonances (LSPR) which can be tuned through the size and shape of the nanoparticles, which are hence ideal candidates for biosensing applications. ***Marianna Fighera*** (SCHeMA PhD, EPFL) presented the microtechnology contribution to the SCHeMA developments which include the manufacturing of interconnected microelectrode arrays and on-chip integrated three electrode systems under various geometries for voltammetric detection of trace metals; microfluidic platforms for on-line desalination, VOCs detection and toxin-preconcentration.

2.7 *Environmental Regulation and Monitoring*

Ingrid Puillat (Ifremer, Brest-France) introduced the needs raised by the European policies and the society as well as the underlying scientific targets. ***Laurent Delauney*** (Ifremer, Brest-France) gave some examples of the existing equipment and infrastructures and of the related challenges.

Emmanuele Magi (SCHeMA PI, UNIGe-IT) then presented the current approaches used for the monitoring of trace volatile organic compounds based on sample collection, sample separation/pre-treatment prior to laboratory analysis. Emphasis was put on the challenges related to the preservation of the original sample composition. Then he introduced indirect approaches based on biomonitoring and passive samplers. Theoretical and analytical approaches for calibration of passive samplers were illustrated using the Polar Organic Chemical Integrative Sampler (POCIS) in particular analyte detection at ultra-trace levels (below ng/L).

2.8 *Data Management*

Patrick Gorringe (Senior Operations Officer at EuroGOOS) presented the past, present and future of the existing marine operational observing networks, their organization and showed examples of existing portals where free and open data are accessible to all possible users. Marine observations are crucial to further the current understanding of the oceanic environment and to supply scientific data to meet society's needs (*e.g.* weather forecasts, modelling of the climate and of its evolution). The existing portals are often built on initiatives at local, regional, European and Global scale. There is a requirement for increased integration and coordination of those activities within the community.

Paolo D'Angelo (SCHeMA PI, ETT) thus introduced the concepts of Sensor Information Service and discussed requirements for worldwide access and interoperability of such a service. The different standards developed to fulfil these requirements and their functionalities were explained. The approach selected, the standards used and the interfaces designed to develop the SCHeMA Sensor Web Interface and Sensor Web Portal infrastructure were presented.

Fig. 5. Practical session on data management animated by Paolo D'Angelo (SCHeMA PI, ETT) and Corinne Nardin (SCHeMA PI, UPPA). Left: Training on access to the data *via* the SCHeMA portal. Right: international trainee group who won the contest, *via* the best presentation of their data analysis.

The practical session was led by ***Paolo D'Angelo*** and ***Corinne Nardin*** (SCHeMA PI, UPPA). Data corresponding to the *in situ* monitoring of the diurnal cycling of dynamic metal species in a stream under contrasting photobenthic biofilm activity and hydrological conditions were made available to the students *via* the SCHeMA website with which they could get familiar (Fig. 5). Literature was as well given to the students prior to the summer school for them to be able to understand and analyse the data.

This practical was associated to a competition. The students had to prepare a short oral presentation on the conclusions they made on the data which they downloaded from the SCHeMA website and analysed. The best presented analysis was awarded a prize.

3. Conclusion

Overall, the SCHeMA summer school reached the main objectives, *i.e.* to educate the attendees on the current scientific and legal issues related to ocean observing capabilities. Moreover, the SCHeMA ESR who prepared short oral communications and practical sessions demonstrated good teaching skills. Attendees participated with enthusiasm to lectures, practical sessions and social events.

Acknowledgements

The success of the Summer School was ensured by the SCHeMA and local organising committees which are greatly acknowledged. From the SCHeMA consortium, special thanks are addressed to Melina Abdou (University of Bordeaux), Mary-Lou Tercier-Waeber (University of Geneva), Jörg Schäfer (University of Bordeaux) and Corinne Nardin (Université de Pau et des Pays de l'Adour). The support of the local organizing committee and of the local and remote staff members of the PiE UPV/EHU is greatly acknowledged for several aspects, in particular Manu Soto (Deputy Director), Ionan Marigomez (Director), Urtzi Izagirre (researcher). Irune Valenciano (PiE, UPV/EHU) is also especially thanked for the support provided during the whole Summer School.

The success of the Summer School has also been ensured by the participation of the partners of the SCHeMA consortium (University of Geneva-Switzerland; Idronaut s.r.l.-Italy; University of Ulm-Germany; Technical University of Graz-Austria; EPFL SAMLAB – Switzerland; University of Bordeaux – France; ETT S.p.A. – Italy; University of Genoa – Italy).

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