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Environmental Sensing of Aquatic Systems at the University of Geneva

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Abstract: Aquatic environments are complex living systems where biological and chemical constituents change rapidly with time and space and may exhibit synergistic interactions. To understand these processes, the traditional approach based on a typically monthly collection of samples followed by laboratory analysis is not adequate. It must be replaced by high-resolution autonomous *in situ* detection approaches. In our group at the University of Geneva, we aim to develop and deploy chemical sensor probes to understand complex aquatic systems. Most research centers around electrochemical sensing approaches, which involves: stripping voltammetry at gel-coated microelectrode arrays for direct measurements of bioavailable essential or toxic trace metals; direct potentiometry for the measurement of nutrients and other species involved in the nitrogen and carbon cycles; online desalination for oceanic measurements; the development of robust measurement principles such as thin layer coulometry, and speciation analysis by tandem electrochemical detection with potentiometry and dynamic electrochemistry. These fundamental developments are combined with instrument design, both in-house and with external partners, and result in field deployments in partnership with environmental researchers in Switzerland and the European Union.

Keywords: Electrochemical sensors · Environmental monitoring · (Micro-)nutrients/pollutants · Nitrogen and carbon species · Optodes

1. Introduction

Significant biological and chemical changes in the water column of aquatic systems can be observed on the time scale of minutes to hours and on the depth scale of centimeters. Time-dependent gradients of temperature, light and chemical species influence the competition between biological organisms that eventually result in the development of algal blooms and a drastic change in biological diversity over time. To understand the mechanisms resulting in such changes, the traditional approaches of discrete sampling followed by an off-site laboratory analysis are not sufficiently adequate: the chemical and biological composition of a sampled aliquot will invariably change when taken out of its environment, and the achievable sampling rate does not reflect the highly dynamic bio-geochemical properties of aquatic systems. In an ideal world, one may imagine to solve this analytical challenge with chemical probes that exhibit the same ease of use as conductivity, temperature and depth (CTD) probes. Indeed, in clini-

cal diagnostics situations where samples are relatively uniform and where frequent recalibration runs and temperature control are easily achieved, electrochemical sensors have been exquisitely successful. Can we learn from this success to make progress in environmental monitoring?

Today, a range of environmental sensors is available commercially for automated and/or continuous monitoring of aquatic systems.^[1] Commercially available sensors can be combined and sometimes integrated in a common platform. So far, most monitoring platforms only poorly integrate systems for biological monitoring with sensors for chemical and physical profiling, which include pressure, temperature, conductivity, pH, O₂, NO₃⁻, chlorophyll-*a*, phycoerythrin and phycocyanin.

The wet chemistry approaches currently available are normally based on flow injection analysis using traditional chromogenic reactions that requires sampling, fluidic handling, mixing, storage and resupply of reagents, and instrumental readout.^[2] Their acquisition and operation is rather costly and their profiling speed is limited due to the slow response time on the order of minutes. *In situ* instruments (<http://www.subchem.com/>) are offered for a limited number of analytes, mainly NO_x nitrogen species, silica and phosphate, and are instrumentally very different from the ones required for measurement of pH (electrochemical) and oxygen (electrochemical,

optical). Carbon dioxide is detected with Severinghaus probes, which requires the passage of the analyte gas across a membrane for re-equilibration at the inner side where a pH measurement is performed.^[3] The response time of such sensors is between 1 and 3 min, which is rather slow for chemical profiling.

Other types of electrochemical sensors (besides the ones mentioned for pH, dissolved O₂ and *p*CO₂) exist and have been successfully used for the detection of nitrogen nutrients and carbon species in surface waters^[4] and sediments.^[5] Significant progress in the development of membrane electrodes (interrogated potentiometrically or with dynamic electrochemistry) has been made in recent years, with the realization of ultra-low detection limits, new chemical recognition elements, new membrane materials and all-solid-state sensing configurations.^[6]

Our group at the University of Geneva aims to form an arch between fundamental sensor research and environmental application. While approaches such as stripping voltammetry on gel integrated sensors originally developed by Tercier-Waeber and Buffle are considered reasonably mature, other concepts based on membrane electrode chemistry or (bio-)polymer functionalized gel-integrated sensor arrays are only now being explored for *in situ* monitoring work.

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2. *In situ* Freshwater Chemical Sensing Tools to Help Understand Rapid Microscale Plankton Dynamics

This project is supported by a SNSF Sinergia grant between the University of Geneva (Bakker and Tercier-Waeber), EAWAG (Pomati) and ETH Zurich (Wehrli). There exist a number of mechanisms by which small-scale environmental heterogeneity may affect biodiversity, productivity and impact on the carbon cycle in aquatic environments. By creating a large number of microhabitats, small-scale heterogeneity may favor coexistence of many organisms with different growth requirements. In aquatic systems, the vertical structure of the water column represents the most heterogeneous dimension of phytoplankton spatial ecology because horizontal mixing is normally 2–3 orders of magnitude faster than vertical mixing.^[7] This allows partitioning of phytoplankton species along the opposing gradients of light and nutrients over a stratified water column.^[8,9] Microscale heterogeneity can influence biodiversity and productivity by favoring species that are mobile or buoyant, such as many cyanobacteria, and are therefore able to reach the most favorable microhabitat for their proliferation.^[7,10] This results in an enhanced growth of some dominant species over a small depth interval where, for example, light intensity and nutrient concentration are optimal.^[11] Consumers compete for locally available resources, which alters local and overall lake resource availability.^[12] Aggregation of phytoplankton biomass may affect biogeochemical dynamics, particularly concerning the feedback between primary production and remineralization. By clustering near phytoplankton, heterotrophic bacteria may not only accelerate remineralization of algal biomass but also enhance plankton productivity by mobilizing inorganic nutrients.^[13] Moreover, phytoplankton aggregates with heterotrophic bacteria may favor microenvironments for anaerobic bacteria such as methanogens, whose metabolism may have an important impact on the carbon budget.^[14]

Ecological evidence for triggers of fast phytoplankton blooms is controversial and the temporal and spatial scales at which local gradients and processes are acting on planktonic communities are not yet known. One reason is that phytoplankton microenvironments remain difficult to interrogate *in situ*. Researchers at EAWAG have developed an automated monitoring platform based on a scanning flow-cytometer that features individual level resolution in the phytoplankton cells allowing for an in-depth analysis of how organisms change with their growth environment.^[15]

In this cooperative project, a suite of electrochemical (and finally fluorescent) sensors for macronutrients, micronutrients/pollutants, and physicochemical parameters are tested in the laboratory, validated, then deployed in the field and used in tandem with scanning flow-cytometry thanks to the EAWAG automated monitoring platform, which operates on Lake Greifen. Ecological monitoring will set the requirements for sensor development, and sensing tools will influence monitoring strategies in what we hope to be a truly interactive and adaptive approach.

This project will provide new tools to interrogate plankton micro-environments at high resolution and evaluate the ecosystem implications of microscale gradients and rapid biodiversity dynamics, using electrochemical sensors. As shown in Fig. 1, the sensors will be first deployed on the platform in parallel with the scanning flow cytometer after tubular sampling at depth, followed by submersible electrochemical sensor probes, and finally the integration of sensing beads into the flow cytometry readout for a comprehensive instrument that allows one to observe biological and chemical parameters simultaneously.

3. Integrated *in situ* Oceanic Chemical Sensing Probes

This project forms part of the EU FP7-OCEAN 2013 SCHeMA project (www.schema-ocean.eu), which is coordinated by the University of Geneva (Tercier-Waeber), and aims to develop oceanic sensor systems for a range of trace metals, nutrients, anthropogenic organic compounds, algae, biotoxins as well as species relevant to the carbon cycle.

Problems with man-made organic pollutants are mainly related to their toxicity, long degradation period and/or liability to bioaccumulate. Trace elements are ubiquitous and diverse components of the earth's

geochemistry, and play critical roles in the functioning of ecosystems. Some metals (*e.g.* Hg, Cd, Pb) and metalloids (*e.g.* As) exhibit 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. Trace metals are inherently persistent, *i.e.* they are neither created nor destroyed by anthropogenic or biological processes.^[16] 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 bio-available.^[17,18] Metals transported to the sediment can be either buried or remobilized *via* various diagenetic processes, *e.g.* reduction of manganese and iron minerals during mineralization of natural organic matter, reaction with sulfides produced during sulfate reduction or species transformation such as reduction (As) or methylation (Hg), which may strongly increase their solubility and/or toxicity. Natural (*e.g.* estuarine currents) and/or anthropogenic (*e.g.* dredging) sediment resuspension also play an important role in contaminant recycling.

Transformations among the various metal species are usually reversible, with the important consequence that the speciation of a metal is a function of the bio-physicochemical condition of the medium. It is therefore obvious that standard procedures based on the measurements of total, or total dissolved metal concentrations alone do not yield sufficient information. The measurements of specific metal species or groups of homologous metal species coupled to master bio-physico-chemical parameters (temperature, pH, conductiv-

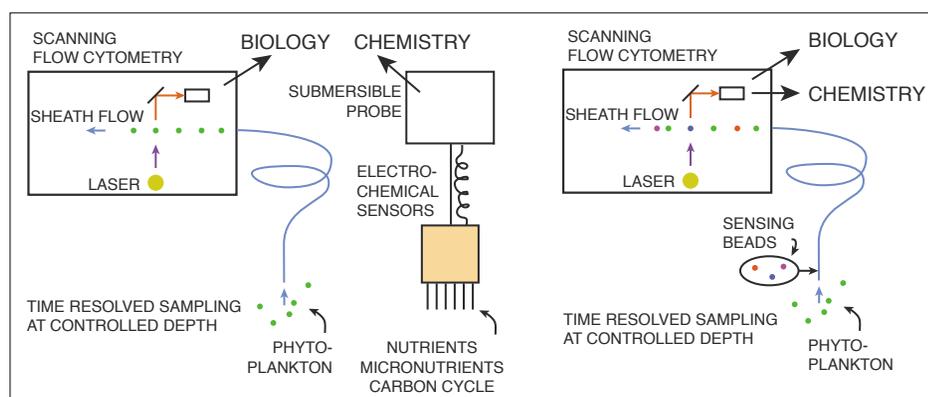


Fig. 1. Two parallel efforts to improve chemical sensing capabilities for plankton studies: Left: Nutrient and micronutrient sensing based on independent profiling technology supplementing the biological data from the flow cytometry. Right: Chemical sensing using sensing beads and the flow cytometry as integrated biological and chemical detector for the same sample volume.

ity, dissolved oxygen, primary productivity), are required to assess the influence of habitat-specific constraints on the speciation of metals and thus on their potential ecotoxicological impacts which may occur long after their release. For example, an increase in temperature may increase bacterial activity, 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.^[18] Note that redox potential is no longer considered a master variable, as *in situ* accurate measurements and rigorous interpretation of this parameter are often not possible in complex media,^[19] although it may still provide useful information on the oxidizing or reducing character of the medium.

A better understanding of these processes will be offered by the development of appropriate sensor networks allowing one to monitor hazardous substances over the long-term, at the appropriate time scale, in the marine environment. This project aims to develop, apply and field validate an autonomous system for monitoring marine ecosystems and water quality. We are developing together with partner researchers a system that consists of a plug-and-play adaptive wireless chemical sensor network serving as a front-end for gathering detailed spatial and temporal information (seconds to hours) on water quality and status based on a range of chemical hazardous compounds coupled to master bio-physicochemical parameters. An ad-hoc ICT (Information and Communication Technologies) wireless networking solution will allow remote control of data transfer and system reconfiguration according to the OGC (Open Geospatial Consortium) standard. The gathered data will be reported back to a web-based data information system for data stamping, storage, standardization, modeling and for user-friendly accessibility. The sensing tools are being optimized throughout their development *via* short field tests and inter-comparison with data obtained using established laboratory techniques. Long-term field applications in estuary and coastal systems will be performed to evaluate their ruggedness and reliability for high resolution spatial and temporal monitoring, define their suitability for different applications and commercial production, and demonstrate monitoring capability and feature to end-users and policy decision makers.

Toward this aim, we are involved in i) the analytical and technical developments

of the sensors and probes for the mapping of trace metals, nutrients and species relevant to the carbon cycle, ii) the validation of both individual chemical probes and the complete integrated system through systematic tests under controlled conditions in laboratory and field time series investigations in estuaries and coastal sea areas, iii) the application and demonstration of the SCHeMA system to biogeochemical studies and potential end-users through long-term field monitoring in marine environments.

Chemical strategies to achieve the above mentioned goals are briefly outlined below.

4. Chemical Strategies for Environmental Sensing

4.1 Stripping Voltammetric Sensors

Two types of voltammetric sensors have been applied *in situ* in various environmental studies. The Au/Hg amalgam electrode developed by Luther^[20] and the gel integrated microsensors (GIME) developed by Tercier-Waeber *et al.* (see ref. [17] for a recent review). The Au/Hg amalgam electrode allows one to directly measure Mn(II) and Fe(II) and other redox species ($O_2(aq)$, $H_2O_2(aq)$, $S_2O_3^{2-}$, S^0 , S^{2-} in S_x^{2-} , $FeS(aq)$). This sensor, integrated in various sub-

mersible devices, was successfully applied to fresh and marine aquatic systems. The latter class of electrodes was developed in Geneva and is covered by an agarose gel that acts as a dialysis membrane to separate most of the fouling components and also insure analyte transport by pure diffusion (*i.e.* no influence of the ill-controlled hydrodynamic condition of the media on the sensor response). Moreover when a GIME is used with anodic stripping technique, the metal flux (or current) during the pre-concentration step selectively represents the so-called dynamic metal species (*i.e.* the sum of the free metal ion and the labile and sufficiently mobile metal complexes) which also determines the flux of metal^[21] toward organisms. GIME are thus of particular interest to study the role of trace metals as micronutrients or micropollutants. They are today already integrated in submersibles probes allowing high resolution spatial and temporal simultaneous monitoring of the dynamic fraction of Cu, Pb, Cd, Zn or Mn(II) (Fig. 2a,c) coupled to master bio-physicochemical parameters (pressure, temperature, conductivity, salinity, pH, dissolved O_2 , chlorophyll-*a*).^[17,22] The results revealed that phytoplankton blooms and their photosynthetic/respiration processes, coupled to other physicochemical processes such as sorption and photoreduction processes, may induce

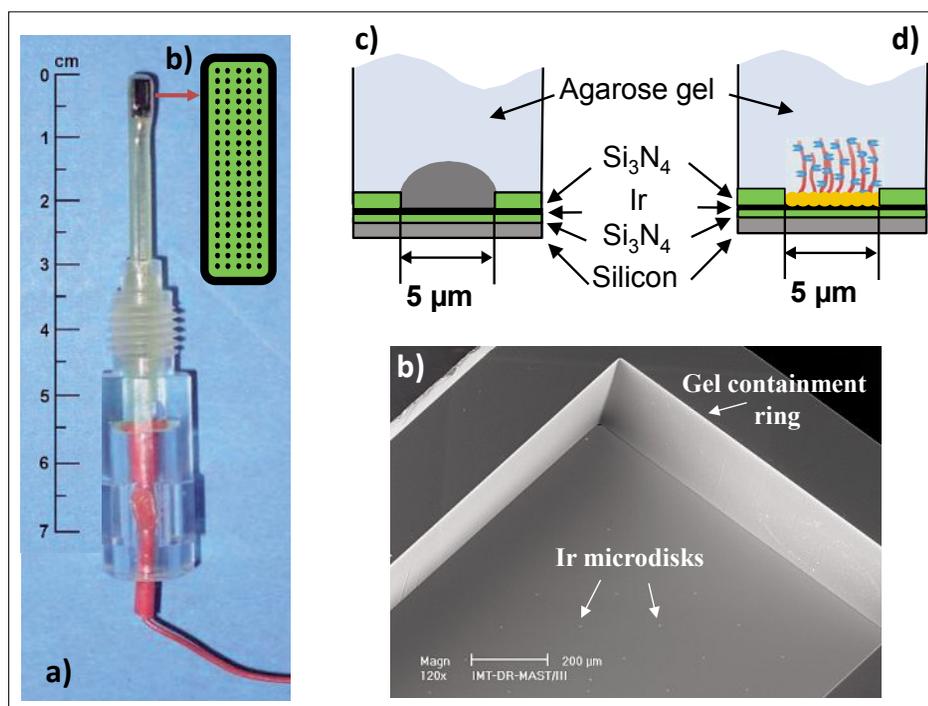


Fig. 2. Picture of a GIME sensor mounted in a Plexiglas holder to allow its incorporation in the flow-through measuring cell of the Voltammetric *in situ* Profiling system (VIP).^[17] The GIMEs, produced by thin-film microtechnology, are based on a 5×20 interconnected Ir microdisk chips (b) wire bounded and encapsulated on a printed circuit board (a). The surface of the chip is covered by a $300 \mu m$ thick pure agarose gel (c, d). The Ir microdisk substrates are electrochemically plated with Hg (c) or AuNP (e.g. for detection of respectively Cu(II), Pb(II), Cd(II), Zn(II), Mn(II), Fe(II) and As(III)). Electrochemically plated AuNP can be chemically functionalized with (bio-)polymers (d)^[24] (e.g. for selective recognition and chemical preconcentration of target analytes prior their voltammetric detection).

short-term (daily and bi-hourly) variations in bioavailable metal concentrations similar in magnitude to those previously thought to occur only at the seasonal timescale^[22] (see Fig. 3). Such diurnal variation, not measurable with classic sampling and total dissolved measurement strategies, may lead to toxicological stress for biota.^[23]

GIME sensors for Fe(II) and As(III) and (bio-)functionalized GIME for As(V) and Hg species are being optimized/developed to further enrich the palette of chemical species that can be determined with this platform. The originality of these sensors is not only the efficiency of the gel against fouling but also the potential to perform all analytical steps (separation, chemical and electrochemical pre-concentrations, buffering, redox state modification) inside the gel (*i.e.* mm³ volume) or at the sensor surface without the need of reagent addition.

4.1.1 Fe(II) and As(III) GIME

Analytical methodology for square wave cathodic sweep voltammetric (SWCSV) detection of Fe(II), with a LOD (lower detection limit) of 1 μM, using a 10 μm in diameter GIME single microelectrode has been already developed and validated in laboratory for direct measurements in freshwater natural samples. With a view to improve detection limits, and include Fe(II) measurements to the micronutrients/pollutants measured simultaneously with the VIP, the methodology is

being adapted to the GIME microsensor arrays. The GIME arrays is based on a microchip of 100 interconnected microelectrodes (Fig. 2b); the voltammetric current measured is the sum of the current generated at each individual microelectrode. Conditions for anodic stripping square wave voltammetric detection (SWASV) will be optimized to further improve the detection limit and insure long-term reliability.

A gold nanoparticle plated gel integrated single microelectrode (AuNP-GIME) is being developed for SWASV measurements of As(III). Using this sensor, direct As(III) measurements in freshwater, without interference of Cu, can be performed for pH ≤ 8. The methodology is adapted to a 100 interconnected AuNP-GIME arrays. Moreover to insure a controlled pH at the sensor surface without the need of reagent addition in the sample (*i.e.* which significantly increase complexity for field deployment and may influence natural equilibrium), a methodology is being developed to trap a buffer in the gel covering the sensor and acting as antifouling membrane.

4.1.2 (Bio-)polymer-functionalized GIME

We are also exploring the development of (bio)polymer-functionalized GIMES for selective and sensitive voltammetric quantification of As(V), Hg(II) and CH₃Hg(I). For Hg species, sensors based on poly-

mer brushes AuNP-GIME functionalized with compounds for selective recognition of the target analytes are explored (Fig. 2d). While promising results have been obtained in the laboratory for detection of Hg(II) using peptide-functionalized polymer brushes microelectrode arrays,^[24] further studies are required to improve selectivity and sensitivity. For As(V), a polymer, chemically synthesized on a AuNP- or C-GIME, to catalyze the reduction of As(V) in As(III) *via* the electrochemical tuning of its RedOx state will be explored. Analytical and voltammetric conditions will be optimized to allow sequential AuNP-GIME measurements of As(III) prior and after As(V) reduction (*i.e.* detection of As(III) and As(III) + As(V)).

4.2 Membrane Electrodes

4.2.1 Desalination Module

For a number of membrane-electrode based sensing approaches, the high salt content of seawater (*ca.* 0.6 M NaCl) is a serious interferent. The high salt concentration can be reduced with an electrochemical thin layer desalination principle developed in our group,^[25] see Fig. 4. This involves an electrochemical plating of the halides (chloride and bromide) from the sample to a silver electrode, while the counterions are transferred across a cation permselective membrane (Nafion) from the sample to an outer solution. For seawater as the outer solution, the salt concentration can be reduced down to the millimolar level. If more dilute solutions can be used, micromolar salt levels are achievable. Anions that do not form insoluble salts with silver are not removed, hence allowing one to detect these species downstream with less interference.^[25] This type of desalination is reversible (desorption is achieved electrochemically), requires very low power because of the small sample volume (thin layer sample) and utilizes robust materials.

4.2.2 Nutrient Sensors

The nutrients nitrite, nitrate and phosphate are detected using solid-state sensors based on ion-selective membranes containing selective receptors (ionophores). For measurement in seawater samples, these sensors are coupled to the desalination module described above. We are also exploring flow-through ion-exchanger modules in the acid form to achieve online acidification of the sample to a pH of about 3 to reduce hydroxide interference. Three different readout approaches are being developed in view of optimal sensitivity and robustness for *in situ* analysis. Zero current potentiometry will continue to be used and optimized for direct nutrient detection. But a promising methodology is thin layer coulometry, as a calibration-free approach that

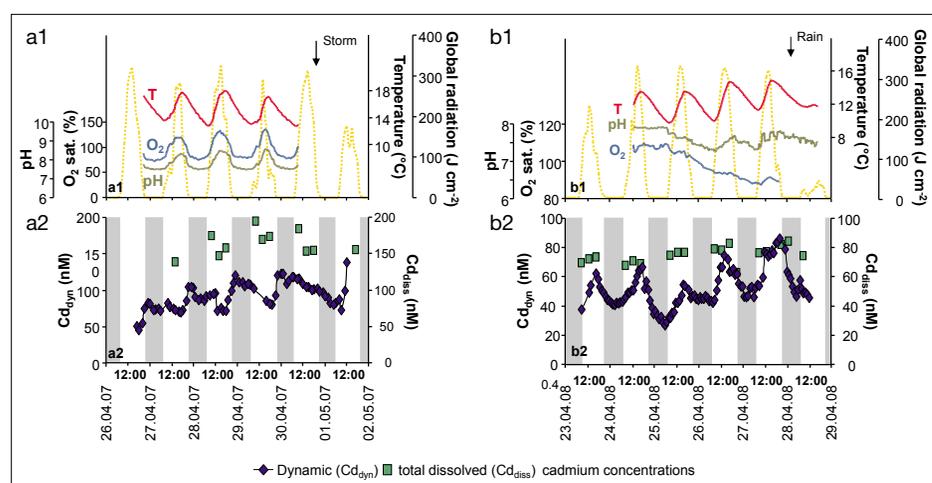
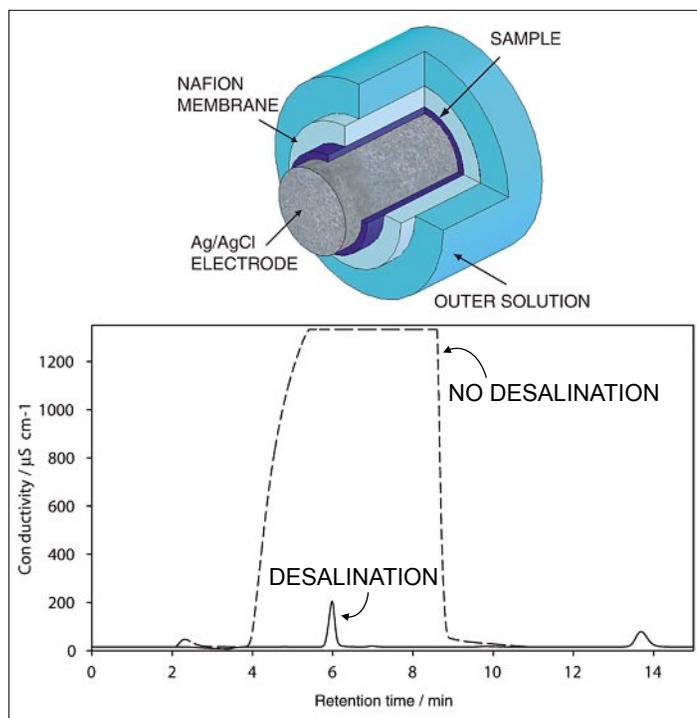


Fig. 3. Summary of continuous ancillary measurements (conductivity, temperature, pH, and oxygen saturation) (a1, b1), hourly global radiation data (a1, b1) and dynamic and total dissolved Cd concentrations (a2, b2) monitored in the Riou-Mort River (Joanis site) during two field campaigns characterized by the presence (a) and the absence (b) of important photobenthic biofilm communities. Shaded bars correspond to nighttime. Diurnal T cycle is induced by diurnal cycle of solar radiation. Well defined diurnal pH and dissolved oxygen cycles observed during the first campaign (a1) reflect photosynthetic/respiration activity of benthic biofilm. The diurnal cycling of Cd_{dyn} was found to be controlled by the balance between two distinct, competitive processes: biofilm-induced sorption processes and photoreduction of small (<20 nm) colloidal Mn oxides.^[22] In the presence of optimum conditions for biofilm photosynthesis, sorption processes prevail due to the increase in pH (a1) leading to minimum Cd_{dyn} concentration during the afternoon (a2). In the absence of significant biofilm activity, photoreduction of colloidal Mn controls the Cd_{dyn} concentration leading to maximum concentration in the afternoon (b2). These latter processes are not detectable from measurements of Cd_{diss} in collected samples (b2). Modified from ref. [22].

Fig. 4. Electrochemical desalination module based on the plating of halides as silver halide onto the electrode and transfer of the counter cation across the tubular Nafion membrane (top).^[25] Injection of artificial seawater sample into an ion chromatograph before (broken line) and after (solid line) online desalination (bottom).



is attractive for autonomous sensing.^[26] Chronopotentiometry is explored to eliminate influences of the speciation of the ion in the sample,^[27] which may be especially attractive for phosphate.

4.2.3 Probes for Species Relevant to the Carbon Cycle

A number of attractive sensor principles to detect species important to understanding the carbon cycle have recently been developed by our group and are being adapted and optimized for use in an aquatic environment. The detection of total alkalinity is explored by chronopotentiometry and thin layer coulometry at ion-selective membranes.^[28] In this approach, a flux of hydrogen ions from the membrane into the seawater sample is instrumentally imposed and the pH change is monitored at the same interface over time (see Fig. 5). Alternatively, the direct detection of carbonate with a selective tweezer-type ionophore containing trifluoroacetyl groups is explored by electrochemistry.^[31] Calcium is detected by membranes containing highly selective ionophores, thereby exhibiting sufficient selectivity for analysis in complex samples. Carbon dioxide is measured by direct potentiometry between a pH electrode and a carbonate-selective electrode,^[29] giving much faster response times compared to most other CO₂ measurement principles (see Fig. 5).

4.3 Bead-based Sensing Approaches

An optical readout with chemical sensing beads is being explored for possible integration with scanning flow cytometry (see above). Traditional bead-based ion

sensors are based on a competitive ion-exchange or cooperative co-extraction of two ions, making it difficult to measure the activity of just one ion.^[32] This limitation can be overcome for dilute samples if one operates the beads exhaustively, removing a large fraction of the analyte from the sample.^[33] For this purpose, sample aliquots of defined volume must be treated with the sensing beads. This approach allows one to detect the available (extractable) analyte fraction from the sample.

In an alternative approach under study in our group, a direct potentiometric read-

out of sensing beads is being explored by the use of potential sensitive dyes. While preliminary (and yet unpublished) results suggest a response behavior analogous to an electrochemical readout, the role of matrix effects must be further explored and the underlying response mechanism must be fully understood before a possible implementation in environmental sensing systems.

5. Conclusions

The projects we have recently embarked on mark a departure for the benchtop scientist, who is often smitten by the beauty of chemical principles. The real world is not as forgiving and the process of bringing new analytical principles to the field and in the hands of practicing environmental scientists is very challenging. But the journey brings its own rewards and the cooperation of the many researchers coming together to solve important, complex problems is satisfying and ultimately the only mechanism to bring true progress to fruition. We are looking forward to new discoveries in this interdisciplinary effort.

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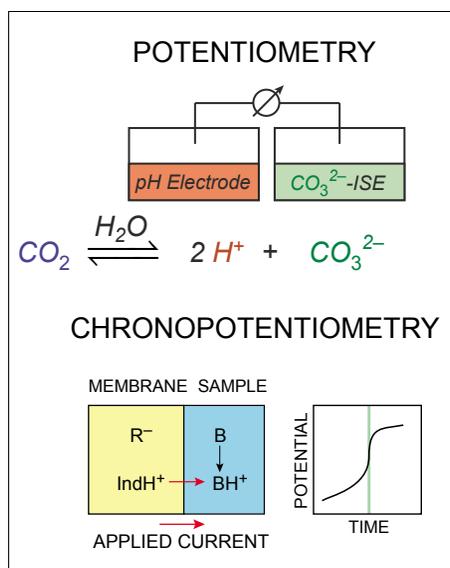


Fig. 5. Direct detection of carbon dioxide by direct potentiometry, using a carbonate electrode with (in theory) sufficient selectivity for seawater analysis (top).^[29] Electrochemical (constant current) perturbations at ion-selective membranes for direct alkalinity sensing (bottom).^[30]

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