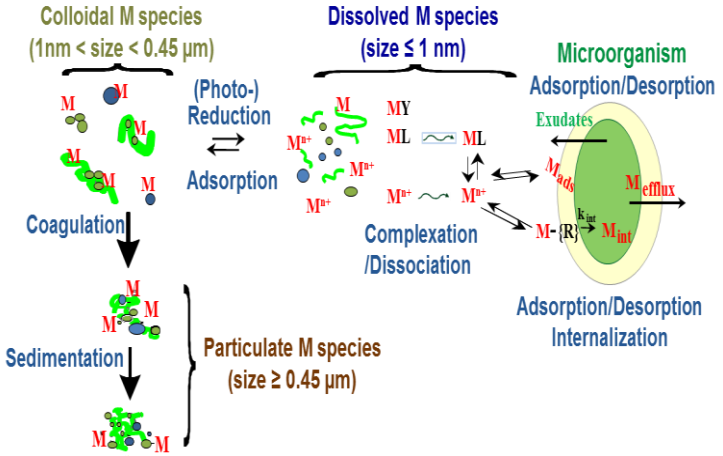
In situ detection of the bioavailable fraction of a range of toxic/essential trace metals

Motivation

Trace elements 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 low concentrations, while others are either essential or toxic (e.g. Fe, Cu, Zn), depending on their concentrations and the nature of the organisms.

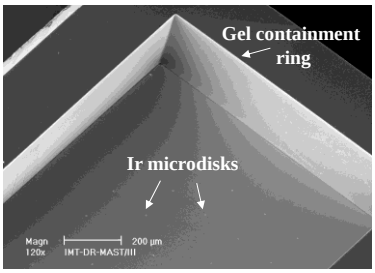
Assessing the risk of metal contaminations is difficult [1]. Indeed, trace metals are persistent. Once they enter the ecosystem, they are involved in bio-geochemical processes and distributed under various physical-chemical forms (speciation). The dissolved metal species includes the so-called dynamic metal species, defined as the sum of the free metal ions (M^{n+}) and small complexes (ML), that are potentially available for bio-uptake [2]. Colloidal/particulate materials play a key role in term of residence time and transport properties. Transformations among the various metal species are usually reversible, with the consequence that the speciation of a metal is a function of the bio-physicochemical condition of the medium and may change continuously in space and time [3].

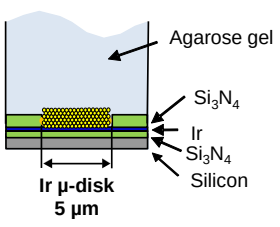


Biogeochemical processes regulating metal cycling in the aquatic systems[1]

The recording of high resolution data sets of specific metal fractions coupled to master variables is essential to enable more reliable understanding and assessment of trace metal biogeochemical cycles and ecological risk. Stripping voltammetry at antifouling gel coated microelectrode arrays is well suited for this purpose.

Antifouling Gel-Integrated MicroElectrode (GIME)

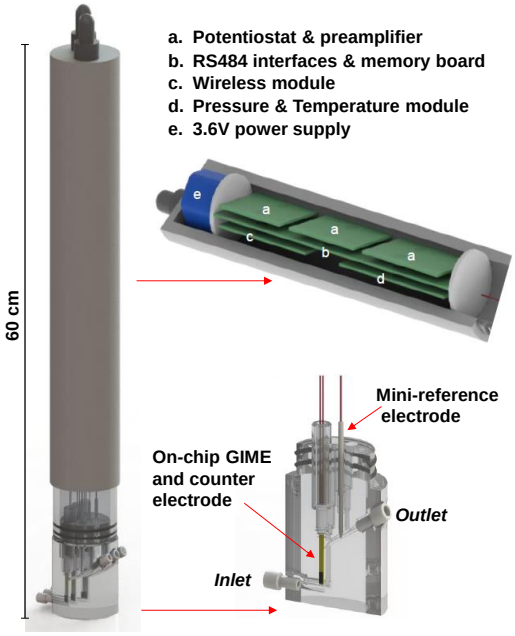




GIME sensors are based on on-chip 100 to 500 interconnected Ir microdisk arrays electrochemically plated with appropriate transducing element and covered by an agarose gel. The agarose gel acts as a dialysis membrane to eliminate the fouling components and also insure metal transport by pure diffusion, i.e. no influence of the ill-controlled hydrodynamic condition of the media on the sensor response.

When a GIME sensor is interrogated using anodic stripping voltammetry, the metal flux (or current) during the electrochemical pre-concentration step selectively represents the dynamic metal species which are potentially bioavailable [2,3]. GIME are thus of particular interest to study the role of trace metals as micronutrients or micro-pollutants.

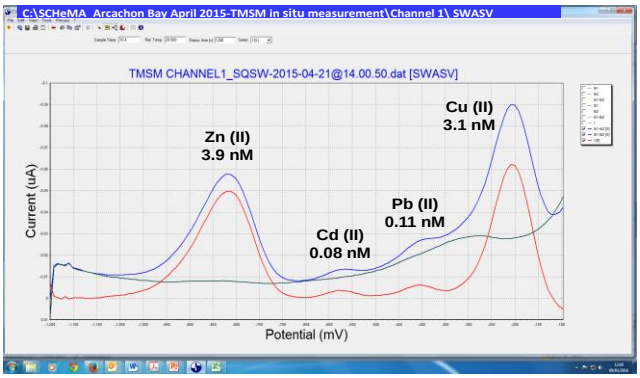
Submersible Three-Channel Trace Metal Sensing Module



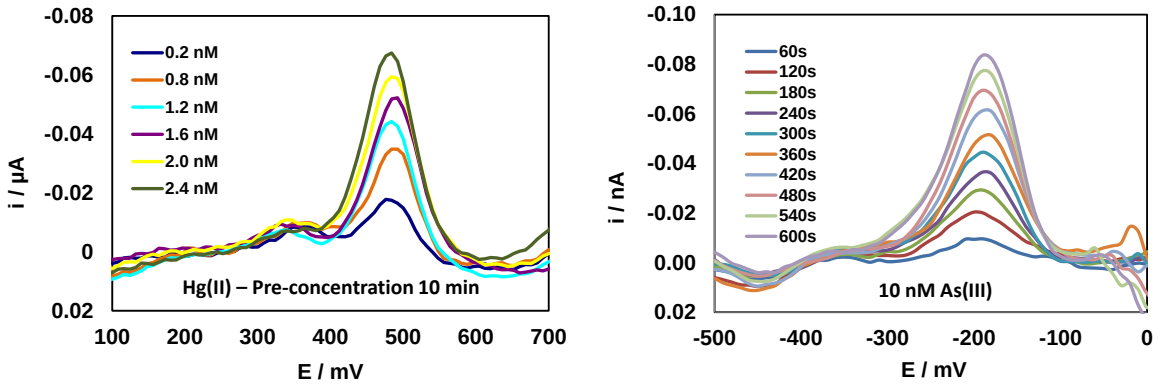
Our submersible Trace Metal Sensing Module (TMSM) is comprised on an electronic housing (upper part), a three-channel flow-through cell (lower part part) and an external peristaltic pump module. The electronic housing incorporate three potentiostats and pre-amplifiers, a 3.4V power supply as well as 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. Each individual channel of the flow-through cell incorporates an on-chip GIME and counter electrode and a mini-reference electrode.

Application in Seawater Analysis

Presently the TMSM allows simultaneous stripping measurements of the dynamic fraction of Cadmium, Lead, Copper and Zinc (Cd(II), Pb(II), Cu(II), Zn(II) - channel 1), arsenite (As(III) – channel 2) and inorganic Mercury (Hg(II) – channel 3). The stripping voltammetric peak currents are directly proportional to the concentrations of the metals in the media and to the electrochemical preconcentration time. Sub-nanomolar (ng/L) detection limit are reached using a 10 min electrochemical pre-concentration time.



GIME-TMSM stripping (blue), background (green), and stripping-background voltammograms recorded in situ in the Arcachon Bay



GIME-TMSM voltammograms of Hg(II) present at various concentrations and As(III) monitored using various electrochemical preconcentration time.

(Bio-)polymer functionalized GIME are under investigation to lower detection limit for Hg(II) as well as to extend the capability of the TMSM to the direct detection of arsenate (As(V)) and possibly methyl-mercury.

References

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[2] Buffle J. and Tercier-Waeber M.-L. *TrAc.* 24, 2005, 172.

[3] Tercier-Waeber M.-L., Hezard T., Masson M., Schäfer J. *Envronmental Science and Technology* 43, 2009, 7237.

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