

EXECUTIVE PUBLISHABLE SUMMARY, RELATED TO THE OVERALL PROJECT DURATION

Contract n° EVK3-CT-2000-00036

Project duration: 01.12.2000 - 30.11.2003

Title: In-situ automated Monitoring of Trace metal speciation in Estuaries and Coastal zones in relation with the biogeochemical processes (IMTEC)

Objectives

Coastal ecosystems are threatened by anthropogenic activities and in particular by chemical pollution. Assessments of the impact of chemical pollutants are presently very difficult, because their speciation, i.e. the distribution of the various chemical forms of a given compound, cannot be determined accurately enough or at a sufficiently high time frequency. The overall objective of the IMTEC project was: 1) to develop an *automated real-time, in-situ monitoring buoy supported Multi Physical-Chemical Profiler (MPCP)* for trace metal speciation measurements coupled to master variables in natural aquatic ecosystems; 2) to extensively deploy the Voltammetric In Situ Profiling System (VIP System), which was developed recently by several partners of this project (VAMP-MAST-III project), and the novel MPCP and collect samples for laboratory complementary measurements in three complementary coastal ecosystems for i) field validation of the new developments, and ii) pollution monitoring and corresponding biogeochemical studies. The long term objective of this project is for end-users (research institutions, water quality regulatory organizations and industry) to apply the MPCP in coastal water systems and use the results for trace element water quality evaluation and legislation development of the European Union.

Scientific achievements

The major scientific and technical results obtained during the three year IMTEC project are summarized below.

a) Analytical and technical developments and their laboratory characterisation.

MPCP. The development of the Buoy supported MPCP has been successfully achieved. The MPCP probe is based on the VIP System. The heart of the VIP probe is a gel integrated microelectrode (GIME) which allows the specific measurement of the concentrations of the dynamic fraction of trace metals, defined as the sum of the free metal ions and the small labile complexes with size of few nanometers. To improve the capability of the VIP, the following work has been performed in the IMTEC project: 1) development of i) a complexing gel integrated microelectrode (CGIME) for voltammetric measurements of free metal ion concentrations; ii) a submersible FIA system for automatic, on-line sample pre-treatment and subsequent GIME measurements of total extractable metal concentrations; iii) an improved probe based on three independent voltammetric measuring channels, iv) an improved buoy controller module (BCM); 2) integration of i) the CGIME, the submersible FIA, a multiparameter and fluorescence probes in the MPCP voltammetric probe and ii) the MPCP to a buoy profiler. Characteristic and performance of the main components of the buoy supported MPCP are summarized below.

The CGIME consists of an 100-interconnected Hg plated Ir-based microelectrode array covered by a thin 3.5 µm layer of complexing resin, itself covered by a thick 300 µm antifouling agarose gel layer. During equilibration with the test water, metals accumulate on the resin proportional to free metal ion concentrations. After equilibration, the metals fixed are released by acid and immediately measured by the voltammetric microelectrode. Systematic tests have been performed in synthetic and real natural samples to characterize and optimize this sensor. The results demonstrated the potentiality of the CGIME for direct, simultaneous detection of free metal ion concentration of Cu, Pb and Cd.

The submersible FIA comprised mixing, heating and cooling coils, reagents and waste eva-bag containers, and a submersible heater and three channels sampling peristaltic pump. Its coupling to voltammetric probes allows automatic, on-line pre-treatment of the sample -based on an analytical procedure involving ligand exchange, followed by acidification and heating of the pre-treated sample- and subsequent GIME measurements of total extractable metal concentrations. Systematic tests using the submersible FIA system coupled to a VIP probe than the MPCP channel 3 using freshly collected fresh and sea water samples were performed to characterize and optimise the system. Comparison with results obtained for trace metal concentrations measured in i) pH 2 acidified samples (acidification time for maximum Me release: 1 hour for sea water and ≤ 60 hours for river samples) and ii) pH 2 acidified + UV irradiated samples, showed that,

using an on-line pre-treatment time of 8 min, the system allows in situ measurements of the total concentrations of the metals which may be released in case of important variation of the physico-chemical conditions of the media (e.g. problem of acidification), i.e. only Me strongly bonded on some organic complexes, which are present mainly in freshwaters and can be dissociate only under drastic chemical conditions, are not detected.

The MPCP probe developed is comprised of distinct specific modules: an electronic housing, three pressure compensated VIP flow-through voltammetric cells and sampling submersible peristaltic pumps, integrated standard physical, chemical and optical sensors. The electronic housing contains all the hardware and firmware necessary to manage: i) the simultaneous control of the fluidic system and the SWASV measurements of each cell, i.e. simultaneous measurements of dynamic metal concentrations (channel 1 – GIME), free metal ion concentrations (channel 2 – CGIME) and total extractable metal concentrations (channel 3 – GIME+FIA); ii) the interfacing of the integrated standard physical, chemical and optical sensors allowing, simultaneously to the three trace metal fraction monitoring, the measurements of master variables (conductivity, temperature, depth, pH, dissolved oxygen, redox E, turbidity and chlorophyll *a*); and iii) the data acquisition and transfer via RS232 or telemetry. A user friendly Windows management software allows the user to control and set up the MPCP probe operating parameters and functions, such as: i) fluidic and electrochemical parameters, ii) data acquisition, transfer and graphical display, iii) calibration, and iv) maintenance operations.

Remote control of the MPCP has been achieved by coupling it to the improved *Buoy controller module* (BCM). The BCM, via a stack of communication protocols and a remote management software, supervises the monitoring activities, collects and stores data from the IMTEC-MPCP measuring probe at pre-set time intervals, forwarding them, via wireless connection using GSM network, to the control node land based station. Systematic laboratory tests have allowed to optimise the analytical procedure/conditions for the simultaneous measurements of the three specific metal fractions. Optimisation of the fabrication process of the micro-sensor arrays allowed reproducible and reliable continuous trace metal speciation measurements over extended period of time (typically 1 week) without renewal of the Hg layers.

PLM technique and micro-analytical developments. In parallel to the development of the MPCP, development and characterisation of permeation liquid membrane technique for trace metal speciation has been performed for comparison purpose with MPCP measurements and evaluation of micro-analytical system, based on this technique, for future in situ applications. For this purpose, a speciation model predicting the metal flux through the PLM for a test solution containing free metal ions M, free ligand L and hydrophilic complexes ML has been defined. It showed that, by modifying experimental parameters, the transport through the PLM can be set up to separate and pre-concentrate specifically free metal ions or dynamic metal species. Based on this, novel PLM devices have been developed. Theoretical and analytical characterization as well as optimization of a *PLM multi-channel flow cell device* was successfully achieved for Cu speciation laboratory studies. Improvement of the system for Pb, Cd and Zn analysis and speciation have begun. A submersible pump was developed to allow preliminary field tests of this device. The mechanic, electronic and software of a laboratory *FIA-PLM-VMC modular integrated micro-analytical system*, for automatic on-line PLM separation and preconcentration of metal species followed by their voltammetric detection, has been achieved and the fabrication process and geometry of the voltammetric micro-cell (VMC) optimised. Promising results were obtained from the preliminary laboratory tests performed without coupling of the PLM.

b) Field measurements in complementary coastal ecosystems

Inter-calibration of common analytical techniques and analytical procedures.

Common analytical procedures have been defined and adopted for sampling, sample pre-treatments, laboratory total metal concentrations measurements, Hg-plated Ir-based microelectrode array preparation and calibration, and in situ SWASV measurements to insure the reliability of the comparison and the interpretation of the field and laboratory complementary data obtained in the three complementary area. Two inter-calibration exercises, involving laboratory measurements of total metal concentrations in pH 2 +UV irradiated samples using VIP probes and laboratory based analytical techniques were carried out. Measurements were performed in i) filtered, stabilized samples collected from the River Tamar and its estuary, encompassing the full range in salinity and ii) certified natural waters. Furthermore, intercalibration exercises incorporating in situ and laboratory speciation analysis of fresh (unacidified) samples using VIP, MPCP, HFPLM and conventional laboratory techniques, involving all IMTEC partners, were undertaken during fieldworks in Sweden (August 2002), Italy (November 2002) and the UK (April 2003). The results have demonstrated the comparability of the metal speciation data obtained by all partners.

Field tests and validation of the MPCP and Buoy supported MPCP. The MPCP was successfully applied for in situ measurements of the free, dynamic and total extractable metal concentrations as well as master variables in i) macro-tidal contaminated estuaries and coastal waters in southwest England and ii) the highly contaminated Po micro-tidal estuary and its corresponding plume in the Adriatic sea during IMTEC field campaigns performed conjointly by several partners (Plymouth - April 2003, Ancona - August 2003). Good agreement in the results were obtained between the MPCP and the in situ VIP and laboratory complementary measurements performed by the other partners, demonstrating the proper functioning of the MPCP at depth and its capability for in situ monitoring of spatial and temporal variations of trace metal speciation and master variables. The Buoy supported MPCP was deployed for unattended monitoring/profiling cycles with automatic data transfer during a third IMTEC fieldwork at the Venice CNR Acqua Alta Platform located in the Northern Adriatic Sea in July 2003. The results obtained demonstrated the potentiality of the system for a remote monitoring and early warning system.

Pollution monitoring and biogeochemical studies. In addition to the IMTEC common field campaigns mentioned above, time series of field deployments of VIP probes and complementary laboratory measurements in macro-tidal estuaries in south west England were performed in December 2002, March and July 2003. The datasets of trace metal species and hydrological/biophysicochemical parameters in the complementary aquatic ecosystems showed that there are marked temporal and/or seasonal variations in metal concentrations and speciation related to freshwater discharges, riverine metal inputs, phytoplankton stocks. This work has also demonstrated a clear link between the concentrations of bioavailable metal in the water column and the production of chelating agents in phytoplankton, which are thought to be involved in the intra-cellular detoxification of trace metals.

Main deliverables

The main deliverables of the IMTEC project are: i) optimisation of sampling and in situ and laboratory analytical procedures for trace metal speciation studies in natural aquatic systems, including successful intercalibrations; ii) development and field validation of the MPCP based on an improved VIP probe integrating GIME and CGIME sensors, submersible FIA system and other probes allowing in situ simultaneous measurements of trace metal speciation and master variables; iii) evaluation of the VIP and MPCP systems as a tool for pollution monitoring and early warning system; iv) field estimation of the role of metal speciation on biological response to metal stress; v) provision of datasets of trace metal species and hydrological/biophysicochemical parameters in macro and micro-tidal estuaries and coastal area available for intercomparison and modeling.

Socio-economic relevance and policy implications

The work has demonstrated that the MPCP system is a cost effective tool for simultaneous, continuous monitoring of relevant specific fractions of Cu, Pb and Cd and master variables at time resolutions appropriate for highly dynamic waters. In addition the technical and analytical developments of the MPCP have been done so that the system is adaptable to measure a wider range of metals, other than the ones studied here, e.g. arsenic and mercury. The IMTEC inter-comparison exercises have allowed integration and co-ordination of methodologies resulting in accurate and precise measurements of specific metal fractions of trace metals and bio-physicochemical parameters by several European laboratories and, by extension, training of several PhD and Post-Doc students in trace metal environmental and pollution control studies. Data collected during the various field campaigns have shown that physical and geochemical processes may readily influence the speciation of trace metal. Hence, the determination of total dissolved concentrations of metals alone, as traditionally performed for water quality control, is a poor indicator of potentially bioavailable metal species concentrations, with subsequent implications to our current understanding of metal toxicity and environmental fate. These findings have implications for the routine monitoring of contaminant metals prescribed in the Water Framework Directive. It highlights the usefulness of the MPCP system developed as a end-user tool for more efficient trace metal water quality evaluation and legislation development.

Conclusions

The scientific and technologic results obtained have allowed to fulfill successfully the main objectives of the project. A sophisticated, but easy handled, submersible system for reliable automated studies of temporal and spatial evolution of trace metal speciation and master variables monitoring has been successfully developed and field validate. The results obtained during several field campaigns in various coastal ecosystems have demonstrated the usefulness of such system for, cost effective, more efficient water quality monitoring and provided an important first link between in situ measurements of trace metal fractions, and their ecotoxicological effects.

The IMTEC project is a clear example of the high quality of novel R&D work, which can be efficiently achieved by a consortium of European Universities and Private Company having complementary expertise.

Dissemination of results

The methods and results have been or are being published in peer reviewed journals/books (7 published papers and 5 to be submitted; 3 published book chapters). Information has also been disseminated via more than 30 national and international conferences. Field demonstration of the MPCP to a Governmental Institution was also performed.

Keywords: Gel-integrated microsensor, Submersible probe, In situ monitoring, Remote control, Trace metal, Speciation, Pollution control, Biogeochemical studies, Aquatic systems.