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

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Objectives

The aims of the IMTEC project were:

- to develop an **automated real-time, in-situ monitoring buoy supported Multi Physical-Chemical Profiler (MPCP)** for simultaneous measurements of specific trace metal species (trace metal speciation) together with important bio-physico-cochemical parameters (master variables) for trace metal data interpretation
- to undertake field trials, using the MPCP system in complementary marine coastal ecosystems to:
  - verify the ruggedness, reliability and validity of the new analytical and instrumental developments;
  - verify the capability of the MPCP for long-term operation
  - assess the potentiality of the MPCP system for pollution monitoring and as early warning system in response to discharge events
  - collect datasets of trace metal species and hydrological / bio-physico – chemical parameters in the complementary coastal ecosystems available for intercomparison and modelling to improve our understanding of (a) the behaviour and transport of trace metals in relation to hydrological/physico chemical conditions and (b) the relationship between trace metal speciation and biological responses in coastal ecosystems.

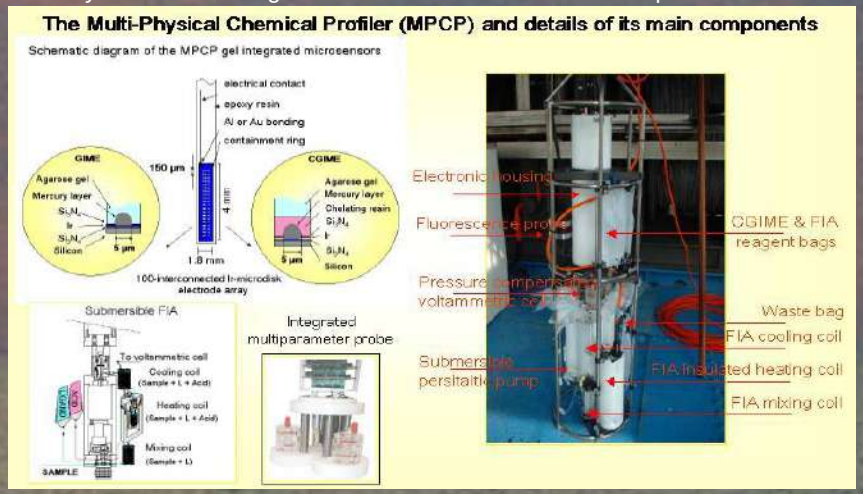
The long-term objective is to provide **a remote monitoring system to end users for cost effective monitoring of water quality, ecotoxicological assessments, legislation development.**

Results (1)

The development of the MPCP has been successfully achieved. It allows simultaneous in situ, autonomous monitoring of three specific fractions of Cu(II), Pb(II), Cd(II), i.e.: free ions, dynamic and total extractable concentrations, which play important role in term of toxicity, transport properties and residence time, as well as master variables (P, T, pH, O_2, conductivity, salinity, redox E and chlorophyll a) down to 150 meters.

The MPCP probe is based on the VIP System (VAMP-MAST III project). The heart of the VIP probe is a gel integrated microelectrode (GIME) which allows the specific measurement of the **dynamic fraction of trace metals**, defined as the sum of free metal ions and small labile complexes with size of few nm. The following analytical and technical developments were performed to improve the capability of the VIP:

- Chelating resin gel integrated microsensor (CGIME) for monitoring of **free metal ion concentrations**
- Submersible mini-FIA system for automatic, on-line sample pre-treatment and subsequent GIME in situ measurements of **total extractable Me concentrations**
- Improved voltammetric probe based on 3 potentiostats and flow-trough cells integrating respectively the GIME, the CGIME and the FIA-GIME as well as all hardware and firmware to manage the **simultaneous real-time in situ measurements of the three specific fractions of trace Me as well as the master variables**
- User friendly Windows management software to control and set up the MPCP



Remote control of the MPCP was achieved by coupling it to a Buoy controller module (BCM) which, via a stack of communication protocols and management software, supervises the monitoring activities, collects/stores data from the MPCP probe forwarding them, via a **GSM network wireless connection, to a land station.**

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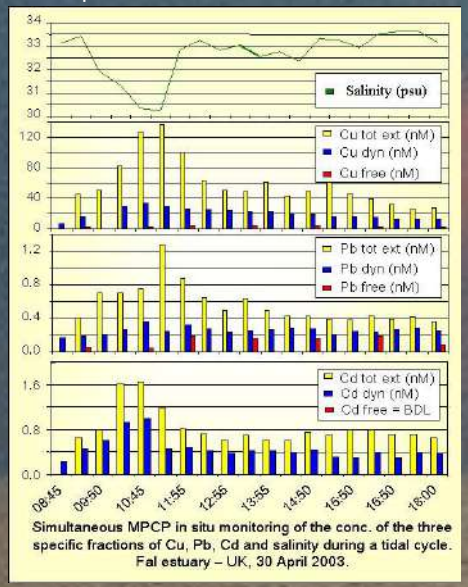
Results (2)

Field measurements in complementary coastal ecosystems. Intercalibration exercises, involving all IMTEC partners, undertaken during fieldworks in Sweden, Italy and UK have allowed **co-ordination, integration and standardisation of sampling and common in situ and laboratory measurement methodologies** resulting in accurate/precise measurements of specific metal fractions and biophysicochemical parameters by several European laboratories. They have also allowed **evaluation of the suite of the MPCP speciation-sensitive measurement techniques** which showed a **good agreement with our present knowledge of trace metal speciation** and field characterisation/ validation of the new analytical and technical developments.

The whole MPCP system was successfully applied for in situ measurements of the free, dynamic and total extractable metal concentrations as well as master variables during IMTEC fieldworks and oceanographic cruises in south west England micro-tidal estuaries (Tamar, Fal) and in the Po estuary and its coastal plume.

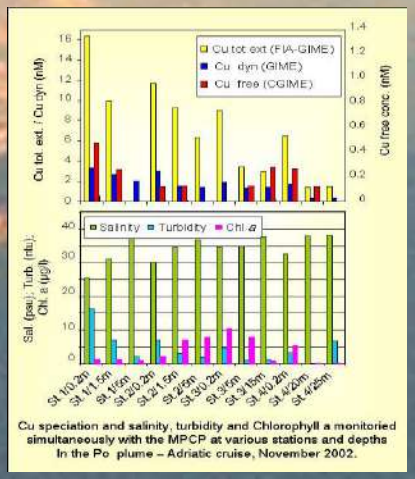


Simultaneous MPCP in situ monitoring of the conc. of the three specific fractions of Cu, Pb, Cd and salinity during a tidal cycle. Fal estuary – UK, 30 April 2003.

This Figure shows typical example of the in situ MPCP trace metal speciation data obtained in the Fal esturary during a tidal cycle. A significant increase of in particular the total extractable concentrations of the three metals as well as of the Cu and Cd dynamic fractions, with potential toxicity impact, were observed at ebb-tide. The variation of the dynamic fraction of Pb was found to be less significant. The ratios of dynamic and free metal ion to total extractable concentrations for the different metals were found to vary under various proportions over the tidal cycle (e.g. at ebb-tide, colloidal and non electroactive species are predominant for Cu and Pb while Cd is in majority under the dynamic form). Free Cd concentrations were found to be below the CGIME detection limit.

These results demonstrated the **interest of metal speciation vs total metal concentration monitoring for toxicological impact assessment of metal pollutant** riverine inputs on coastal area.

Higher concentrations of total extractable and dynamic fractions of the three metals were also observed in the Po mouth and surface water of the Po plume.



Cu speciation and salinity, turbidity and Chlorophyll a monitoried simultaneously with the MPCP at various stations and depths In the Po plume – Adriatic cruise, November 2002.

Decrease, under various proportions, were observed for Cu, Pb and Cd (not shown) total extractable and dynamic concentrations as a function of both the distance from the Po mouth and the depth. Increase in salinity and decrease in turbidity, measured simultaneously, suggests that this is mainly related to the mixing of the Po river and the Adriatic Sea waters. Cu free ion concentrations were found to be more related to Chlorophyll a, i.e. to primary productivity, suggesting that a significant proportion of Cu free is either assimilated by the biota or complexed by their exudates. Pb free concentrations were found to be very low (typically 0.01 nM) and relatively constant.

These examples demonstrated the **capability of the MPCP for remote in situ monitoring** of the **temporal**, under appropriate time scale, as well as **spatial variations of trace metal speciation** and master variables and its potentiality for i) more **efficient environmental monitoring and rigorous interpretation of trace Me cycles** and **their ecotoxicological impact**, ii) **pollution control** and iii) **early warning system**.

Relevance for Society

Results obtained during the IMTEC project for long-term biogeochemical studies and pollution monitoring have confirmed that **physical and bio-geochemical processes may readily influence the potentially biologically available fraction of trace metals**, for which total metal concentrations are poor indicator. The 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. These results provide an important first link between in situ measurements of specific trace metal fractions, and their ecotoxicological effects. All these findings demonstrated **the need and the usefulness of a system such as the buoy supported MPCP system** developed **as cost effective tool** for the member state institutions **for more efficient water quality evaluation**, **trace metal ecotoxicological assessment** and **legislation development**. This is **vital to maintain the high productivity and nursery grounds** for a high proportion of commercial fish and shellfish species **of the coastal zones** which, ultimately, will also **maintain the quality of the life of the population** living in the surrounding area.