

TECHNICAL ANNEX

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VAMP - Voltammetric Autonomous Measuring Probes for trace metals in the water column (500 m, max depth) and at water-sediment interfaces (6000 m, max depth)

Participants in the project

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CABE Group - Analytical Biophysical Environmental Chemistry University of Geneva	- Switzerland
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Technical Annex

**“VAMP - Voltammetric Autonomous Measuring Probes
for trace metals in the water column (500 m, max depth)
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TABLE OF CONTENTS

§1. OBJECTIVES AND METHODOLOGY	1
§1.1 SUBPROJECT I: VOLTAMMETRIC PROBE FOR THE WATER COLUMN	1
§1.2 SUBPROJECT II: VOLTAMMETRIC PROFILER FOR SEDIMENT-WATER-INTERFACE	3
§1.3 RATIONALE FOR COMBINING SUBPROJECTS I AND II	5
§2. TASK STRUCTURE OF THE PROJECT	7
§3. ROLE OF PARTICIPANTS	11
§4. DETAILED DESCRIPTION OF TASKS	12
§5. MANAGEMENT OF THE PROJECT	28
§5.1 DIAGRAM SHOWING THE KEY ACTIVITIES IN THE PROJECT	28
§5.2 DATA MANAGEMENT	29
§5.3 MEETINGS AND WORKSHOPS	29
§5.4 MILESTONES	29
§5.5 REPORTS	29
§6. DISSEMINATION AND EXPLOITATION OF RESULTS	30

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§1. OBJECTIVES AND METHODOLOGY

The purpose of this project is to develop, by means of several new technologies, a voltammetric sensor assembled in probes allowing automatic measurements, at great depths, of trace metal concentration profiles, in the water column and at the sediment-water interface. The present project will focus on the simultaneous measurement of Cu(II), Pb(II), Cd(II) and Zn(II). The analysis of Mn(II), Fe(II) and O₂ will result as "side-products" of this development, as it has already been shown in laboratory conditions that they are measurable by means of the same sensor and techniques. Other compounds such as S(-II), Se(IV), and organic compounds are potentially measurable with the same technique and system.

The development of the two measuring systems will be referred to below as i) the voltammetric probe for the water column (Subproject I), and ii) the voltammetric profiler for the sediment-water interface (Subproject II), respectively.

§1.1 Subproject I: Voltammetric probe for the water column

The probe will be developed for automatic, autonomous measurements of trace metal concentrations, in the water column, down to 500 m, i.e. in the most important part of the photic zone. The probe will be equipped with data memory and signal transmission by cable telemetry to a surface vessel or to a buoy equipped with a radio or cellular telephone or a satellite system for autonomous data transmission to a land-based station during 1 - 2 weeks of continuous use. Sensitivity limits $\leq 10^{-11}$ mol/l (~ 0.001 $\mu\text{g/l}$) is expected for Cu, Pb, Cd and Zn. Sensitivities close to 10^{-9} mol/l (0.1 $\mu\text{g/l}$) are expected for Fe(II) and Mn(II).

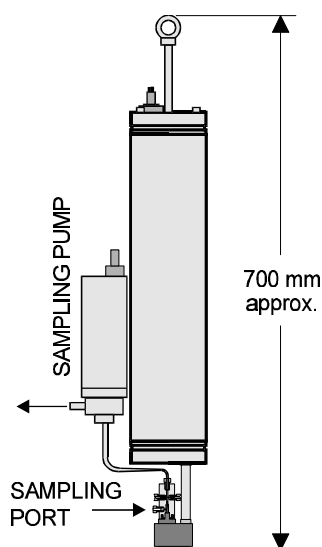


Figure 1 - The Voltammetric Probe.

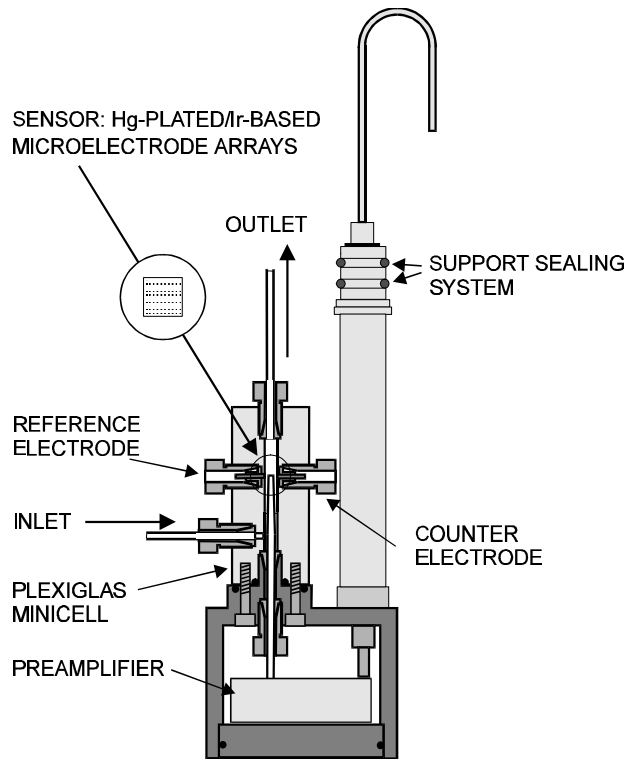


Figure 2 - The Voltammetric Cell.

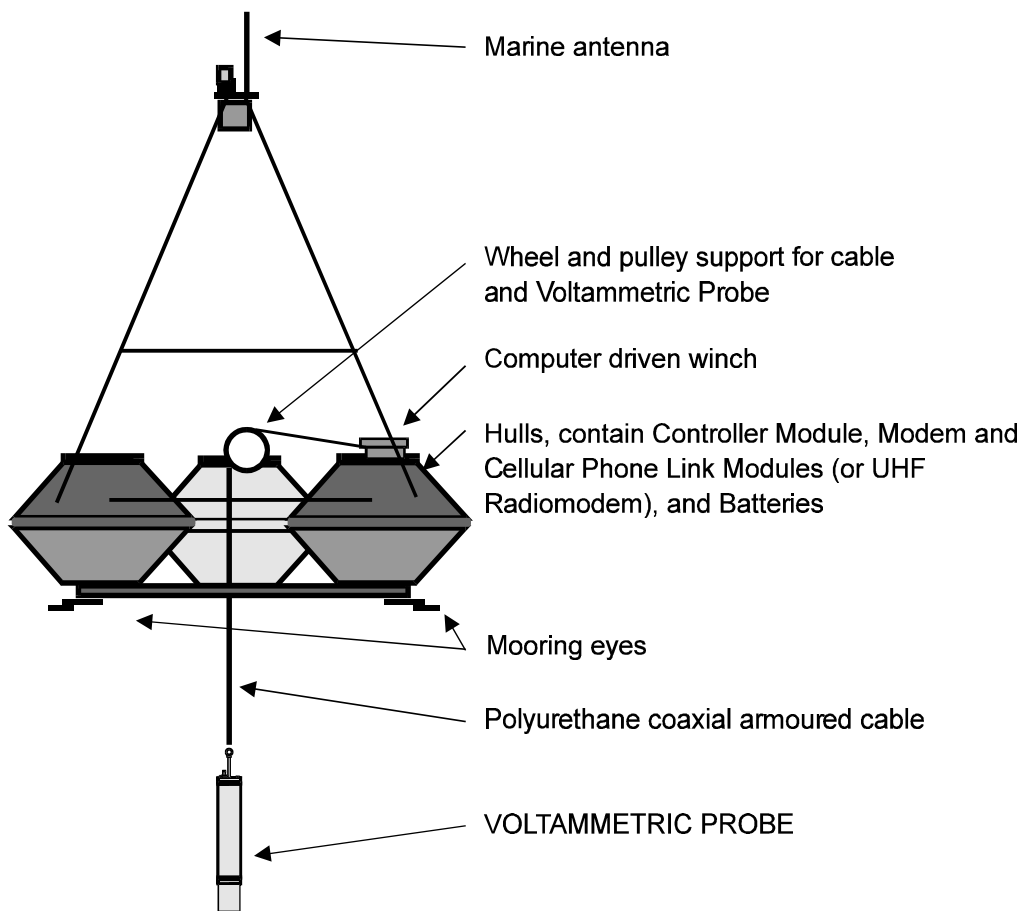


Figure 3 - Possible autonomous and profiling measurement system.

§1.2 Subproject II: Voltammetric profiler for sediment-water-interface

This profiler will be based on voltammetric electrode arrays. It will be developed for remote measurement of trace metal concentration profiles at the sediment-water interface, at high spatial resolution (100-200 μm), for estimation of fluxes. The corresponding voltammetric probe will be installed on the Lander developed by IDRONAUT in the frame of the BIMS project (Benthic Instrumentation and Monitoring System for investigation of physical, chemical and geotechnical properties of the water-sediment interface; project EU408, EUROMAR-BIMS). The Lander will be modified and equipped with a system allowing slow vertical penetration of the voltammetric electrode array in the sediment, to avoid perturbation. After penetration of the electrode array and reequilibration of the sediment, concentration profiles will be determined by performing voltammetric measurements on each individually addressable electrode of the array.

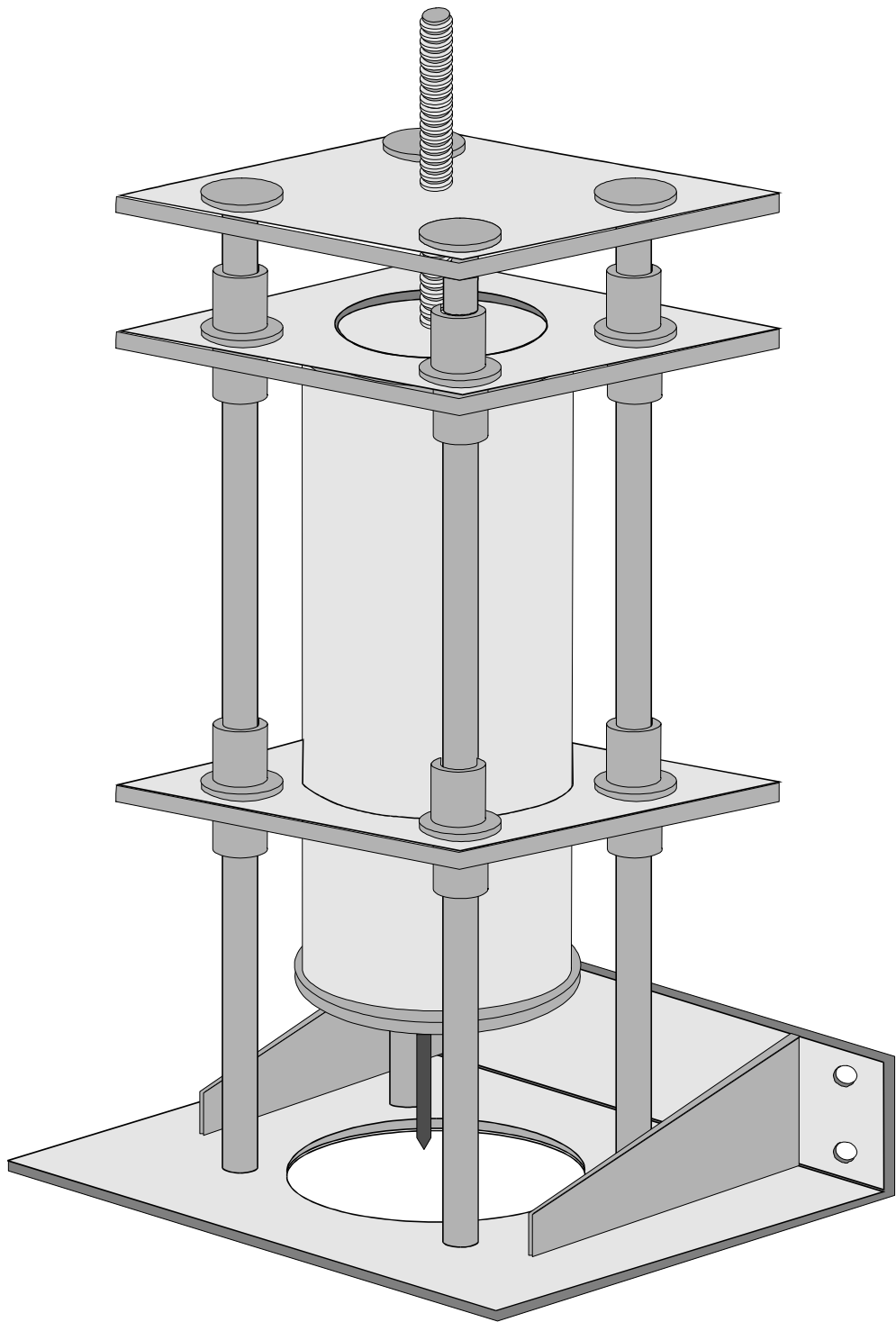


Figure 4 - The Voltammetric Profiler.

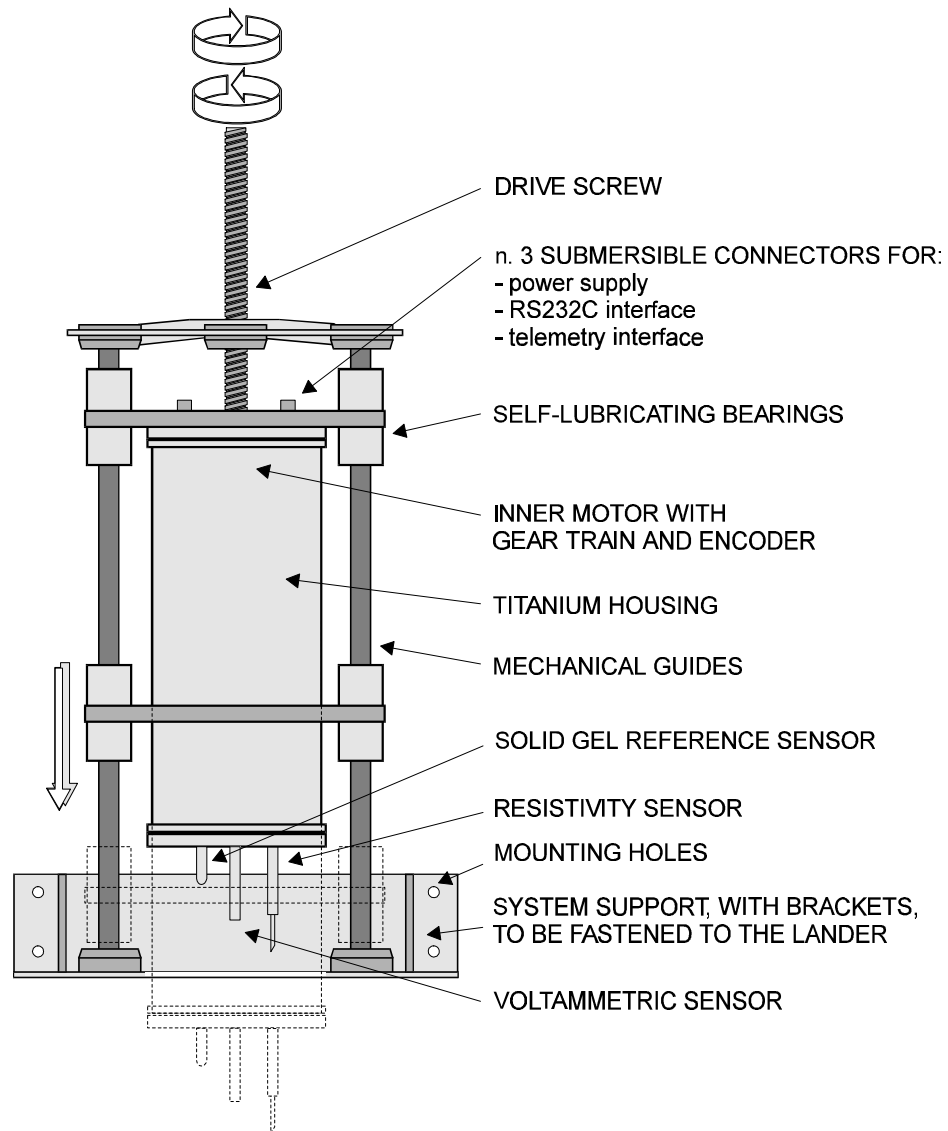


Figure 5 - The Voltammetric Profiler.

§1.3 Rationale for combining subprojects I and II

Successful development of the voltammetric probes, largely depends on the quality and reliability of the measuring sensor. As mentioned above, this is related to the choice of the best manufacturing technology with respect to the reliability of the sensor and to the ability of finding a good protection of the sensor against fouling components.

These developments are very similar for both subprojects I and II. Reliable electrode arrays with an antifouling gel will have to be prepared in both cases.

However, Subproject II is more demanding than Subproject I, and it is therefore its logical continuation. The main difference is that in Subproject I, a single electrode or an array of interconnected electrodes can be used together with a classical potentiostat. In Subproject II, an array of individually addressable electrodes must be prepared, and a special multichannel potentiostat must be built, in order to allow the measurement of high resolution concentration profiles. The same protective gel can be used in both Subproject I and II, but conditions are more drastic in Subproject II because of the larger concentration of fouling material in sediment than in the water column.

Although Subprojects II can be seen as continuation project of Subproject I, it is also very important that they be associated from the beginning in one single project. In this way, the developments to be done in Subproject I will take into account, as far as possible from the very first stage, the additional difficulties which will be encountered in Subproject II. Much time and efforts will then be saved for Subproject II.

Another important reason for combining Subprojects I and II, is that both of them include three types of development: i) microtechnology of sensor manufacturing, ii) specific analytical chemistry developments related to the complexity of sea water and sediment chemistry, and iii) technological developments related to data acquisition and transmission in extreme conditions. These developments cannot be fully done in parallel, since development of one type may require that other developments should have been done previously. Due to the complementary of the two subprojects, their combination allows maximum time optimisation and therefore an optimum cost efficiency for the whole development.

§2. TASK STRUCTURE OF THE PROJECT

Although the project concerns two instrumental developments, the tasks describing the planning of the project have been grouped. They are:

- 1 - Specification of the whole project
- 2 - Development of the voltammetric probe for the water column
- 3 - Laboratory and field tests on the voltammetric probe for the water column
- 4 - Development of the voltammetric profiler for the water-sediment interface
- 5 - Laboratory and field tests on the voltammetric profiler for the water-sediment interface

Task 1 - Specification of the whole project

Activities of this task will be focused on the realisation of all specifications of the: voltammetric sensors array, measurement methodology, protective gels, probe electronics, mechanics, firmware and laboratory and field tests. Said specifications will be discussed with the project Partners and a final document will be issued by the coordinator.

Sub-task 1.1 - This task concerns the accomplishment of the specification of sensor array and multichannel potentiostat.

Sub-task 1.2 - The measurement methodologies and methods for the water column voltammeter probe and for the water-sediment voltammetric probe will be accomplished.

Sub-task 1.3 - The specification of the sensor protective gels and the probe sterilising system will be prepared.

Sub-task 1.4 - The mechanical drawings and the selection of the constructional material will be accomplished. Besides the electronics and firmware specification, data telemetry and communication protocol specifications will be prepared.

Sub-task 1.5 - The field tests will be planned and the required resources (site, vessel, etc.) will be selected. Different sites will be selected for the different typologies of the tests that must be carried out. Moreover, the validation and comparative tests methodologies will be defined for the laboratory and field tests.

Task 2 - Development of the voltammetric probe for the water column

The activities of this task are finalised with the development of the voltammetric probe for water column measurements. At the end of the activities, a prototype of the above probe will be ready for laboratory and field tests.

Sub-task 2.1 - The micro-electrode gel will be developed in laboratory. Moreover, laboratory tests will be carried out on the chemical and physical efficiency of the protective gel.

Sub-task 2.2 - The sensor array for the water column probe will be developed. Furthermore, the coating of the micro-electrode array with the gel will be accomplished.

Sub-task 2.3 - The probe housing together with the voltammeter cell mechanics will be realised, while, the electronics and management firmware of the probe will be developed. Furthermore, the data transmission telemetry system and the communication protocol will be accomplished.

Sub-task 2.4 - Tests of the sensor array assembled in the voltammeter cell will be carried out in laboratory.

Sub-task 2.5 - Assembling and integration of the whole voltammeter probe parts will be performed. The water column voltammetric probe will be ready for the laboratory tests.

Task 3 - Laboratory and field tests on the voltammetric probe for the water column

This task concerns both laboratory and unattended field tests and qualification of the voltammetric probe for its validation.

Sub-task 3.1 - Laboratory tests on the whole probe will be carried out. Furthermore, the laboratory tests will be also performed in simulated pressure conditions.

Sub-task 3.2 - Methodologies for the measurement of the mobile and total metal concentration will be developed and tested.

Sub-task 3.3 - Tests will be carried out in the field by using an oceanographic vessel. The tests will be focused on the short and mid-term accuracy and reproducibility of the measurements. Furthermore, tests will be carried out at different sites and depths. Comparative tests will be performed by means of other analytical methods.

Sub-task 3.4 - If necessary, analytical improvements on the probe will be accomplished based on the evaluation of the tests performed in field, and methodology for mobile and total metal concentration will be improved.

Sub-task 3.5 - By means of a moored system (IDRONAUT Buoy Profiler 701), the probe will carry out extensive unattended and remote controlled tests. The mid-term accuracy and stability of the measurement will be evaluated.

Sub-task 3.6 - The sterilising system will be developed and applied to the voltammetric probe; comparative tests will be performed to investigate the possible influence of the sterilising system on the measurements accuracy.

Sub-task 3.7 - The voltammetric probe for the water column, complete with the sterilising system, will be deployed for the final long-term validation tests. They will be carried out by means of the moored system used for the sub-task 3.5. A scientific and technical report about the performance of the voltammetric probe will be issued.

Task 4 -Development of the voltammetric profiler for the water-sediment interface

- Sub-task 4.1** - An IAMA based sensor for the water-sediment interface probe will be manufactured. The multichannel potentiostat and a multiplexer system will be built according to the sensor array geometry. Tests of the multichannel potentiostat at high sensitivity will be performed. Fabrication and tests of various types of reference electrodes will be performed.
- Sub-task 4.2** - The measurement methodologies for the water-sediment interface probe will be developed, while, an initial evaluation of the individually addressable microelectrode array will be accomplished.
- Sub-task 4.3** - The electronics of the probe for water column will be partially adapted to the new sensor array, while, the microprofiler electronics will be developed. The management firmware together with the microprofiler mechanics will be accomplished.
- Sub-task 4.4** - The voltammetric probe for the water-sediment interface will be assembled and integrated. Preliminary tests on the micro-profiler will be performed.
- Sub-task 4.5** - The Benthic Lander will be adapted to support the micro-profiler and to support all the parts required to fulfil one voltammetric probe measurement mission. The balancing of the buoyancy and the landing speed of the Lander will be adapted for the voltammetric probe.

Task 5 - Laboratory and field tests on the voltammetric profiler for water-sediment interface

- Sub-task 5.1** - The tests of analytical measurement methods and probe penetration, in a simulated bed of sediment at atmospheric pressure, will be performed. Also tests on the protective gel resistance in living sediment, and the efficiency of the sterilising system will be accomplished.
- Sub-task 5.2** - The probe will be tested at various simulated pressures in the sediment in laboratory. Furthermore, tests with a classical reference electrode and with reference electrode on chips will be performed.
- Sub-task 5.3** - Tests will be performed in field using an oceanographic vessel. Tests will be performed in shallow water, and the communication with the probe will be set by means of an umbilical cable while the Lander is placed *in situ* through the vessel facilities. Tests will focus on the short and mid-term accuracy and reproducibility of the measurements. Furthermore, the tests will be performed at different sites and depths. Comparative tests will be performed by means of other analytical methods.

Sub-task 5.4 - Field tests of the probe for the water-sediment interface assembled on the Lander will be performed. The landing and the insertion of the sensor array in the sediment will be semiautomatic. Data and diagnostics information will be stored in the probe.

Sub-task 5.5 - Technical and measurement methodologies of both probes will be improved. Furthermore, a final project scientific report will be issued.

§3. ROLE OF PARTICIPANTS

The project will involve the four following partners:

- 1- IDRONAUT S.r.l. (Brugherio (MI) / Italy) will be responsible of the development of probes electronics, firmware and mechanics. Furthermore, it will participate to the laboratory tests and will be responsible of the management of the whole project.
It is involved in the following sub-tasks: 1.4, 2.3, 2.5, 3.1, 3.4, 3.5, 3.6, 3.7, 4.1, 4.3, 4.4, 4.5, 5.1, 5.2 and 5.5. It is responsible for the following sub-tasks: 1.4, 2.3, 2.5, 3.1, 3.6, 4.3, 4.4, 4.5, 5.2 and 5.5.
- 2- CABE (Group of Analytical and Biophysical Environmental Chemistry of University of Geneva, Switzerland) will be responsible of the characterization of the measurement methodology and sensor, of the protective gel development. Moreover, as scientific coordinator, it will be also responsible of the laboratory tests and of the scientific coordination of the whole project.
It is involved in the following sub-tasks: 1.1, 1.2, 1.3, 1.5, 2.1, 2.4, 2.5, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 4.2, 4.4, 5.1, 5.2, 5.3, 5.4 and 5.5. It is responsible for the following sub-tasks: 1.2, 1.3, 2.1, 2.4, 3.2, 3.3, 3.4, 4.2 and 5.1.
- 3- IMT (Institute of Microtechnology, University of Neuchatel, Switzerland) will be responsible of the development of the microsensor array for both sub-projects and of the development of the single and multichannel potentiostat. It will also participate to the laboratory tests.
It is involved in the following sub-tasks: 1.1, 2.2, 2.5, 3.1, 4.1, 4.4, 5.1, 5.2 and 5.5. It is responsible for the following sub-tasks: 1.1, 2.2 and 4.1.
- 4- AMK (Analytical and Marine Chemistry, Goteborg, Sweden) will be responsible for the attended and unattended field tests of both sub-projects. Moreover, it will participate to the realization of the specification of the whole project.
It is involved in the following sub-tasks: 1.1, 1.2, 1.3, 1.5, 3.3, 3.5, 3.7, 4.5, 5.3, 5.4 and 5.5. It is responsible for the following sub-tasks: 1.5, 3.5, 3.7, 5.3 and 5.4.

§4. DETAILED DESCRIPTION OF TASKS

The following paragraph resumes the details about tasks and sub-tasks.

Task 1 - Specification of the whole project

Sub-task 1.1

- *Title:* Sensor specification
- *Partner responsible:* IMT
- *Partners involved:* CABE, AMK
- *Duration (in months):* 4,25
- *Specific objective:*

Graphite, glassy carbon, platinum, gold, and mercury have been the most widely used electrode substrates. Reliability of solid electrodes is poor because of the time evolution of their surface state. For that reason Mercury Film Electrodes (MFE), and Hanging or Sessile Mercury Drop Electrodes (HMDE or SMDE) are the most widely used for accurate and reproducible analytical purposes. The drawback of classical Hg electrodes for *in situ* measurements is that Hg film or drops have to be renewed for each determination. In addition, the above substrate are not good for making mercury films, because i) they dissolve in Hg (Au, Ag), ii) cohesion between substrate and Hg is not good, so that a true, reproducible film is not formed, or iii) interference's occur due to intermetallic compounds formation with the test metal. Since, Ir is the only substrate allowing true reproducible Hg film formation, no dissolution in Hg, and no intermetallic compound formation. Moreover, interconnected Ir-based micro-electrode arrays allows significant increases in sensitivity limits (by factors of 10-100). Ir-based micro-electrode array fabrication methodologies and steps will be investigated during this sub-task.

- *Methodology:* None
- *Deliverables:*

The sensor specifications relatively to both sub-projects I and II will be realized and made known among the project partners.

- *Interdependence and links with other tasks:*

Link and relationship with the other sub-tasks of the task 1 are foreseen.

Sub-task 1.2

- *Title:* Measurement methodology
- *Partner responsible:* CABE
- *Partners involved:* AMK
- *Duration (in months):* 1,25
- *Specific objective:*

A wide number of current-potential-time functions have been developed for the analysis of trace compounds. Each one has its limitations and advantages. Different compounds can be measured by different techniques thanks to their differences in sensitivity and selectivity. For the analysis of trace metals (like Cu, Pb, Cd, Zn), the so-called stripping techniques: Anodic Stripping Voltammetry and Adsorptive Cathodic Stripping Voltammetry are the more appropriate because they involve a preconcentration step and thus have a better sensitivity. When the concentration of the measured compound is not too low ($\geq 10^{-7}$ M or ca 10 $\mu\text{g/l}$), techniques without pre-concentration step can be

used. For instance Mn(II) and Fe(II) in sediment or anoxic water can be measured by a single Cathodic potential scan Mn (II) however, can also be measured at lower concentrations by ASV. ASV, AdCSV and CSV techniques can be combined to various potential times modulations to improve their sensitivity and selectivity. The Square Wave techniques are often more sensitive than other techniques and above all they are unique by allowing, in adequate conditions, the determination of trace metals at extremely low concentrations in an oxygen saturated solution. For these reasons, SWASV will be used for Cu, Pb, Cd, and Zn determination in this project, whereas SWCSV will be used for Mn(II) and Fe(II) analysis. Objective of this sub-task will be the characterization of such measurement methodology when applied to the Ir-based micro-electrode arrays.

- *Methodology:* None
- *Deliverables:*

The measurement methodology specifications relatively to both sub-projects I and II will be realized and made known among the project partners.

- *Interdependence and links with other tasks:*

Link and relationship with the other sub-tasks of the task 1 are foreseen.

Sub-task 1.3

- *Title:* Protective gels and antifouling system
- *Partner responsible:* CABE
- *Partners involved:* AMK
- *Duration (in months):* 1,25
- *Specific objective:*

Voltammetric measurements performed directly in non pre-treated natural waters are often much perturbed by electrode fouling by organic and inorganic colloidal material, leading to drastic changes in peak characteristics. Although this problem is sometimes reported as being less important in sea water than in fresh waters, it may be a drastic limitation for long term monitoring, and for measurements in sediments. The use of renewable Hg drops or Hg films may minimise this problem in the laboratory. This type of electrode however, cannot be used at depth in the water column or in sediments. Although a number of workers have tried to protect the electrodes by means of various membranes their efficiency and reliability have been found to be rather poor until now and insufficient for developing reliable sensors working automatically *in situ* for long periods of time. The use of micro-electrodes makes it possible to cover them with protective gels thicker (hundreds of microns) and more efficient than the above membranes. Objective of this sub-task is the characterization of a protective gel compatible with the measurement methodology and with the Ir-based micro-electrode array.

- *Methodology:* None
- *Deliverables:*

The protective gel and antifouling system specifications relatively to both sub-projects I and II will be realized and made known among the project partners.

- *Interdependence and links with other tasks:*

Link and relationship with the other sub-tasks of the task 1 are foreseen.

Sub-task 1.4

- *Title:* Probes electronics, mechanics, firmware
- *Partner responsible:* IDRONAUT
- *Partners involved:* //

– *Duration (in months):* 6

– *Specific objective:*

Mechanics: The proper material will be carefully selected on the basis of the physical resistance, under varying conditions, to pressure and temperature, water fouling, and to trace metal contamination. Plastic parts will be made of acetal plastic (Delrin), P.T.F.E., polycarbonate or transparent methacrylate. The body of the housing will be made of high purity Titanium. The size of the housing is expected to be about 100 mm diameter, and about 700 mm long. Concerning the sub-project II, the voltammetric sensors will be fitted in the lower cover of a cylindrical body (diameter about 240 mm, length about 600 mm) made of high purity titanium. In correspondence with the centre of the upper cover, a drive screw protruding about 450 mm rotates (both directions). The drive screw rotates inside the threaded upper flange of the microprofiler. In this way, the rotation of the drive screw is transformed into an axial movement of the probe (both directions).

Electronics: To obtain the high performance and integration required by both sub-project a join of innovative technologies will be used. Low power (CMOS) SMT devices, ASIC (Application Specific Integrated Circuits), FPGA (Field Programmable Gate Array) and EPAC (Electrically Programmable Analog Circuits), specifically developed for this project, will characterize the electronics. Moreover, an advanced telemetry system, will be specifically developed to equip the measurement probe, and will be able to sustain the rather high transfer rate requested when the probe operates during on-line continuous monitoring. Furthermore, this telemetry system can also communicate through cables up to 10 km long. The transfer rate will be automatically adapted by the system, depending on the signal strength. Either FSK (Frequency Shift Keying) or GMSK (Gaussian Minimum Shift Keying) will be used as the transmission modulation technique.

Firmware: The complete specifications of the management firmware for both sub-project will be realized, besides a firmware development tools for the target management microprocessor will be individuated. The probes firmware will be characterized by built-in autodiagnosics capabilities, firmware remote upgrading functions and automatic management of the data processing and data acquisition functions. Moreover, a communication protocol able to guarantee the communication between the probe and the management systems, under extreme conditions, will be individuated and adapted or realized.

– *Methodology:* None

– *Deliverables:*

The mechanical, electronics and firmware specifications relatively to both sub-projects I and II will be realized and made known among the project partners.

– *Interdependence and links with other tasks:*

Link and relationship with the other sub-tasks of the task 1 are foreseen.

Sub-task 1.5

– *Title:* Field tests planning

– *Partner responsible:* AMK

– *Partners involved:* CABE

– *Duration (in months):* 2,25

– *Specific objective:*

The field tests will be planned and the required resources (site, vessel, etc.) will be selected. Different sites will be selected for the different typologies of the tests that must be carried out. Moreover, the validation and comparative tests methodologies will be defined for the laboratory and field tests. About, the unattended field tests will be defined the test site, the support platform or buoy, finally, the mooring will be designed.

– *Methodology:* None

– *Deliverables:*

The specifications of the field test planning concerning both sub-projects I and II will be realized and made known among the project partners.

– *Interdependence and links with other tasks:*

Link and relationship with the other sub-tasks of the task 1 are foreseen.

Task 2 - Development of the voltammetric probe for the water column

Sub-task 2.1

– *Title:* Protective gel synthesis

– *Partner responsible:* CABE

– *Partners involved:* //

– *Duration (in months):* 8

– *Specific objective:*

The following major problems may affect the voltammetric signals in a non-reliable way, during the measurements:

- electrode **fouling** by organic and inorganic colloidal or macromolecular material;
- irregular ill-controlled **convective currents** at the electrode surface, particularly on the water side of the sediment-water interface;
- change of **chemical conditions at the electrode surface**, compared to sea water due, in particular, to the reduction of O₂ (with the concomitant increase of pH).

Objective of this sub-task will be the developing of a protective gel which overcomes these problems by covering the micro-electrodes by a gel layer, in which the metal ions under test can freely diffuse. The gel layer should be much thicker (hundreds of microns) than the electrode size (a few microns). The electrode with the gel is then preequilibrated with the water sample for a few minutes. The test compound (as well as most small molecules and ions) diffuses in the gel but not the colloidal organic and inorganic fouling material. The test compound is then measured *within* the gel by voltammetry on micro-electrodes, without physical or chemical influence of the fouling material of the test solution. Polysaccharide and Polyacrylamide gels will be evaluated, in fact both gels present the following advantages: i) natural convection does not penetrate it and then does not influence the voltammetric signal. Anyway, electrodes with a size of a few microns are little affected by solution convection; the gel will minimise even further this effect.; ii) pH buffers may be chemically attached within the gel, to avoid pH change at the electrode surface during oxygen reduction.

– *Methodology:*

The best conditions for gel fabrication will be found in order to get a reproducible gel, adhering to the electrode, with antifouling properties but not perturbing for the diffusion of the analyte. These diffusion properties and gel structures will be tested.

– *Deliverables:*

A protective gel will be realized and a report presenting the achieved results will be made known to the other partners.

– *Interdependence and links with other tasks:*

This sub-task is strictly linked the micro electrode array fabrication, sub-task 2.2.

Sub-task 2.2

– *Title:* Microelectrode array

– *Partner responsible:* IMT

– *Partners involved:* //

– *Duration (in months):* 11

– *Specific objective:*

Microelectrode arrays will be produced in this sub-task. Ir based (Hg) micro-electrodes are particularly appropriate for *in situ* measurements in fresh waters, for the following reasons:

- they are able to give reliable results over long-term periods;
- they can be used as Hg electrodes, without pollution risk, for compounds in the range of 0 to -2V (in particular Cu, Pb, Cd, Zn down to at least 10⁻¹¹M, and Mn(II), Fe(II) down to 10⁻⁹M);
- they can be potentially used as Ir electrodes for analysing compounds in the range of 0 to +2V (e.g. O₂, Hg, As, Se(IV));
- they can be used in unstirred medium, i.e. without perturbing the test medium, e.g. in sediments (as for the sediment-water profiler) or gels;
- they can be produced under the form of electrode arrays, by means of modern micro-technologies which is a key feature for high resolution concentration profile measurements in Subproject II.

– *Methodology:*

The fabrication of the Ir-micro-electrode array will be based on thin film technology. The bulk insulation of a clean 3 inch silicon wafer is obtained by 2000 Å of Low Pressure Chemical Vapour Deposition (LPCVD) silicon nitride (Si₃N₄). A metallic layer of 2000 Å is deposited by e-gun evaporation of iridium. An additional 2000 Å of LPCVD Si₃N₄ constitutes the top insulation layer. A positive photoresist is spun on the substrate and patterned under UV exposure to produce the openings defining the microelectrode arrays and the connection pads. The unprotected Si₃N₄ surfaces are etched in a CHF₃ plasma, thus freeing the surfaces of the Ir microelectrodes. The photoresist is removed in acetone.

– *Deliverables:*

A sensor array ready to be installed in the measurement cell and a report will represent the deliverables of this sub-task.

– *Interdependence and links with other tasks:*

This sub-task is linked with the tasks which foresee the development of the protective gel (2.1) and the probe electronic and mechanics (2.3).

Sub-task 2.3

– *Title:* Development of probe housing, electronic and firmware

– *Partner responsible:* IDRONAUT

– *Partners involved:* //

– *Duration (in months):* 24

– *Specific objective:*

The measurement cell, the probe housing and the mechanical support for the probe electronics internal to the probe housing will be developed. The complete electronics of the voltammetric probe will be developed, ASIC, FPGA and EPAC devices will be also designed and realized during this sub-task. A modular approach will be used to provide simultaneously single channel potentiostat required in Subproject I, with a straightforward extension to multichannel potentiostat for Subproject II. The management firmware of the voltammetric probe and the communication protocol will be developed. Furthermore, to accomplish the laboratory and field test a management software running on a PC will be realized. A surface deck unit will be built to power and interface the voltammetric probe. It will contain a rechargeable 12V lead battery which will allow more than one week of continuous operation without any external AC power. The deck unit will provide the battery recharger, the power supply devices to power the voltammetric probe and a transceiver necessary for the telemetry system. The surface deck unit will allow control of the voltammetric probe, by means of a portable Personal Computer through an RS232C interface. The voltammetric probe mechanics, electronics and firmware will be built to be interfaced to an automatic Buoy Profiler, enabling to automatically monitor the whole water column.

– *Methodology:*

Up to date electronic devices and mechanics materials and parts will be used. The firmware will be realized in high level language, “C” language. CAD CAE and CAM tools will be used to realize the mechanical drawings and electronic schemes and P.C.B. (Printed Circuit Boards).

– *Deliverables:*

A complete prototype of the probe mechanics, electronics and firmware will represent the deliverables of this sub-task.

– *Interdependence and links with other tasks:*

This sub-task will depend from the sub-task 2.2.

Sub-task 2.4

– *Title:* Test on the sensor array and protective gel

– *Partner responsible:* CABE

– *Partners involved:* //

– *Duration (in months):* 5

– *Specific objective:*

Ir-based Hg "film" micro-electrodes arrays will be tested in this sub-task. Until now, they have never been applied to sea water and sediments. As a matter of fact, in such electrodes, the Hg "film" is an Hg hemisphere, whose stability is much improved compared to classical Hg film, and which can be used for days without renewal. This also allows preparation of the electrode ex-situ, thus avoiding polluting the test medium. It must also be noted that the amount of Hg forming such small size hemispheres is of the order of 1 ng, i.e. equivalent to Hg ions naturally dissolved in no more than a few tens of ml of pelagic sea water. Therefore, even accidental oxidation of the electrode would not be a pollution problem, in particular because most Hg would form insoluble Hg oxide or calomel.

The micro-electrode arrays covered with a polysaccharide or Polyacrylamide gel 100-1000 µm thick, will be inserted in a flow-through cell with a very small dead volume, through which the sea water under test will be pumped.

– *Methodology:*

Voltammetric techniques will be used to prepare the mercury film and analyse the trace metals. Tests will be made in synthetic and natural waters to find the best analytical conditions.

– *Deliverables:*

A report, presenting the results achieved during the laboratory test, will represent the deliverables of this sub-task.

– *Interdependence and links with other tasks:*

Links are foreseen with sub-task 2.2, 2.3 and 2.5.

Sub-task 2.5

– *Title:* Assembling and integration of the probe

– *Partner responsible:* IDRONAUT

– *Partners involved:* CABE, IMT

– *Duration (in months):* 15

– *Specific objective:*

The specific objective of this sub-task will be devoted to the assembling of all the parts which constitute the voltammetric probe. In details, the following actions are foreseen: i) Joining of the measurement cell with the sensor array covered with the protective gel; ii) Assembling of the management and data conversion electronics; iii) Integration of the management electronics with the sensor array and with the potentiostat; iv) Mechanical assembling of the measurement cell on the probe housing; v) Static depth test on the probe will be realized in order to guarantee that the probe sustain the maximum operating pressure.

– *Methodology:*

The assembled probe will be tested in a pressure chamber available at the IDRONAUT laboratory.

– *Deliverables:*

The voltammetric probe relatively to the sub-project I will be assembled, and will be ready for tests in laboratory and in field.

– *Interdependence and links with other tasks:*

This task depends mainly from all the sub-tasks of the task 2 “Development of the voltammetric probe for the water column”.

Task 3 - Laboratory and field tests on the voltammetric probe for the water column

Sub-task 3.1

– *Title:* Laboratory tests

– *Partner responsible:* IDRONAUT

– *Partners involved:* CABE, IMT

– *Duration (in months):* 9

– *Specific objective:*

Specific objective of this sub-task will be the characterization and improvement of the probe answer to meet the project specifications. Laboratory tests will focus on the characterization of the: i) electronic noise emission and immunity from the ambient EMI (Electromagnetical Interference) /RFI (Radio Frequency Interference) and ESD (Electrostatic Discharge) disturbance; ii) potentiostat and compliance voltage, respect to the sensor array; iii) real time diagnostics to be done during the measurement and stand-by

cycles; iv) calibration and maintenance methodologies and frequency; v) fluidics performance of the measurement cell. The above tests will be performed at different depth, by means of a pressure chamber.

– *Methodology:*

The tests will be performed in synthetic and natural waters, by using the voltammetric techniques characterized in the previous sub-task.

– *Deliverables:*

A report describing the results achieved by the laboratory tests will be realized and made known to the other partners. Real time diagnostics, calibration methods and maintenance procedures will be defined.

– *Interdependence and links with other tasks:*

Links are foreseen with the activities of task 2.

Sub-task 3.2

– *Title:* Development of the measurement methods

– *Partner responsible:* CABE

– *Partners involved:* //

– *Duration (in months):* 8

– *Specific objective:*

The experimental work made with the probe developed in this project will be primarily based on Square Wave Anodic Stripping Voltammetry (SWASV), for Cu,Pb,Cd,Zn, and on Square Wave Cathodic Sweep Voltammetry (SWCSV), for Mn(II) and Fe(II), without deoxygenating.

Primary objective of this sub-task is the optimisation of the measurement methods by using the above measurement technique, to get the concentrations of mobile metal species and the total metal concentration.

Speciation of metal ions is not really the goal of this project. Nevertheless, any *in situ* sensor is sensitive to some of the metal species, but not to the total metal concentration. Therefore, to ultimately give reliable results and allow meaningful interpretation of data, speciation aspects must be taken into account from the very first stage of *in situ* probe developments. Since only the small quick diffusing metal species are detected by voltammetry, in unmodified water, the probe specifically determines the truly dissolved (or mobile) metal species. Voltammetry is the only technique allowing specific determination of their concentration without sample handling. Furthermore, the total metal concentration is readily measured (by voltammetry or any other technique) after sample acidification. The colloidal + particulate bound metal may then be obtained by subtraction. Indeed, both parameters are necessary to understand and model biogeochemical cycles: i) colloidal + particulate metal concentration is a key parameter to determine metal fluxes in the ocean and ii) the truly dissolved metal concentration is the only experimental metal concentration which can be readily linked by computation, to the free metal ion concentration, which is itself an indicator of metal bioavailability.

– *Methodology:*

Direct measurements will be combined with measurements after acidification or addition of a complexing agent. The best conditions will be developed.

– *Deliverables:*

A report describing the measurement conditions will be realized and made known to the other partners.

– *Interdependence and links with other tasks:*

This sub-task depends on the availability of the whole voltammetric probe hardware and firmware, since it depends upon all the development sub-tasks.

Sub-task 3.3

- *Title:* Attended field tests
- *Partner responsible:* CABE
- *Partners involved:* AMK
- *Duration (in months):* 5
- *Specific objective:*

Test deployments will take place partly on the AMK research vessel, which within short steaming time from Göteborg can reach a range of different marine environments including coastal fjords, the shallow coastal waters of the Kattegatt (of the order of 20m depth), and the deep waters of the Skagerrak (> 600m depth).

Following laboratory tests of the sensor in sea water, initial deployments in the water column will involve lowering the sensor package on a clean (kevlar) line. Samples for the analysis of total trace metal will be taken for comparison.

– *Methodology:*

The following methodology will be used during the attended field test: i) The Hg films will be formed on the surface of the Ir micro-electrodes of the array. This will be done on board a vessel, by electrolysis of an Hg(II) solution, directly in the voltammetric cell fixed on the probe; ii) the probe will be used for at least a week, without additional maintenance; iii) during normal operation (measurement of truly dissolved metal species), the probe will be deployed to the desired depth, and the sea water will be pumped directly through the cell, without pre-treatment other than filtration through a sieve with a very large pore size (50-100 µm); iv) before measuring, equilibration of the voltammetric cell walls with sea water will be done by circulating it in the flow-through cell, to avoid contamination or losses by adsorption; v) repetitive measurements will be made using several circulation steps, to ensure that equilibrium is reached between the bulk water and the cell; vi) thanks to the long-term stability of the sensor array, calibration will be only done on the surface during maintenance, at weekly intervals.

Moreover the correct functioning of the probe *in situ* will be checked in several ways: by analysing and following the time evolution of the characteristics of the base line of the voltammograms, as well as peak width and peak potentials, and/or by checking the constancy of the ratio of the reduction current of oxygen measured on the electrode array, to the signal of an independent oxygen electrode.

– *Deliverables:*

Prototype of tested probes with a list of problems to solve or technical improvements to do.

– *Interdependence and links with other tasks:*

Links are foreseen with sub-tasks 3.2 and 3.4.

Sub-task 3.4

- *Title:* Measurement methods improvements
- *Partner responsible:* CABE
- *Partners involved:* AMK, IDRONAUT
- *Duration (in months):* 8

– *Specific objective:*

To improve the methods and technical developments performed in 3.1 and 3.2, after the field attended tests.

– *Methodology:*

As in sub-tasks 3.1 and 3.2.

– *Deliverables:*

A report describing the measurement methods and system will be realized and made known among the project partners.

– *Interdependence and links with other tasks:*

The activities concerning this task depend on the availability of the complete voltammetric probe and upon the availability of the preliminary results of the laboratory and field tests.

Sub-task 3.5

– *Title:* Unattended mid-term field tests

– *Partner responsible:* AMK

– *Partners involved:* CABE, IDRONAUT

– *Duration (in months):* 6

– *Specific objective:*

Primary objective of this sub-task will be to test the mid-term monitoring capabilities of the voltammetric probe. It will be installed on a moored automatic Buoy Profiler and left in place to automatically perform a profile of the water column at configurable intervals. The acquired data will be transferred to a shore stations which will manage and control the voltammetric probe operations.

– *Methodology:*

As in sub-task 3.3

– *Deliverables:*

A report on the performance of the probe during the unattended field test will be realized and made known to the project partners.

– *Interdependence and links with other tasks:*

Links with sub-tasks 3.3 and 3.4.

Sub-task 3.6

– *Title:* Development of the sterilising system

– *Partner responsible:* IDRONAUT

– *Partners involved:* CABE

– *Duration (in months):* 20

– *Specific objective:*

A sterilising system based on the electro-oxidation of Cl^- will be the specific objective of this sub-task. To this end, sea water electrolysed will be performed close to the voltammetric cell, by means of Pt or Ru cathodes, and anodes in Ti oxide, Ru oxide, or Ir oxide. This electrolysis will be repeated at regular intervals, between voltammetric measurements.

– *Methodology:* None

– *Deliverables:*

At the end of the activities of this sub-task, a sterilising system ready to be installed on the voltammetric probe will be ready.

- *Interdependence and links with other tasks:*

This sub-task depends somewhat upon the result achieved by the field attended and unattended tests.

Sub-task 3.7

- *Title:* Final field unattended long-term validation tests
- *Partner responsible:* AMK
- *Partners involved:* CABE, IDRONAUT
- *Duration (in months):* 6
- *Specific objective:*

The purpose is to check that the whole probe is working automatically for long periods of time. The probe will be installed on the same moored buoy used to perform the activities of sub-task 3.5. Moreover the probe will be equipped with the sterilizing system developed in sub-task 3.6.

- *Methodology:*

The probe will operate automatically thanks to the developed software and record metal concentration profiles. The frequency and cause of failure will be recorded and the system will be improved.

- *Deliverables:*

A report on the performance of the system.

- *Interdependence and links with other tasks:*

Links are foreseen with sub-tasks 3.4, 3.5 and 3.6.

Task 4 -Development of the voltammetric profiler for the water-sediment interface

Sub-task 4.1

- *Title:* Fabrication of an individually addressable microelectrode array
- *Partner responsible:* IMT
- *Partners involved:* IDRONAUT
- *Duration (in months):* 24
- *Specific objective:*

In Subproject II, voltammetric measurements will be done on a large number of individually addressable electrodes to get a spatial resolution of 100-200 μm . The voltammetric sensors will be based on similar micro-electrode arrays as those developed for Subproject I, but each micro-electrode will be independently addressable. At first, the sensors will be formed on strips of a 3 inch silicon containing 64 microelectrodes with their individual interconnections. On chip multiplexing will be integrated later if necessary. The geometry of the array will be such that i) trace metal concentration profiles at the water sediment interface will be measurable over a centimetre with the high resolution of 100 - 200 μm , in particular at the sediment-water interface region, ii) measurements on one electrode does not interfere with its neighbours. The optimum geometry will be determined by mathematical simulation and literature data. A multichannel potentiostat will be developed to allow simultaneous measurement on 8 channels by addressing successively the 8 electrodes.

- *Methodology:*

Individually addressable electrode with “on-chip” multiplexing requires additional technological steps, respect to the one used to develop the micro-electrode for the sub-project I. A simple NMOS analog multiplex approach is considered. A clean 3 inch

p-doped silicon wafer with a bulk resistivity of 5-7 $\Omega\text{-cm}$ is used. Diffusions for the channel stop, the source and the drain of the transistors are obtained by driving the impurities from 4000 Å doped Chemical Vapour Deposition (CVD) oxides. A gate oxide of 800 Å is thermally grown in an oxidizing ambient at 1100° C. Contact holes are wet etched using solution buffered fluoric acid 1:7. The metal gate and the address lines are made of 6000 Å evaporated aluminium and patterned in an aluminium etch solution. Electrodes are realized with 1000 Å e-gun evaporated iridium, patterned by lift off.

A 6000 Å thick Plasma Enhanced Vapour Deposition (PECVD) Si₃N₄ layer is deposited as a passivation layer. Openings for the electrodes are obtained by using a plasma etch.

– *Deliverables:*

A sensor array ready to be installed on the sediment probe housing, a multichannel potentiostat and a report will represent the deliverables of this sub-task.

– *Interdependence and links with other tasks:*

This sub-task links with the task which foresees the development of the sediment probe electronic and mechanics (4.3).

Sub-task 4.2

– *Title:* Measurement methods

– *Partner responsible:* CABE

– *Partners involved:* //

– *Duration (in months):* 20

– *Specific objective:*

Hg plated Ir based micro-electrodes, covered with a protective gel layer will be used as in Subproject I. The purpose of sub-task 4.2 is to develop the methodology of preparation of Hg plated microelectrodes of gel-coating and the optimum analytical conditions to get high spatial resolution of metal concentration profiles, in synthetic solutions or suspensions.

– *Methodology:*

The same methodology as in sub-tasks 2.1, 2.4 and 3.2 will be used.

– *Deliverables:*

A report on optimal conditions of analysis.

– *Interdependence and links with other tasks:*

Links with sub-task 4.1 and task 5.

Sub-task 4.3

– *Title:* Development of the probe and microprofiler mechanics, electronics, firmware

– *Partner responsible:* IDRONAUT

– *Partners involved:* //

– *Duration (in months):* 25

– *Specific objective:*

Mechanics of the microprofiler will be realized by means of high purity titanium and AISI 316 stainless steel, while the plastic parts will be made of acetal plastic (Delrin), polycarbonate or transparent methacrylate. Particular care will be devoted to the realisation of the vertical mechanical guides which allow the axial movement of the probe and its sensors. This will prevent the sensor tip from being damaged during the penetration in the sediments.

Special attention will be taken during the realization of the **electronic** to avoid electrical coupling between the sensing elements (sensors) and to separate the analog from the digital ground. Due to the presence of a DC motor inside the probe housing, special care will be taken in shielding and immunizing the electronics devices from the EMI/RFI radiated by the motor itself. Since analog systems are inherently more susceptible (about 40 dB) to these disturbances, because unlike digital systems, their input/output characteristics are continuously variable. Therefore, a small change in environmental EMI/RFI translates into a corresponding change in the output of an analog device multiplied by its gain.

Moreover, the integration of the DC motor PWM control, the encoder and the additional sensors (Temperature, Resistivity) used by the Subproject II with the multi-potentiostat and digital electronics will be a specific objective of this sub-task. However, the use of microelectrode arrays will provide larger currents than a single microdisk, hence simplifying the design of the current to voltage converter. Voltammetric measurements will be done on a large number of individually addressable electrodes to get a spatial resolution of 100 - 200 μm . The number of channels of the potentiostat will be set to 8 in order to benefit from the existing logic integrated circuits. For the same reason the number of electrodes within the channels will also be set to 8, giving an overall number of 64 addressable microelectrodes (i.e. 8 sets of 8 microelectrodes). The voltammetric response will be collected simultaneously from the 8 channels by addressing successively the 8 electrodes. To operate simultaneously a set of individually addressable microelectrodes, a multichannel potentiostat will be used. A low power consumption approach will be adopted to increase the autonomy of the battery-operated system.

The **firmware** development will focus on i) the automatic management of the microprofiler during the measurement phase; ii) the data acquisition from the multichannel potentiostat, and the addressing of the sensors array; iii) the management of the system once installed on the Benthic lander. The communication protocol, the operator interface and the data processing will be based on those developed for the Subproject I.

– *Methodology:*

Up to date electronic devices and mechanics materials and parts will be used. The firmware will be realized in high level language, “C” language. CAD CAE and CAM tools will be used to realize the mechanical drawings and electronic schemes and Pcb.

– *Deliverables:*

A complete microprofiler mechanics, electronics and firmware will represent the deliverables of this sub-task.

– *Interdependence and links with other tasks:*

This sub-task will depend from sub-task 4.1.

Sub-task 4.4

– *Title:* Assembling and integration of the probe

– *Partner responsible:* IDRONAUT

– *Partners involved:* CABE, IMT

– *Duration (in months):* 9

– *Specific objective:*

Objective of this sub-task is the assembling and the integration of all the parts of the microprofiler probe. The voltammetric sensors and the temperature, reference and resistivity sensor will be fitted in the lower cover of the cylindrical body. They will be connected to the management electronics and preliminary laboratory test will be performed. Moreover, the microprofiler will be assembled and the moving parts tested.

– *Methodology*: None

– *Deliverables*:

As result of the activities of this sub-task the microprofiler will be ready for the laboratory and field test.

– *Interdependence and links with other tasks*:

This sub-task will depend from sub-tasks 4.3 and 4.1.

Sub-task 4.5

– *Title*: Adaptation of the Benthic Lander

– *Partner responsible*: IDRONAUT

– *Partners involved*: AMK

– *Duration (in months)*: 8

– *Specific objective*:

The Benthic Lander is a complex bottom Lander already developed in the frame of the EUREKA-EUROMAR project "EU-408 BIMS", entitled "*Benthic Instrumentation and Monitoring System for Investigation of Physical, Chemical and Geotechnical Properties of the Water-Sediment Interface*". The Lander is designed to be easily assembled on site. The whole frame is made of pure titanium, to avoid contamination at the deployment site. The Lander has a triangular structure whose base dimensions are 2000 mm and height 2500 mm. The system weight is 60-70 kg in air, without the rechargeable batteries and their housing. The Lander is deployed as a free vehicle and its buoyancy is adjusted so as to sink to the bottom at a rate $< 0.5\text{m/s}$. The lower part of the frame will hold the voltammetric microprofiler system and the battery housing, while the upper part holds the buoyancy devices. As for any free-fall vehicle, there is a release of ballast at the end of an experiment to return the instrument to the surface. Additional buoyancy adjustments are provided in order to control landing speed and to drive the voltammetric probe microprofiler system in the sediment, with minimum disturbance. Mechanical and buoyancy adaptation of such lander to the voltammetric microprofiler is the specific objective of this sub-task.

– *Methodology*: None

– *Deliverables*:

The Benthic lander ready to accept the voltammetric microprofiler will represent the deliverables of this sub-task.

– *Interdependence and links with other tasks*:

This sub-task is strictly linked with sub-task 4.3, which foresees the development of the voltammetric microprofiler.

Task 5 - Laboratory and field tests on the voltammetric profiler for water-sediment interface

Sub-task 5.1

– *Title*: Tests of the analytical measurement methods in the laboratory in real sediment

– *Partner responsible*: CABE

– *Partners involved*: IDRONAUT, IMT, AMK

– *Duration (in months)*: 11

– *Specific objective:*

The analytical conditions developed in 4.2 will be used here to make analysis in real sediments, in the laboratory. The conditions will be modified to take into account the properties of real sediments. Tests on the efficiency of the gel will be performed in detail.

– *Methodology:*

The same methodology as sub-task 4.2 will be used.

– *Deliverables:*

A report on optimum analytical conditions.

– *Interdependence and links with other tasks:*

Links with sub-tasks 4.2 and 5.3

Sub-task 5.2

– *Title:* Tests of the probe under pressure

– *Partner responsible:* IDRONAUT

– *Partners involved:* CABE, IMT

– *Duration (in months):* 7

– *Specific objective:*

Primary objective of this sub-task is the testing of the microprofiler complete of each part in real operating conditions. These will be simulated in laboratory by means of pressure chamber. Special attention will be taken to test the reference electrode behaviour in function of the pressure. Moreover, test will be conducted on the positioning of the electrode array with respect to the sediment-water interface by measuring the resistivity, based on the fact that the electrical resistivity in the water column is about 15-20% lower than that in the sediment. Checking of the positioning and of the force will be done at different pressure and with different operating conditions.

– *Methodology:* None

– *Deliverables:*

A report describing the results achieved during the pressure test will represent the deliverable of this sub-task.

– *Interdependence and links with other tasks:*

This sub-task depends on sub-task 5.1 and on the development sub-tasks 4.1 and 4.3

Sub-task 5.3

– *Title:* Attended field tests of the profiler

– *Partner responsible:* AMK

– *Partners involved:* CABE

– *Duration (in months):* 6

– *Specific objective:*

Tests on the spatial resolution and analytical sensitivity and reliability of the sediment-water interface profiler will be done, at small depths, through a sequence of increasingly challenging environments.

– *Methodology:*

The first tests will be carried out in shallow sediments close to the water's edge with toxic or suboxic surface sediments, in other words with chemistry not far removed from that of the water column. Subsequent tests will be made on anoxic sediments. These field comparisons will be complemented where appropriate by laboratory comparisons under controlled chemical conditions.

- *Deliverables:*
Report on the performance of the system at small depths.
- *Interdependence and links with other tasks:*
Links with sub-tasks 5.1 and 5.4.

Sub-task 5.4

- *Title:* Field tests of the profiler at great depth
- *Partner responsible:* AMK
- *Partners involved:* CABE
- *Duration (in months):* 4
- *Specific objective:*

Deployment on a Benthic Lander will allow the sensor to be tested at the sediment-water interface in deeper waters. Comparison of the profiles obtained by the gel systems and by the electrochemical sensors will be especially valuable in assessing the spatial resolution and speciation-sensitive response of the two profilers.

- *Methodology:*
Most of the test deployments will be accompanied by simultaneous deployments of DET or DGT gel accumulation profilers.
- *Deliverables:*
A report on the performance of the system.
- *Interdependence and links with other tasks:*
Links are foreseen with sub-task 5.3

Sub-task 5.5

- *Title:* Technical improvements of the probes
- *Partner responsible:* IDRONAUT
- *Partners involved:* CABE, IMT, AMK
- *Duration (in months):* 16
- *Specific objective:*

Objective of this sub-task will be the collection and classification of all the technical improvements realized on the two sub-project prototypes. They will be reported on the specifications and will be finally implemented on the two probe prototypes in a consolidated form (i.e updating of the probes PCB (Printed Circuit Board) versus manual wiring modifications).

- *Methodology:*
All the reports and technical papers realized by the partners during the whole project will be collected by the coordinator. A draft condensing all the modification and/or improvements brought to the probes will be realised and discussed during a meeting among the partners.
- *Deliverables:*
The revised specification of the sub-projects will be released, while the two prototypes will be updated to the latest modifications.
- *Interdependence and links with other tasks:*
Links are foreseen with all previous sub-tasks.

§5. MANAGEMENT OF THE PROJECT

The overall coordination of the project will be accomplished by IDRONAUT. A scientific sub-coordination will be assured by CABA.

While the management and coordination will be the same for both sub-projects, two working groups will be established, one for each sub-project, addressing different resources and goals. Coordination between the two groups will be maintained through vertical and horizontal issue. Two sub-project coordinators will be responsible of the management of each working group.

The organisation will then be the following:

IDRONAUT

Coordinator

CABA

Scientific sub-coordinator

CABA

Sub-project I coordinator

IDRONAUT

Sub-project II coordinator

Organisation of the two working group

IMT	CABA	IDRONAUT	AMK
Fabrication of microsensors and multipotentiostat	Development of analytical conditions. Lab and field tests.	Technical developments of the probes	Probes specifications Field tests in seawater

§5.1 Diagram showing the key activities in the project

Herein after there are reported the key activities for both sub-projects and the responsible partner.

Sub-Project I

- sub-task 2.1 - Synthesis of the microelectrode protective gel, responsibility of CABA.
- sub-task 2.2 - Development of the microelectrode array, responsibility of IMT.
- sub-task 3.2 - Development of the measurement methods, responsibility of CABA.
- sub-task 3.6 - Development of the sterilising system, responsibility of IDRONAUT.
- sub-task 3.7 - Final field unattended long-term validation tests, responsibility of AMK.

Sub-Project II

- sub-task 4.1 - Fabrication of an individually addressable microelectrode array, responsibility of IMT.
- sub-task 4.3 - Development of the probe and microprofiler mechanics, electronics, firmware, responsibility of IDRONAUT.
- sub-task 5.1 - Tests of the analytical measurement methods in the laboratory in real sediment, responsibility of CABA.
- sub-task 5.4 - Field tests of the profiler at great depth, responsibility of AMK.

§5.2 Data management

Not applicable to the project.

§5.3 Meetings and workshops

About 2-3 meetings/year for coordination have been foreseen.

§5.4 Milestones

The full project is planned for three years. Overall, the cost and time will be distributed equally between the two sub-projects. For both probes, three types of development are needed. Some developments must precede others in a logical order. For this reason, the combination of the two sub-projects I and II allows optimum distribution of time and thus minimisation of costs.

The main milestones are the following:

- 1 - Two months later the project starting:
 - * The whole specification of the voltammetric probe and of the voltammetric profiler will be ready.
- 2 - End of the first year:
 - * Prototype of a probe for automatic measurement of mobile concentrations of metals, ready for the field tests.
- 3 - Two months after the end of the second year:
 - * Probe for automatic measurement of mobile + total concentrations of metals as above, with autosterilizing system.
- 4 - Middle of the third year:
 - * Prototype of probe for voltammetric metal-concentration profiles at the sediment-water interface, ready for the field validation tests.
- 5 - End of the third year:
 - * Probe and Lander for metal concentration profiles at the sediment-water interface.

§5.5 Reports

The following reports will be submitted to the Commission:

- every 6 months: a short management report comparing progress sub-task by sub-task with the technical annex;
- annual scientific and technical progress reports;
- a final report set consisting of
 - a) a final management report,
 - b) a publishable final report,
 - c) a final scientific and technical report,
 - d) an extended abstract for electronic dissemination which shows the objectives and technical results of the project,
 - e) a short report on the dissemination and exploitation of the results,
 - f) 1 reprint of all publications of the project (when available),
 - g) if applicable: EDMED and ROSCOP forms.

§6. DISSEMINATION AND EXPLOITATION OF RESULTS

Dissemination of results will be carried out by organising and/or participating in meetings on oceanographic research or exploitation, related to trace compounds concentration or speciation determinations. IDRONAUT is a member of MAROBOT and EUROLANDER Community which organise discussion meetings. It also takes part regularly to other meetings like OSATES or ECOPS. F. Graziottin (IDRONAUT) is the Italian Contact Participant in the EUROMAR board. J. Buffle (CABE) is Chairman of the IUPAC Commission of Environmental Analytical Chemistry which has recently established links with SCOR (Scientific Committee of Oceanic Research), in particular to promote development of *in situ* probes and sensors in the ocean. He also participates regularly, sometimes as plenary lecturer, in scientific meetings on environmental sciences (e.g. ACS meetings) where the results of the project will be given.

Dissemination of results will also be done by publications in scientific journals, in various fields: marine science, analytical chemistry, environmental chemistry, microtechnology, sensors.

Filed exploitation of the developed devices will be promoted too, in particular in the strategic Programs selected for instance in MAST-III (projects of sections A-1, A-2, A-3 and B-1), in JGOFS and LOICZ, and in ECOPS EUROCONFERENCE (HiBETS, MASTER, GEOGLOW). Exploitation of the Benthic Lander in extreme conditions will be promoted in areas of European interests [11], e.g. at the Eastern Atlantic margin, extending from the Portuguese slope to the deep-sea floor, as well as in the Eastern Mediterranean Sea extending from the continental margin of Greece to the Mediterranean ridge. Other occasions for exploitation are given by the multitude of national and European Programs in progress in the Mediterranean area.

Exploitation of the probes therefore will also be envisaged, possibly after modifications, to monitor pollution of fresh waters, to study biogeochemical processes in fresh water systems and as water quality control in drinking and waste water treatment plants.