

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

CONTRACT NUMBER : MAST3-CT95-0033

COORDINATOR :

Idronaut S.rl.
Via Monte Amiata, 10
20047 Brugherio - (MI)
Italy
Tel. : + 39-39-879656 ; Fax : +39-39-883382
E-mail : idronaut@askesis.it

Flavio Graziottin

OTHER PARTNERS

University of Geneva
CABE, Department of Inorganic, Analytical and Applied Chemistry
Sciences II - 30 Quai E. Ansermet
1211 Geneva 4
Switzerland
Tel. : +41-22-7026431 ; Fax : +41-22-7026069
E-mail : buffle@cabe.unige.ch

Principal investigator

Jacques Buffle

University of Neuchatel
Institute of Microtechnology
Rue Breguet 2
2000 Neuchatel
Switzerland
Tel. : +41-32-7205305- Fax : +41-32-7205711
E-mail : milena.kouldelka@imt.unine.ch

Milena Koudelka-Hep

Goteborg University
Department of Analytical and Marine Chemistry
41296 Goteborg
Sweden
Tel. : +46-31-7722295 ; FAX : +46-31-7722785
E-mail : david@amc.chalmers.se

David Turner

A NOVEL VOLTAMMETRIC *IN-SITU* PROFILING SYSTEM FOR CONTINUOUS, REAL-TIME MONITORING OF TRACE ELEMENTS IN NATURAL WATERS.

Mary-Lou TERCIER-WAEBER* and Jacques BUFFLE

CABE, Department of Inorganic, Analytical and Applied Chemistry, Sciences II,
University of Geneva, 30 Quai E.-Ansermet, 1211 Geneva 4, Switzerland.

Flavio GRAZIOTTIN

Idronaut, Via Monte Amiata 10, 20047 Brugherio (MI), Italy.

SUMMARY.

The aim of the VAMP project is to develop, by means of several new technologies, voltammetric sensors and probes allowing *in-situ* automatic measurements of trace concentration profiles i) in the water column - sub-project I and ii) at the sediment-water interface - sub-project II. The work performed during the first two years of the project has allowed to successfully complete the sub-project I. The main technical developments and analytical tests carried out are summarised in this paper.

I. INTRODUCTION.

There is a growing need to monitor continuously chemical pollutants, and in particular trace elements, in natural aquatic systems both to get deeper insight into natural processes in general and to understand the relationship between anthropogenic releases and their long term impact on man and the environment. Trace elements are not biodegradable but are involved in biogeochemical cycles and distributed under different physicochemical forms (i.e. simple inorganic species, organic complexes and metal ions adsorbed onto a variety of colloidal particles). The proportion of these different forms may vary continuously with space and time due to concurrently occurring physical, chemical and biological processes. Any variation in the speciation of an element will affect its bioavailability, its rate of transport to the sediment and its overall mobility in the aquatic system [1-4]. To understand and predict the role and the fate of these different metal species, new analytical instrumentation capable of performing *in-situ*, real time monitoring of specific forms of elements in continuous and reproducible manner, on a wide spatial network, is required [5].

The design of such a tool is still a challenge for analytical chemists since techniques that combine high sensitivity and reliability, speciation capability, integrity of the samples and unattended operation are prerequisite. This kind of development however is the only way : i) to minimise the large number of artefacts due to sampling and sample handling, ii) to allow rapid detection of pollutant inputs, iii) to accumulate detailed spatial and temporal data banks of complete ecosystems at low cost, and iv) to perform measurements in locations which are difficult to access. Amongst the analytical tools available, the potentiality of voltammetric techniques for trace compound analysis in natural waters has been demonstrated in the past [6-10]. However, most of the development done until now deal with on-line automatic voltammetric analyzers for laboratory or field measurements [9, 11-14]. Very little work has been reported concerning the development of submersible voltammetric probes for *in-situ* monitoring of trace elements [15-17] and none of these systems were usable for automatic, continuous measurements. This is mainly due to the fact that long term *in-situ* monitoring with such systems are limited by insufficient reliability of the commercially available voltammetric sensors and by the fouling of the sensor surface due to the adsorption of organic or inorganic matter.

In this paper the development of a novel **Voltammetric *In-situ* Profiling System (VIP System)**, based on advanced microprocessor and telemetry technology, is reported. This system has been built by taking into account all the important criteria mentioned above as well as the problems related to field deployment, in particular: robustness, ease of handling and flexibility. The heart of the submersible voltammetric probe is a gel integrated either single or array microsensor. These microsensors have been specifically developed to enable continuous, reproducible and reliable measurements of analytes in complex media without physical and chemical interferences of the test solution [18-21]. The VIP system allows to perform direct *in-situ* measurement of the mobile fractions of Cu(II), Pb(II), Cd(II) and Zn(II) as well as Mn(II) and Fe(II) using either Square Wave Anodic Stripping Voltammetry (SWASV) or Square Wave Cathodic Sweep Voltammetry (SWCSV) down to 500 meters depth. Examples of environmental applications of the VIP system for *in-situ* monitoring of Cu(II), Pb(II) and Cd(II) in oxygen saturated sea water and Mn(II) profiling in lake water are given.

II. EXPERIMENTAL SECTION.

VIP System. A detailed technical description of the Voltammetric *In-situ* profiling System is given elsewhere [22]. Briefly, the VIP System consists of: a submersible voltammetric probe, an Idronaut Ocean Seven 301 multiparameter submersible probe (optional), a calibration deck unit, a surface deck unit and a IBM compatible PC (Fig. 1).

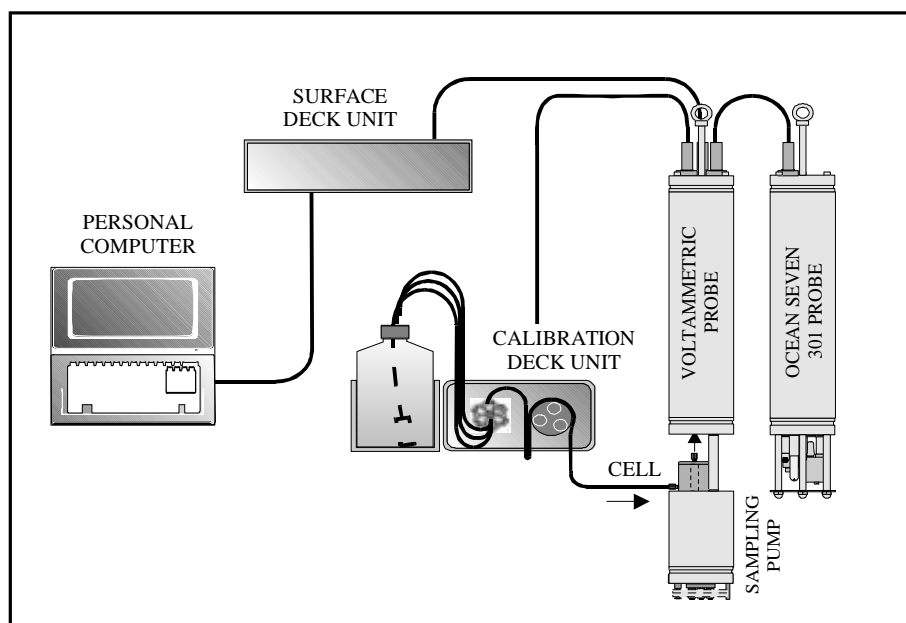


Fig. 1 : Schematic diagram of the whole Voltammetric In-situ Profiling System (VIP System)

The *submersible voltammetric probe* (dimensions : 86 cm length, 10 cm in diameter ; weight : 8 kg in air, 4 kg in water) is comprised of distinct specific modules : an electronic probe housing, a pressure compensated flow-through plexiglas voltammetric cell (internal volume = 1.5 ml) with a platinum ring auxiliary electrode and a home-made Ag/AgCl/KCl saturated gel reference electrode, a pressure case base incorporating the preamplifier for the voltammetric microsensor and a sampling submersible peristaltic pump. The electronic housing contains all the hardware and firmware necessary to manage : i) the voltammetric measurements, ii) the interfacing of the Ocean Seven 301 (via an RS232C interface), the calibration deck unit and the submersible peristaltic pump, and finally iii) the data transfer by telemetry. The interface between the Personal Computer and the voltammetric probe is carried out by using the Terminal Emulator under Windows. The VIP System software is divided in a management software and a firmware. The firmware, stored in a flash memory, allows the user to execute the processing operating functions and the data acquisition. The management software allows the user, through menus and pop-up data entry windows, to

control and configure the voltammetric probe operating parameters and functions such as : electrochemical parameters, data acquisition, calibration and maintenance operations. Data files are stored in a non volatile memory having its own battery which guaranty high data retention and protection. The *Ocean Seven 301* probe allows to control the exact position of the voltammetric probe at depth and to measure simultaneously the following parameters : temperature, conductivity, salinity, dissolved oxygen, pH and Redox potential. The *calibration deck unit* enables to perform in laboratory, on shore or on boat i) the renewal of the microsensor Hg layer (see below), ii) the calibration of the probe, and iii) the measurements of standard and collected natural samples. The *surface deck unit* powers and interfaces, by telemetry, the measuring system with a Personal Computer. The telemetric signals superimposed to the system power supply flow all along the voltammetric probe holding cable. This unit allows an autonomy of about 35 hours and can be recharged either in continuous mode using solar captor or after use.

Gel integrated microsensors. The working sensor of the submersible voltammetric probe is an Agarose Membrane-covered Mercury-plated Ir-based either single or microelectrode arrays (μ -AMMIE and μ -AMMIA respectively) (Fig. 2).

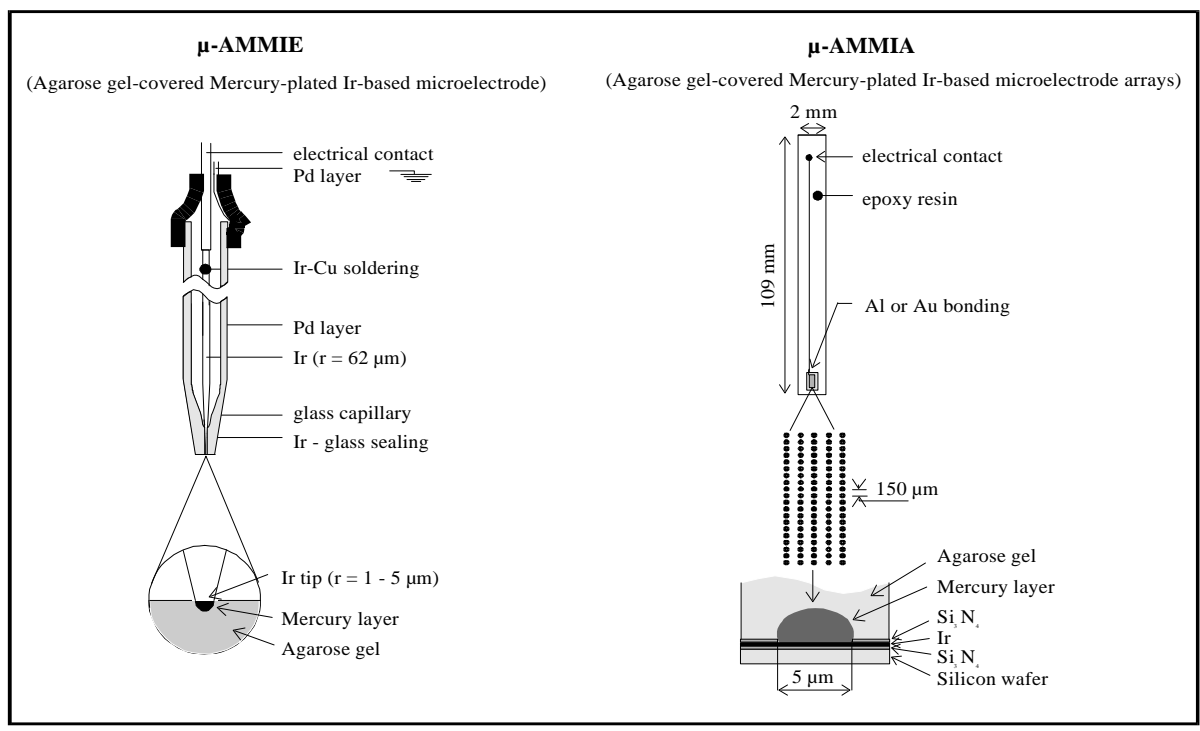


Fig. 2 : Schematic diagram of the single and array gel integrated microsensors

The voltammetric microsensors measure the test compounds within the gel after equilibration of the gel with the sample. Details of the fabrication and characteristics of these microsensors are reported elsewhere [18-21] and thus are only briefly summarised here. The single microelectrode was built by sealing an electroetched Ir wire with diameter of few micrometers in a shielded glass capillary followed by mechanical polishing [18]. The microelectrode arrays was produced by means of thin film technology on chips and photolithographic technique [20]. It consists of 5 x 20 interconnected iridium microdisc electrodes having a diameter of 5 μm and a centre to centre spacing of 150 μm surrounded of a 300 μm thick Epon SU8-8 containment ring. Both sensors are covered with a 1.5% LGL agarose protective gel membrane. Mercury semidrops were plated through the gel layer onto Ir substrates at -400 mV (vs Ag/AgCl/3M KCl/1M NaNO₃) in a deoxygenated 5 mM Hg(CH₃COO)₂ and 10⁻²M HClO₄ solution. Reoxidation of the mercury was carried out by scanning the potential linearly from -300 mV to +300 mV , at 5 mV/s, in a degassed 1M KSCN solution. In both cases, the currents were recorded and, from the electric charge, the diameters of the mercury semidrops were determined by assuming they were parts of spheres. The same agarose antifouling gel membrane was used over an extended period of about one month. This kind of gel integrated microsensor has a number of advantages for in-situ measurements : i) the gel acts as a dialysis membrane, i.e. allows diffusion of small ions and molecules and retains colloidal and particulate material, and thus protects the electrode surface from fouling [19,21] allowing its operation for long periods of time ; ii) the gel membrane protects the electrode from ill-controlled hydrodynamic currents occurring inside the water column, i.e. analysis inside the gel is based on pure molecular diffusion ; iii) microelectrodes have low iR drop and reduced double-layer capacitance, thus direct voltammetric measurements without added electrolyte can be performed in freshwaters even if the ionic strength is as low as 10⁻⁴M ; and iv) voltammetric currents, *i*, at micro-sized electrodes are controlled by spherical diffusion and reach a non zero steady state value at constant potential [23]. This last point is particularly important as it allows : i) to perform the SWASV deposition step without stirring, which is absolutely required to perform SWASV in the protective gel membrane, and ii) to define a maximum size cut-off limit of a few nanometer [5,24] for the so-called mobile species (i.e. free ions and small labile complexes) selectively measurable on the microelectrode. These considerations are important as they show that combination of VIPS *in-situ* measurements with complementary

laboratory measurements of total concentration in raw and filtered samples, performed by using classical techniques, allows to determine three key environmental fraction of trace element species : i) the mobile species (\leq of a few nm) by direct *in-situ* measurements in unperturbed sample which is a key feature to minimize analytical artefacts [10]; ii) the colloidal species (total concentration in filtered samples minus mobile concentration) ; and iii) the particulate species ($> 1 \mu\text{m}$) (difference in concentration between raw and filtered samples). Distinction between these three different fractions is important since the mobile species are the species the most easily bioavailable while the colloidal and particulate fractions play different roles in metal circulation and residence time. These three fractions are considered in the interpretation of the results reported below. Finally, it has been shown [21] that the current amplitude of the gel integrated microsensors is independent of the pressure, even up to pressure as high as 600 bars, and its temperature dependence can be taken into account using Arrhenius equation.

III. RESULTS AND DISCUSSION.

In-situ Mn(II) profiling in anoxic lake waters. The system was first tested for Mn(II) concentration profile measurements within the anoxic hypolimnion of lake Brêt (Switzerland). Lake Brêt is a shallow lake with a maximum depth of 20 meters and it is stratified roughly from May to the end of September. All through the field tests, μ -AMMIE or μ -AMMIA with the same mercury layers were used to calibrate the submersible voltammetric probe the day before and after each deployment as well as for *in-situ* measurements (i.e. no renewal of the mercury semidrops over three days). The calibrations were performed by standard additions in $0.2 \mu\text{m}$ filtered lake water samples degassed with a mixture N_2+CO_2 to maintain the pH at 7.5. Example of the results obtained (Fig. 3) illustrate the excellent stability of the gel integrated microsensor for at least three days and show no memory effect from in-situ measurements performed between both laboratory calibrations. In addition, all the different calibrations curves yielded an average slope of $17.5 \pm 1.2 \text{ pA}/\mu\text{M}$ ($N = 6$, 95% probability) and $30.6 \pm 1.6 \text{ pA}/\mu\text{M}$ ($N = 8$; 95% probability) for SWASV ($t_{\text{dep}} = 5 \text{ s.}$) and SWCSV respectively using the μ -AMMIE (Hg layer radius : 8.8 to $9.3 \mu\text{m}$) and $5.3 \pm 0.29 \text{ nA}/\mu\text{M}$ ($N = 6$, 95% probability) for SWASV using the μ -AMMIA (Hg layer radius : 6.6 to $7 \mu\text{m}$; $t_{\text{dep}} = 10 \text{ s.}$). These results show the

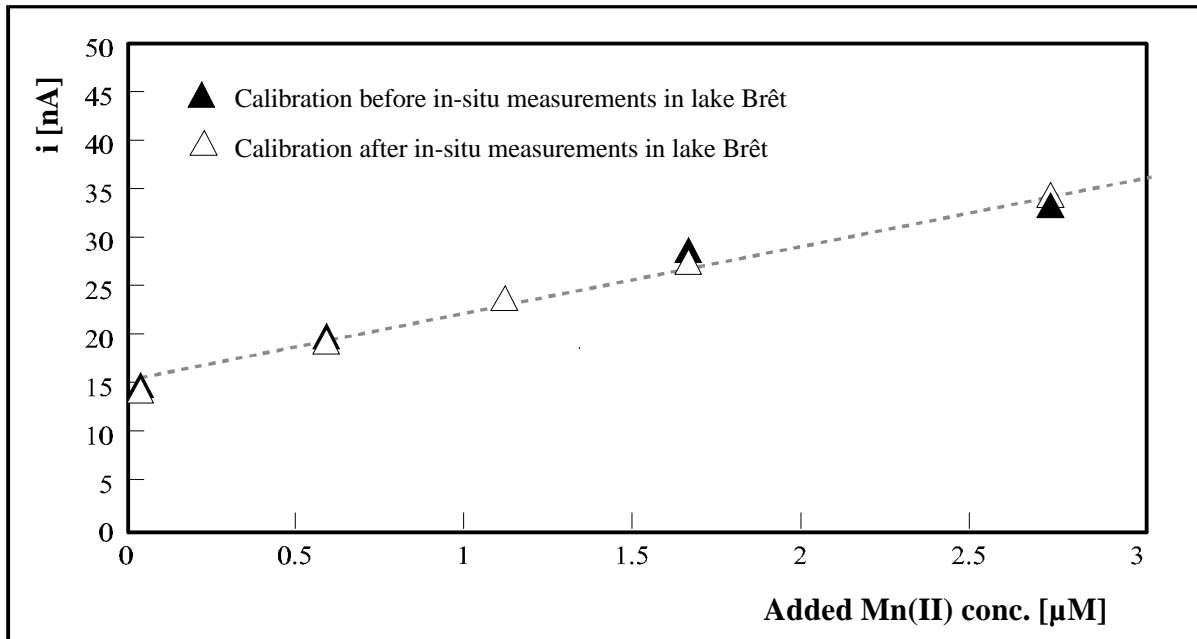


Fig. 3 : Typical SWASV results obtained for laboratory calibrations performed before and after in-situ measurements in lake Brêt using the same Hg layer over the three days. μ -AMMIA Hg radius = 6.7 μm . SWASV conditions : precleaning $E = -800$ mV ; precleaning $t = 30$ s. ; deposition $E = -1600$ mV ; deposition $t = 10$ s. ; final $E = -1300$ mV ; pulse amplitude = 25 mV ; step amplitude = 1 mV ; frequency = 5 Hz.

excellent reproducibility and reliability of both gel integrated microsensors developed. The main objective of field tests in lake Brêt were to check the validity and reliability of the measurements performed with the VIP System in real conditions. For this purpose, concentration profile obtained from *in-situ* voltammetric measurements were compared with on-field voltammetric measurements, performed at a constant temperature of 20°C, using microsensor arrays with and without protective gel layer. For on-field measurements, a Tygon sampling tubing was fixed to the VIP titanium protective cage at exactly the same level that the input of the pressure compensated flow-through cell and samples were pumped at each depth directly in a thermostated plexiglas cell using a peristaltic pump. For comparison purpose, samples were also withdrawn to allow laboratory Mn measurements in acidified (pH 2) raw samples, acidified samples filtered on 0.2 μm pore size membranes and acidified samples ultracentrifuged at 30000 rpm for 15 hours (which allowed to eliminate the species with a size ≈ 5 nm assuming a density of 2) using either Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Typical results obtained for Mn profiles in lake Brêt are shown in Fig. 4. Excellent agreement are observed in particular between:

- Mn(II) concentration profiles determined from *in-situ* voltammetric measurements after temperature effect correction, using the following equation $\ln(i) = 29.68-7091*1/T$ [21], and on-field voltammetric measurements performed at constant temperature of 20°C using microsensor arrays with gel.
- Mn(II) concentration profiles determined from voltammetric measurements with microsensor arrays with gel (mobile species with size of few nm) and ICP laboratory measurements of ultracentrifugated acidified samples (species \bullet 5 nm).

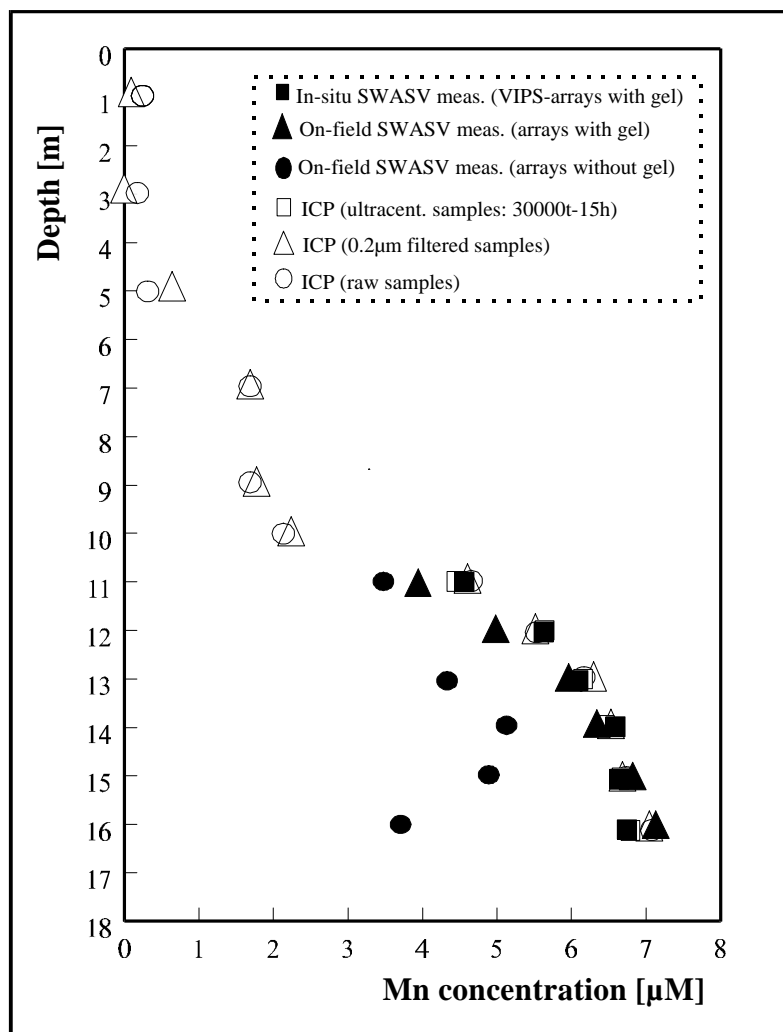


Fig. 4 : Typical profiles of Mn in the anoxic hypolimnion of lake Brêt, August 20 1997. (SWASV conditions as in Fig. 3).

These results demonstrate the reliability of the VIP System using gel integrated microsensors for *in-situ* monitoring. They also confirm that pressure has no effect on the current amplitude as well as the validity of the equation, determined in the laboratory, to take into account the temperature effect [21]. In addition, interesting information regarding the nature of Mn in lake Brêt is also obtained by comparing voltammetric measurements with the results obtained for ICP and AAS laboratory measurements of the raw, 0.2 µm filtered and ultracentrifuged acidified samples (Fig. 4). Since voltammetry measures only the mobile Mn species with sizes of a few nanometers, whereas AAS and ICP techniques measure the total metal concentration in the different samples, the results obtained indicate that Mn in lake Brêt is present predominantly in the mobile form, i.e. most likely Mn²⁺ and probably small inorganic complexes, at this period of the year. The protective role of the agarose gel membrane was also studied by comparing Mn(II) concentration profiles obtained using microsensor arrays with and without gel layer (Fig. 4). It can be seen that systematically too low concentrations are obtained for the unprotected microsensor. A detailed study showed that peak current attenuations observed for unprotected sensors are due to adsorption of lake born iron hydroxide particles, well-known for having strong adsorbing capabilities, onto the sensor Hg surface which then hinder the diffusion of Mn(II). These results clearly demonstrate the efficiency and necessity of the protective gel layer to eliminate fouling problems and thus allow reliable, direct measurements in natural media. It must be emphasised that no other perturbation in voltammetric peaks except a lowering in the current intensity was observed. Thus, in the absence of protective gel, the difference observed between *in-situ* voltammetry and classical techniques might be wrongly attributed to the presence of colloidal Mn species even though such species are not present in lake Brêt as demonstrated before. A more detailed study comparing the results obtained for Mn(II) profiling with the VIP System in different lakes can be found elsewhere [24].

In-situ trace metal monitoring in oxygen saturated sea water. Continuous trace metal monitoring for quality control is becoming of prime importance in many estuaries and coastal zones. The potentiality of the VIP System for such purpose was tested in Venice Lagoon (Venice-Italy) and in Gullmar Fjord (Sweden). In-situ measurements in Venice Lagoon were performed in three different stations: 1) Breda, which is located in the middle of the industrial area and represents one of the most polluted part of the Lagoon, 2) Fusina, which is at the limit of the southern part of the industrial area in a wide artificial

navigation canal and finally 3) Bocca di Porto, which is located at the main entrance of the Lagoon. In Kullmar Fjord, two types of tests were carried out with the Vip System : i) *in-situ* measurements at different hydrographic stations aboard R/V Arne Tiselius, and ii) unattended, autonomous *in-situ* measurements at Kristineberg Marine Research Station located at the entrance of the Fjord. The probe was calibrated before and after deployment. Average slopes of 0.30 ± 0.01 nA/nM, 0.34 ± 0.01 nA/nM and 0.18 ± 0.02 nA/nM were found for Pb(II), Cd(II) and Cu(II) respectively (Hg layer radius = $7.9\mu\text{m}$; deposition $t = 15$ min; $N = 4$; 95% probability).

Venice Lagoon VIP measurements (average of three replicates) together with total metal concentrations measured in UV irradiated, acidified samples in the laboratory are given in Table 1. As can be seen, the dissolved fraction of trace metals represent in general only 10

Table 1: VIP *in-situ* measurements (C_m = trace metal mobile fraction concentrations) and laboratory measurements (C_{tot} = total metal concentrations measured in UV irradiated, acidified samples) of Cd(II), Pb(II) and Cu(II) in Venice Lagoon (March 12-13, 1997).

Stations	Cd(II) [nM]		Pb(II) [nM]		Cu(II) [nM]	
	C_m (VIP)	C_{tot} (lab)	C_m (VIP)	C_{tot} (lab)	C_m (VIP)	C_{tot} (lab)
Breda	0.18 ± 0.04	1.33 ± 0.03	1.64 ± 0.11	3.03 ± 0.17	3.93 ± 0.86	10.57 ± 1.08
Fusina	0.25 ± 0.04	1.20 ± 0.01	0.42 ± 0.05	3.10 ± 0.10	1.56 ± 0.39	23.33 ± 2.60
Bocca di Porto	0.02 ± 0.005	0.23 ± 0.03	0.06 ± 0.01	1.0 ± 0.10	--	5.97 ± 0.81

to 20% of the total metal concentration and hence, as previously observed for trace metal measurements in freshwater [18], the colloidal/particulate fraction are predominant. Table 1 also shows that concentrations as well as variation in concentrations in the ppt level can be measured *in-situ* with a good reproducibility using the VIP System.

Stability tests of the VIP System for unattended autonomous *in-situ* monitoring performed at Kristineberg Marine Station are shown in Fig. 5. Measurements were automatically performed every hour for 52 hours with a renewal of the Hg layer after 22 hours. Interesting observation can be made from these preliminary results. Indeed, temperature, salinity and conductivity data (Fig. 5), measured simultaneously to *in-situ* VIP Pb(II) concentration

using the Ocean Seven 301 multiparameter probe, show that fresh, warmer water is advected into the measurement site during the experiment. At each of such event, significant variation of in-situ Pb(II) concentration were also observed. Even if more extensive studies are required for rigorous interpretation, these results show the potentiality of the VIP System as a tool to identify and study specific changes.

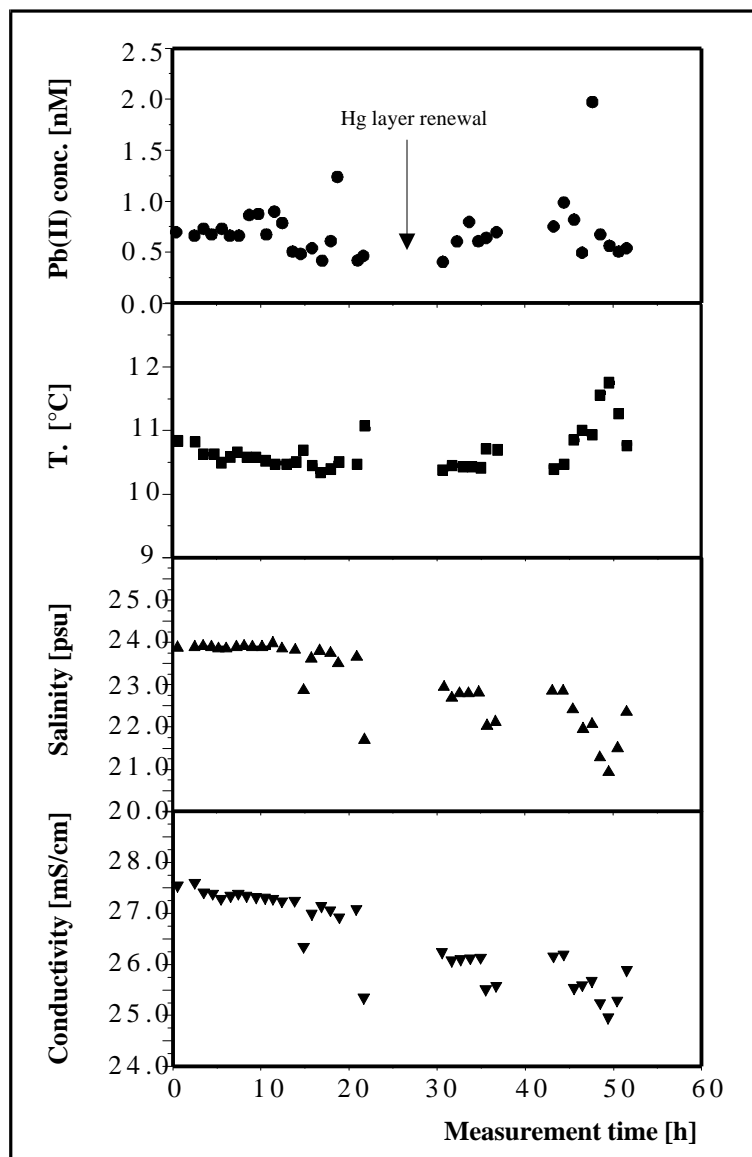


Fig. 5 : Unattended autonomous *in-situ* monitoring performed with the VIP System at Kristineberg Marine Station (Kullmar Fjord-Sweden May 16-18 1997). μ -AMMIE Hg radius = 8.3 μ m. SWASV conditions : precleaning E = -80 mV ; precleaning t = 60 s. ; deposition E = -1300 mV ; deposition t = 15 min ; equilibration E = -1300 mV ; equilibration t = 10 s. ; final E = -80 mV ; pulse amplitude = 25 mV ; pulse step = 8 mV ; frequency = 200 Hz.

IV. CONCLUSION.

The combination of voltammetric principles with recent breakthrough in electronic and micromechanics has allowed the development of a sophisticated, compact, reliable, in-situ analytical device for trace element measurements in natural aquatic systems thanks to the use of reproducible and well characterised gel-integrated microsensors. In particular ppt level of the mobile fraction, which is the most difficult fraction to measure without analytical artefacts, can be determined by direct in-situ measurements, i.e. without perturbing the samples. In addition punctual changes can be identified and studied. Further development are under way to couple flow injection system to the flow-through voltammetric cell and to adapt the VIP System to a Radio Buoy Profiler. These will allow i) in-situ total metal concentration measurements in addition to the mobile fractions and ii) continuous, autonomous, automatic in-situ monitoring over extended period of time respectively. Both points are important for efficient environmental monitoring and more rigorous interpretation of trace element cycles in natural aquatic systems.

ACKNOWLEDGEMENTS.

The authors thank : Fabio Confalonieri, Giuliano Riccardi and Antonio Sina (Idronaut team) who developed the software, the hardware and the submersible pump of the VIP System. Claude Bernard, François Bujard and Serge Rodak (CABE team) who built the flow-through voltammetric cell as well as all the instrumentation needed for constructing the voltammetric single microsensor. G.C. Fiaccabrino, M. Koudelka-Hep (Institute of Microtechnology, University of Neuchâtel) and Cécile Belmont-Hébert (CABE) who have developed the Ir-based microsensor arrays and performed systematic laboratory tests of this microsensor respectively. D. Turner (Department of Analytical and Marine Chemistry, Goteborg University) for providing all the logistic during field tests in Kullmar Fjord-Sweden.

REFERENCES.

1. *Metal Speciation and Bioavailability in Aquatic Systems* ;
Tessier, A. and Turner, D. R., Eds. ; Wiley : New York, **1995**.
2. *Chemical and Biological Regulation of Aquatic Systems* ;
Buffle, J. and De Vitre, R.R., Eds. ; Lewis : London, **1994**.
3. *Trace Elements in Natural Waters* ;
Salbu, B. and Steinnes, E., Eds. ; CRC Press : London, **1995**.
4. Kenneth, S.J. ; Coale, K.H. ; Jannasch, H.W. *Anal. Chem.* **1992**, *64*, 1065A.
5. Buffle, J. ; Tercier, M.-L. ; Parthasarathy, N ; Wilkinson, K.J. *Chimia* **1997**, *51*, 690.
6. Kheifets, L.Y. ; Vasyukov, A.E. *J. Anal. Chem.* **1996**, *51*, 432.
7. Smart, R.B. *Hazard Assess. Chem.* **1987**, *5*, 1.
8. van den Berg, C.M.G. In *Chemical Oceanography* ; Riley, J.P., Ed. ; Academic Press :
London, **1989** ; Vol. 9, Chapter 51.
9. Zirino, A. In *Marine Electrochemistry* ; Whitfield, M. and Jagner, D., Eds. ; Wiley :
New York, **1981** ; Chapter 10.
10. Tercier, M.-L. ; Buffle, J. *Electroanalysis* **1993**, *5*, 187.
11. Hernandez-Brito, J.J. ; Cardona-Castellano, P. ; Perez-Peña, J. ; Gelado-Caballero, D.
Electroanalysis **1990**, *2*, 401.
12. Bond, A.M. ; Luscombe, D.L. ; Tan, S.N. ; Walter, F.L. *Electroanalysis* **1990**, *2*, 195.
13. Mann, A.W. ; Lintern, M.J. *J. Geochem. Explor.* **1984**, *22*, 333.
14. Cagnet, L. ; Linet, P. ; Ribacki, D. ; Loubinoux, M.T. *J. Fr. Hydrol.* **1987**, *18*, 27.
15. Tercier, M.-L. ; Buffle, J. ; Zirino, A. ; De Vitre, R.R.
Anal. Chim. Acta **1990**, *237*, 429.
16. Brainina, Kh. Z. ; Khanina, R.M. ; Forshtadt, V.M. ; Vilchinskaya, E.A. ;
Gaponenko, G.L. In *Proc. of J. Heyrovsky Centennial Congress on Polarography* ;
41th Meeting of the International Society of Electrochemistry : Prague, **1990**, p 175.
17. Wang, J. ; Foster, N. ; Armalis, S. ; Larson, D. ; Zirino, A. ; Olsen, K.
Anal. Chim. Acta **1995**, *310*, 223.
18. Tercier, M.-L. ; Parthasarathy, N. ; Buffle, J. *Electroanalysis* **1995**, *7*, 55.
19. Tercier, M.-L. ; Buffle, J. *Anal. Chem.* **1996**, *68*, 3670.

20. Belmont, C. ; Tercier, M.-L. ; Buffle, J. ; Fiaccabrino, G.C. ; Koudelka-Hep, M.
Anal. Chim. Acta **1996**, 329, 203.
21. Belmont-Hébert, C. ; Tercier, M.-L. ; Buffle, J. ; Fiaccabrino, G.C. ; Koudelka-Hep, M
Anal. Chem., submitted.
22. Tercier, M.- L. ; Buffle, J. ; Graziottin, F. *Electroanalysis*, in press.
23. Zoski, C.G. J. *Electroanal. Chem.* **1990**, 296, 317.
24. Tercier-Waeber, M.-L. ; Belmont-Hébert, C. ; Buffle, J. *Env. Sci. & Techn.*, submitted.