Environ. Sci. Technol. **1998**, *32,* 1515−1521

Real-Time Continuous Mn(II) Monitoring in Lakes Using a Novel Voltammetric in Situ Profiling System

MARY-LOU TERCIER-WAEBER,* CÉCILE BELMONT-HÉBERT, AND JACQUES BUFFLE

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

The application of a novel voltammetric in situ profiling system (VIP System) for real-time continuous monitoring of Mn(II) in anoxic lake waters is described. The heart of the submersible voltammetric probe is a gel-integrated microsensor including either a single or an array microelectrode. The integration of a microelectrode in a gel is a novelty which protects its surface from fouling and allows its application for direct measurements in complex media. The main features of this kind of microsensors for in situ measurements in natural waters are discussed. Reliability and validity of concentration profiles obtained using the VIP System have been demonstrated by comparing in situ and on-field voltammetric data with those obtained using classical techniques. The advantages of combining the VIP System with classical techniques for environmental study are also illustrated. In particular, (i) specific measurements of the mobile forms (i.e., hydrated Mn^{2+} and small complexes with size smaller than a few nanometers), the colloidal forms (a few nanometers to 1 μm) and the particulate forms (>1 μm), which are three key fractions for understanding Mn biogeochemical cycles as well as (ii) the discrimination between seasonal and temporal variations can be performed with minimum sample handling and analysis time.

Introduction

There is a growing need to continuously monitor 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 inpact 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 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 minimize the large number of artifacts 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. Among 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 deals 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 is 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. Recently, a novel voltammetric in situ profiling system (VIP System), based on advanced microprocessor, telemetry, and microsensor technologies, has been developed by taking into account all the important criteria mentioned above (*18*). The heart of the submersible voltammetric probe is a gel-integrated microsensor including either a single or an array microelectrode. These microsensors have been specifically developed to enable continuous, reproducible, and reliable measurements of analytes in complex media (*19*−*22*). The probe can be used for measurements down to 500 m with detection limits of a few parts per trillion for in situ trace metal monitoring in oxygen saturated seawater (*18*).

This paper reports Mn(II) profiling in anoxic lake water with the VIP System and comparison of the results with classical laboratory analysis. The role of Mn on aquatic biota and biogeochemical cycles of many trace compounds and elements strongly depends on its oxidation state as well as the size distribution of complexes, colloids, and particles to which Mn is bound (*2, 23, 24*). Presently, there is no simple technique to discriminate unambiguously between these various forms of Mn. In particular, discrimination between hydrated Mn^{2+} and its labile complexes on one hand and the colloidal forms (size of a few nanometers to 1 μm) of Mn(III)/Mn(IV) on the other, is very difficult. It is shown that the system presented here is much helpful to solve this problem.

Experimental Section

VIP System. A detailed technical description of the voltammetric in situ profiling system is given elsewhere (*18*). 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 an IBM-compatible PC (Figure 1). 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

* Corresponding author. Tel.: ++41-22-7026048; fax: ++41-22-7026069; e-mail: marie-louise.tercier@cabe.unige.ch.

S0013-936X(97)00610-X CCC: $15.00
Published on Web 04/14/1998

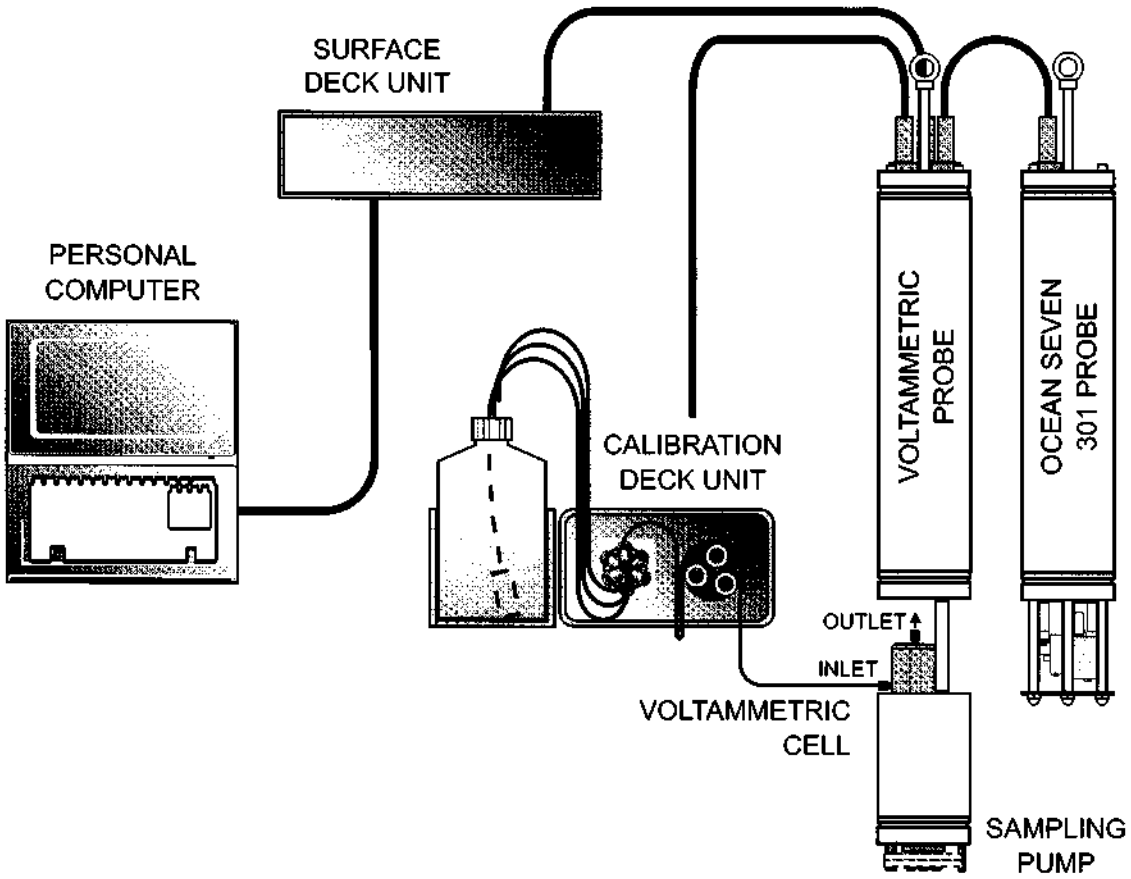

FIGURE 1. Schematic diagram of the whole voltammetric in situ profiling system (VIP System).

voltammetric cell (internal volume = 1.5 mL) with a platinum ring auxiliary electrode and a homemade 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 nonvolatile memory having its own battery, which guarantees 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 h 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) (Figure 2). The voltammetric microsensors measure the test compounds within the gel after its equilibration with the sample (Figure 3). Details of the fabrication and characteristics of these microsensors are reported elsewhere (*19*−*22*) and are only briefly summarized here. The single microelectrode was built by sealing an electroetched Ir wire with diameter of a few micrometers in a shielded glass capillary followed by mechanical polishing (*19*). The microelectrode arrays was produced by means of thin film technology on chips and photolitographic technique (*21*). It consists of 5 × 20 interconnected iridium microdisk electrodes having a diameter of 5 μm and a center to center spacing of 150 μm surrounded of a 300 μm thick Epon SU-8 containment ring. Both sensors are covered with a 1.5% LGL agarose gel layer to protect their surface against fouling (*20, 22*). Mercury semidrops were plated through the gel layer onto Ir substrats at −400 mV (vs Ag/AgCl/3 M KCl/1 M $NaNO_3$) in a deoxygenated 5 mM $Hg(CH_3COO)_2$ and 10−2 M $HClO_4$ 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 1 M 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 portions of spheres. The same agarose antifouling gel membrane was used over an extended period of about 1 month.

Conditions for Manganese Measurements. Votammetric Mn(II) measurements were peformed in situ with the VIP System and on-field with a computer-controlled AMEL 433A

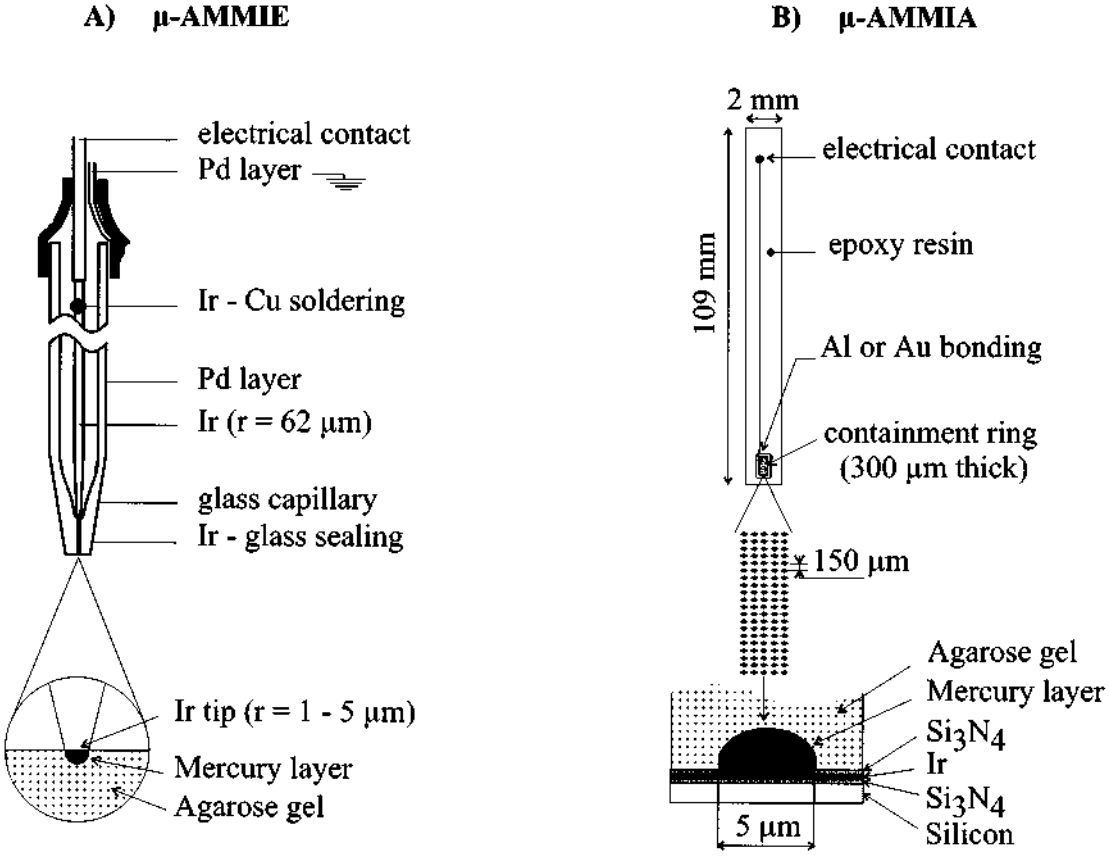

FIGURE 2. Schematic representation of (A) the agarose membrane-covered mercury-plated Ir-based single microelectrode (*μ*-AMMIE) and (B) the agarose membrane-covered mercury-plated Ir-based microelectrode arrays (*μ*-AMMIA).

polarograph coupled to a homemade preamplifier using either square wave anodic stripping voltammetry (SWASV) or square wave cathodic sweep voltammetry (SWCSV). The optimal parameters for Mn(II) SWASV and SWCSV measurements were determined by performing systematic tests in synthetic freshwater solutions as well as in 0.2 μm filtered lake water samples, degassed with a mixture of $N_2 + CO_2$ to adjust the pH in the range 7−8, and spiked with Mn(II) in the range 1−15 μM. Optimal conditions for SWASV were found to be as follows: precleaning $E = -800$ mV; precleaning time = 30 s; deposition $E = -1600$ mV, deposition $t = 5-30$ s; equilibration $E = -1600$ mV; equilibration $t = 0$; final $E = -1300$ mV; pulse amplitude = 25 mV; step amplitude = 1 mV; frequency = 5 Hz. Those for SWCSV were precleaning $E = -800$ mV; precleaning $t = 30$ s; equilibration $E = -1300$ mV; equilibration $t = 5$ s; initial $E = -1300$ mV; final $E = -1600$ mV; pulse amplitude = 25 mV; step amplitude = 1 mV; frequency = 5 Hz. Under these conditions, detection limits of 0.1 and 0.5 μM were obtained for SWASV with deposition times of 30 and 5 s, respectively, and a concentration of 1 μM for SWCSV. Fluidic conditions of the VIP System were flow rate = 7.5 mL/min and circulation time = 1 min. These conditions ensured complete renewal of the solution in the flow-through voltammetric cell as well as equilibration of the cell walls, i.e., no memory effects were observed between the different samples. For comparison purpose, Mn concentrations were also measured using either atomic absorption spectroscopy (AAS; Pye-Unicam SP), inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Perkin-Elmer, Pasma 1000), or colorimetric technique (*25*) (Bran + Luebbe colorimeter) in acidified (pH 2) raw samples, acidified samples filtered on 0.2 or 0.45 μm pore size membranes and acidified samples ultracentrifuged at 30 000 rpm for 15 h (which allowed to eliminate the species with a size > 5 nm assuming a density of 2; Beckman l7−55).

Features and Selectivity of Gel-Integrated Microsensor

Measurements with the gel-integrated microsensors of the submersible voltammetric probe are performed in two successive steps: (a) equilibration of the agarose gel with the test solution and (b) voltammetric analysis inside the gel. The key features of this kind of sensors are the following: (i) the gel acts as a dialysis membrane, i.e., it allows selective penetration of small ions and molecules by diffusion but retains colloidal and particulate material (Figure 3) and, thus, protects the sensor surface from fouling (*20, 22*), allowing its reliable operation for a long period of time; (ii) the gel layer protects the electrode from ill-controlled hydrodynamic currents occurring inside the water column, i.e., analysis inside the gel is based on well-controlled 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^{-4} M; and (iv) voltammetric currents, *i*, at microsized electrodes are controlled by spherical diffusion and reach a nonzero steady-state value at constant potential given by (*26*)

$$i = anFDCr \qquad (1)$$

where $a = 4$ for a disk, 2π for a hemisphere, and 4π for a sphere, D is the diffusion coefficient of the redox species in the gel [note that this value may be smaller in the Agarose gel than in free solution (*20*)], C is the total concentration of the reductible metal species, r is the microelectrode radius, and the other symbols have their usual meanings. Equation 1 holds when $Dt/r^2 > 100$, which is fulfilled for deposition time $t > 10$ s and $r \leq 10$ μm. The characteristic iv is particularly important as it allows (i) to perform the SWASV deposition step without stirring, which is absolutly required

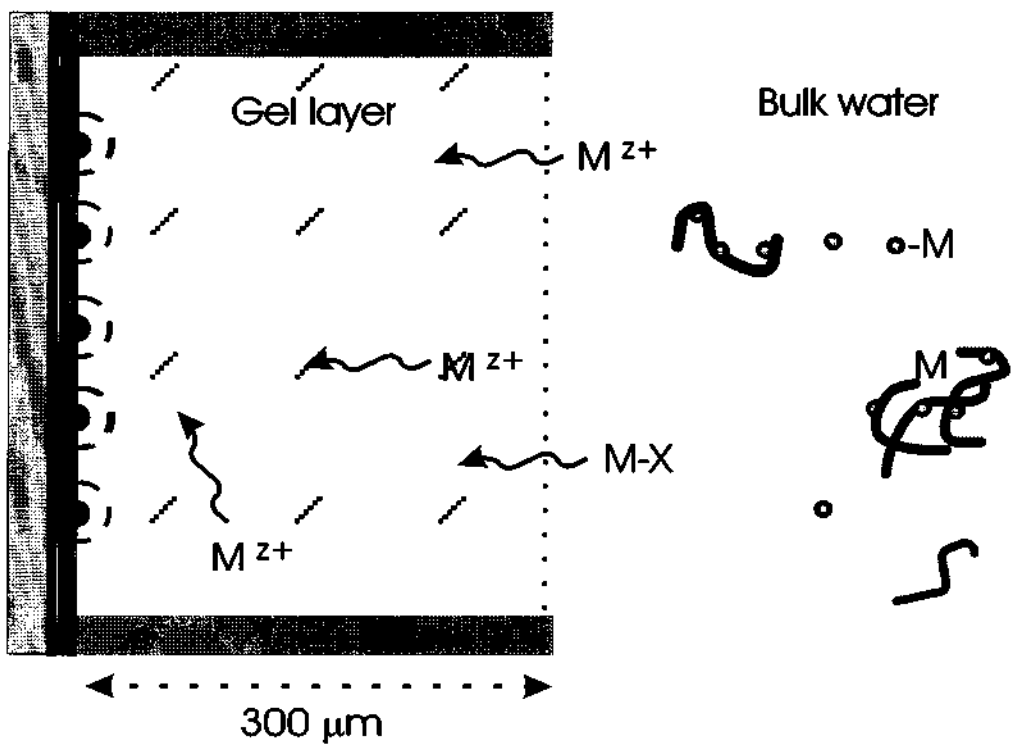

FIGURE 3. Schematic representation of the diffusing species in solution and in the agarose gel layer.

to perform SWASV in the protective gel membrane, and (ii) to define a maximum size cutoff limit for the so-called mobile species (i.e., free ions and small labile complexes) selectively measurable on the microelectrode. Indeed, since D is inversely proportional to the radius r_M of the reacting metal species (Stokes−Einstein relationship), at the same concentration, a metal species with $r_M = 4$ nm will give rise to a current 10 times lower than the free hydrated ion ($r_M \approx 0.4$ nm). Thus, the cutoff size limit between the measured mobile and nonmeasured colloidal species in this technique can be roughly estimated to be a few nanometers. 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 fractions of trace element species: (i) the mobile species (less than or equal to a few nanometers) by direct in situ measurements in unperturbed sample (which is of uppermost importance for anoxic waters at large depth and pressure); (ii) the colloidal species (total concentration in filtered samples minus mobile concentration); and (iii) the particulate species (>1 μm) (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 (*22*) that the current amplitude of the gel-integrated microsensors is independent of the pressure, even up to pressure as high as 600 bar, and its temperature dependence can be taken into account using Arrhenius equation.

Results and Discussion

Mn(II) concentration profiles were measured within the anoxic hypolimnion of two Swiss eutrophic lakes, Bret and Lugano, using the VIP System with either the μ-AMMIE or the μ-AMMIA. Lake Bret is a shallow lake with a maximum depth of 20 m, and it is stratified roughly from May to the end of September. Lake Lugano consists of two basins, north and south basins, separated by the Melide dyke. The south basin is particular in that its bottom floor is formed by a series of mountains and valleys and thus has wide variation of depths (30−100 m). Field tests were performed at Figino station, which is the deepest part of the South basin with a maximum depth of 95 m. 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 3 days). The calibrations were performed by standard additions in 0.2 μm filtered lake water samples degassed with a mixture N_2 + CO_2 to maintain the pH at 7.5. The average slopes of the calibrations curves were found to be (17.5 ± 1.2) pA/μM (N = 6, 95% probability) and (30.6 ± 1.6) pA/μM (N = 8; 95% probability) for SWASV (tdep = 5 s) and SWCSV, respectively, using the μ-AMMIE (Hg layer radius = 8.8−9.3 μm) and (5.3 ± 0.29) nA/μM (N = 6, 95% probability) for SWASV using the μ-AMMIA (Hg layer radius = 6.6−7 μm; tdep = 10 s.). These results show the excellent reproducibility and reliability of both gel integrated microsensors developed.

Field Tests in Lake Bret: Reliability of VIPS in Situ Measurements. The main objective of field tests in Lake Bret was to check the validity and reliability of the measurements performed with the VIP System in real conditions. For this purpose, concentration profiles obtained from in situ-

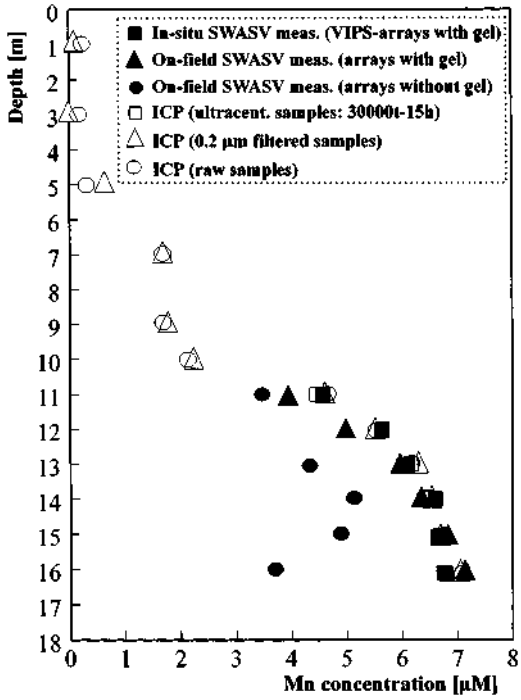

FIGURE 4. Typical profiles of Mn in the anoxic hypolimnion of lake Bret, August 20, 1997. In situ measurements were corrected for temperature effect. On-field measurements were done at 20 °C. Voltammetric measurements: microsensor arrays with and without protective agarose gel membrane; Hg radius = 6.7 and 7 μm for in situ and on-field measurements, respectively. SWASV conditions used: precleaning $E = -800$ mV; precleaning $t = 30$ s; deposition $E = -1600$ mV; deposition $t = 10$ s; equilibration $E = -1600$ mV; equilibration $t = 0$; final $E = -1300$ mV; pulse amplitude = 25 mV; step amplitude = 1 mV; frequency = 5 Hz.

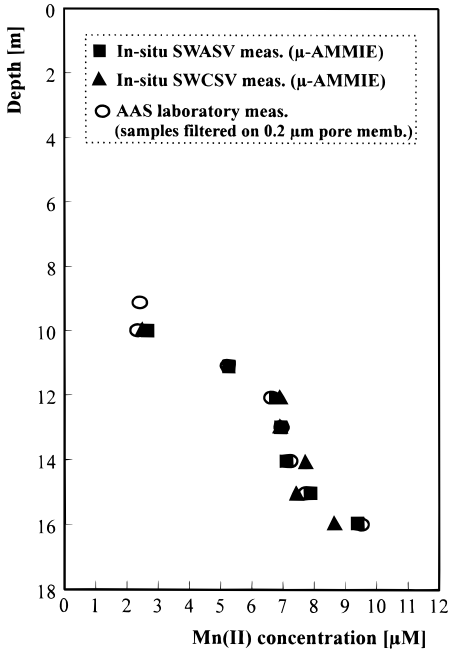

FIGURE 5. Typical profiles of Mn in the anoxic hypolimnion of lake Bret, August 20, 1996. Voltammetric measurements: μ-AMMIE Hg radius = 9.46 μm. SWASV conditions used as in Figure 4 excepted deposition $t = 5$ s. SWCSV conditions used: precleaning $E = -800$ mV; precleaning $t = 30$ s; equilibration $E = -1300$ mV; equilibration $t = 5$ s; initial $E = -1300$ mV; final $E = -1600$ mV; pulse amplitude = 25 mV; step amplitude = 1 mV; frequency = 5 Hz.

voltammetric measurements, after temperature effect correction, were compared with those obtained by on-field voltammetric measurements, performed at a constant temperature of 20 °C, using microsensor arrays with and without protective gel layer. The temperature effect correction was made by using eq 2 (*22*):

$$\ln(i) = 29.68 - 7091\frac{1}{T} \qquad (2)$$

where T is in kelvin. It has to be noted that the temperature effect on Mn(II) voltammetric currents is important as an average temperature coefficient of (8.35 ± 0.1)%/°C, computed from the derivative of eq 2 $\mathrm{d}\ln(i)/\mathrm{d}T = 7091/T^2$, is obtained in the temperature range 4−20 °C. For on-field measurements, a Tygon sampling tubing was fixed to the VIP System 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 raw, 0.2 μm filtered and ultracentrifugated samples, acidified at pH 2 with HCl suprapur, using either atomic absorption spectroscopy (AAS) or inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Typical results obtained for Mn profiles in Lake Bret are shown in Figures 4 and 5. Excellent agreements are observed in particular between the following: (1) Mn(II) concentration profiles determined from in situ voltammetric measurements, after temperature effect correction, and on-field voltammetric measurements performed at constante temperature of 20 °C (Figure 4: full squares and triangles, respectively), (2) Mn(II) concentration profiles determined from in situ measurements, after temperature effect correction, using either SWASV or SWCSV techniques (Figure 5), (3) Mn(II) concentration profiles determined from in situ voltammetric measurements (mobile species with size of few nanometers) and ICP laboratory measurements of ultracentrifugated acidified samples (species ≤ 5 nm) (Figure 4, full and open squares, respectively).

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 (*22*). In addition, interesting information regarding the nature of Mn in Lake Bret 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/or ultracentrifuged acidified samples (Figures 4 and 5). 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 Bret is present predominantly in the mobile form, i.e., most likely Mn^{2+} and possibly a small proportion of inorganic complexes, at this period of the year. The protective role of the agarose gel membrane was also assessed by comparing Mn(II) concentration profiles obtained using microsensor arrays with and without gel layer (Figure 4, full triangles and circles, respectively). It can be seen that systematically too low concentrations are obtained for the unprotected microsensor. Similar problems were already encountered previously when performing in situ Mn(II) measurements by anodic stripping voltammetry (ASV) using a prototype submersible voltammetric cell with a standard metrohm hanging mercury drop electrode (HMDE) (*15*). A detailed study showed that for both the HMDE and the Hg-plated Ir-based microelectrode the attenuation of voltammetric peak amplitude was correlated with the concentration of lake born

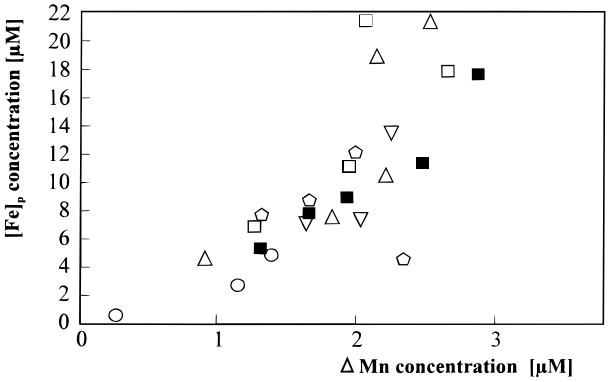

FIGURE 6. Variations of Mn concentrations (ΔMn) observed between laboratory AAS measurements of 0.2 μm filtered acidified lake Bret water samples and in situ voltammetric measurements, using a HMDE (open symbols) and a Hg-plated Ir-based microelectrode (full symbols), as a function of iron hydroxides particle concentration $[Fe]_p$. ($[Fe]_p = [Fe]_{tot}$ measured by AAS in raw acidified samples − [Fe(II)] measured by colorimetry [28]). Lake Brêt, August to September 1990.

iron hydroxide particles (Figure 6) characterized elsewhere (*28*). This result strongly suggests that peak current attenuations observed for unprotected sensors are due to adsorption of these particles, well-known to have strong adsorbing capabilities, onto the Hg-plated microelectrode surface which then hinder the diffusion of Mn(II). These results thus clearly demonstrated the efficiency and necessity of the protective gel layer to eliminate fouling problems and to allow reliable, direct measurements in natural media. It must be emphasized 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 Bret as demonstrated before.

Field Tests in Lake Lugano: Daily versus Random Measurements. In Lake Lugano, replicate daily profiling of dissolved and colloidal Mn fractions was performed in situ using the VIP System and in the laboratory by colorimetric measurements in 0.45 μm filtered samples, respectively. The results in south basin of Lake Lugano were quite different from those obtained in Lake Bret as shown in Figure 7. All Mn(II) profiles measured in situ with the VIP System were similar over the measured period while colorimetric measurements, performed in 0.45 μm filtered samples, show large variations of concentration from 1 day to another. Over the same period, the depth position of temperature, pH, dissolved oxygen, and conductivity gradients changed drastically (see for example Figure 8a). Similar daily changes, influenced by weather conditions, have been already observed in north basin of Lake Lugano, and a model was proposed to describe the corresponding internal wave pattern (*27*). Significant variations in conductivity were also observed in the vicinity of the sediment (Figure 8b). The salient feature is that the variations in conductivity profiles close to the sediment are similar to those observed for Mn concentration profiles determined by colorimetry (Figures 7 and 8b). In addition, colorimetric values are always higher or equal to the values obtained by in situ voltammetric measurements, which only measure the mobile Mn(II) concentration, i.e., a parameter closely related to free Mn^{2+}. These observations suggest that the difference in the Mn concentration measured in situ by the VIP System on one hand and by colorimetry in filtered 0.45 μm samples on the other hand is due to colloidal Mn originated from resuspension of sediments by submarine currents. This is supported by the available data on the

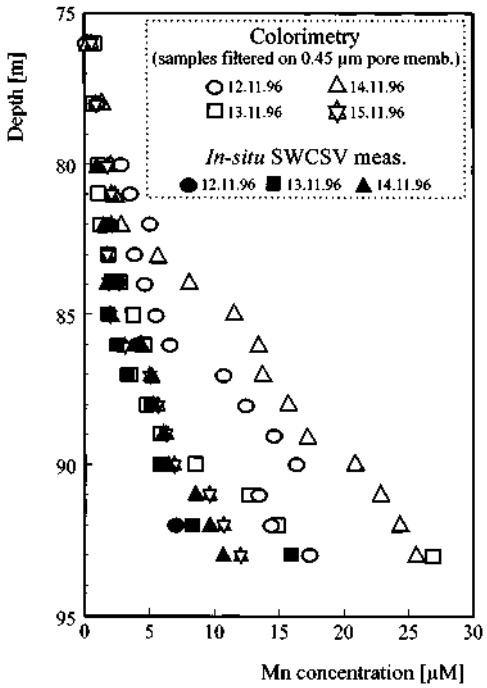

FIGURE 7. Profiles of Mn(II) in the anoxic hypolimnion of lake Lugano South basin. Figino station, November 12−15, 1996. μ-AMMIE Hg radius = 8.74 μm for in situ measurements of November 12 and 13 (same mercury layer) and 8.78 μm for in situ measurements of November 14. SWCSV conditions used as in Figure 4.

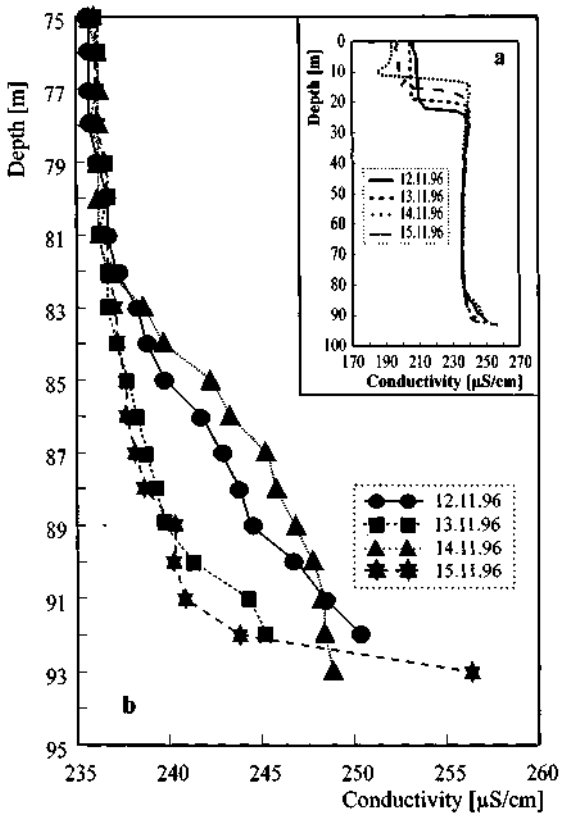

FIGURE 8. Profiles of conductivity in (a) the whole water column and (b) at the bottom of lake Lugano South basin. Figino station, November 12−15, 1996, max depth 93 m.

characteristics of the Figino site sediment. Indeed, conductivity and Mn concentration of sediment pore water increase from 350 to 560 μS/cm and from 400 to 500 μM (*29*) from top sediment down to 20 cm and deeper, respectively.

This is much larger than the conductivity and Mn concentration of the water above the sediment (Figures 7 and 8) and, thus, sufficient to increase both parameters in the observed range, by a punctual resuspension of a few tens centimeters of sediment, in a 10 m thick water layer above the sediment. Moreover, the concentration of Mn in sediment pore water was measured by dialyzers. Interestingly, by combining these Mn data with pH and bicarbonate values, rhodocrosite [$MnCO_3$(s)] is found to be largely oversaturated (*29*). Since most resuspended Mn in the water layer above the sediment is found to be in the colloidal form (colorimetric minus VIPS measurements) and not as mobile species (VIPS measurements), this seems to suggest that probably Mn^{2+} in sediment pore water is in equilibrium with $MnCO_3$(s) and that the Mn species measured in the dialyzers are not only Mn^{2+}, but mostly colloidal $MnCO_3$(s) with size < 40 nm (i.e., the colloids small enough to diffuse in the dialyzers during 2 weeks). If Mn^{2+} is in equilibrium with $MnCO_3$(s), the mobile concentration measured by the VIP System is not expected to vary significantly with mixing event, whereas the colloidal concentration of Mn will directly depend on dilution as experimentally observed in Figure 7. At any rate, the purpose of the above discussion is not to find the precise nature of Mn species, which can only be done on the basis of more systematic studies. It just intends to illustrate the importance of unambiguous discrimination between colloidal and ionic forms and the capability of the VIP System in that respect. The results of Figure 7 also illustrate the importance of continuous measurements over extended period of time, compared to random sampling, to distinguish between seasonal and temporal variability and, in turn, to avoid misinterpretation of the seasonal element species distribution due to temporal situation. For both purposes, there are several advantages to combine the VIP System with classical techniques. In particular, the VIP System allows the elimination of the need of drastically perturbing and time-consuming separation techniques such as cascade ultrafiltration or ultracentrifugation, which must be used to discriminate colloidal Mn from Mn^{2+} and its small organic complexes when using classical detection methods. In situ real-time measurements (i.e., in nonperturbed samples) of the Mn mobile fraction with the VIP System can be performed in parallel with on boat sampling of raw and filtered acidified samples for colloidal and particulate measurements which, in turn, can be analyzed during the night by connecting an automatic sampler to the detection device. Thus, a complete set of data for each successive sampling day can be obtained without and with minimum sampling storage for the mobile and colloidal/particulate fractions, respectively. The future study will focus on the availability of the VIP System to perform unattended, autonomous in situ Mn(II) measurements over an extended period (typically between a week and a month). For this purpose, the submersible voltammetric probe will be adapted to a Radio Buoy Profiler (Idronaut-Milan) and its behavior daily controlled from a land station by using cellular phone link.

Acknowledgments

The authors thank Idronaut Srl (Milan) who has developed the software, the hardware, and the submersible pump of the VIP System. G. C. Fiaccabrino and M. Koudelka-Hep (Institute of Microtechnology, University of Neuchâtel) who have fabricated the Ir-based microsensor arrays. Dr. A. Barbieri (Laboratorio Studi Ambienti-Sezione Protezione Aria e Acqua, Lugano-Paradiso) for providing all the facilities and performing colorimetric laboratory measurements during the field survey at lake Lugano. A. Sina (Idronaut, Milan) for his technical assistance during field tests at Lake Lugano. Dr. K. W. Hanselmann for the complementary data measured in sediment pore water. This work was supported by the European Commission (Marine Science and Technology—MAST III program, contract no. MAS3-CT95-0033).

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Received for review July 9, 1997. Revised manuscript received February 20, 1998. Accepted February 22, 1998.

ES9706108