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A study of iron and manganese transformations at the O_2/S(-II) transition layer in a eutrophic lake (Lake Bret, Switzerland): A multimethod approach

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Abstract—The usefulness of an analytical scheme based on the simultaneous use of various analytical methods (differential pulse polarography, colorimetry, atomic absorption, and filtration) for the study of Fe and Mn species at a mid-water O_2/H_2S redox transition layer has been investigated. The relative abundance of particulate, colloidal and electroactive species as well as their redox state has been determined, across the interfacial zone. The relevance of polarographic results in unmodified anoxic lake water was tested by performing measurements both directly in the field and the laboratory after sample storage. Significant differences in the signals of Fe(II) and S(-II) species have been observed. The concentration of manganese oxyhydroxide (MnO_x) was measured using three different analytical techniques and the results suggest that natural lacustrine MnO_x contains a reactive and a less reactive fraction. Use of the multimethod approach, has enabled us to demonstrate a spatially well resolved chemical make-up of the water strata at the transition layer and peaked profiles for dissolved Mn(II) and particulate and colloidal Fe(III) and Mn(IV) species. The most probable reactions between O_2, Mn(II)/Mn(IV), Fe(II)/Fe(III) and S(-II) are discussed on the basis of these results.

I. INTRODUCTION

BOTH IRON AND MANGANESE are ubiquitous elements in natural aquatic systems. The physical and chemical factors governing their behaviour in lakes are of interest to limnologists, geochemists and scientists dealing with water supply and quality (BISWAS, 1981; STUMM and MORGAN, 1981; WETZEL, 1975). The chemistry of the latter elements is important owing to the strong adsorption affinity of their naturally occurring oxyhydroxides for both trace metals and organics (ANDERSON and RUBIN, 1981; BENJAMIN and LECKIE, 1981; TIPPING, 1981; LION *et al.*, 1982) and because of their redox transformations (DAVISON, 1985) at the pE boundaries found in natural aquatic systems. A considerable amount of data on the transformations of iron (DAVISON *et al.*, 1981, 1982; LIDEN, 1983) and manganese (DELFINO and LEE, 1968; DAVISON and WOOF, 1984; STAUFFER, 1986; STAUFFER and ARMSTRONG, 1986) in both oceanic and lacustrine systems are available, and our understanding of the geochemistry and biology governing the behaviour of these elements has greatly progressed since the pioneering work of MORTIMER (1941, 1942) and EINSELE (1940) in the early 1940s. However, in most studies non specific analytical techniques such as atomic absorption spectrometry or colorimetry which enable only the determination of the total concentration of a given element have been used. Filtration using 0.45 μm filters has moreover been generally adopted to distinguish between dissolved and particulate iron and/or manganese species. Considering the growing body of evidence pertaining to the existence of broad size distributions for both iron (MILL, 1980; TIPPING *et al.*, 1982; LAXEN and CHANDLER, 1983) and manganese (HOFFMANN *et al.*, 1981; LAXEN and CHANDLER, 1983; LAXEN *et al.*, 1984) in natural waters and the diversity of the possible complexed species with various oxidation states, these types of analytical approaches give only a rough description of the chemical composition of a given water sample. This paper discusses a refined multi-method approach developed to obtain more detailed information on the nature of Fe and Mn species by minimizing the possible artefacts often produced by separation or preconcentration techniques. Emphasis has been particularly laid on some of the analytical aspects such as the characterization of species present at the O_2-H_2S transition layer in a eutrophic lake, without sample modification by means of voltammetry. Since this type of multi-method approach entails the use of operationally defined parameters, both the analytical and the limnological meaning of the results are discussed here.

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II. EXPERIMENTAL

II.1. Site description

Lake Bret is situated 10 km to the east of Lausanne in the Canton of Vaud (Switzerland) and is used as a drinking water reservoir. Its main morphological and hydrological characteristics are given in Fig. 1. The lake's simple morphology and hydrology (one water inlet, the river Grenet, and one water outlet (a water treatment plant) is ideally suited for limnological studies. Land use, in both the lake's and the river Grenet's watershed, is predominantely agricultural which has led to high phosphorus loading and to the lake's current eutrophic state. Pollution from other sources, such as heavy metals or industrial waste organics are negligible and the lake is a protected zone where all motor sports are prohibited. Lake Bret may be classified as a dimictic lake, which is often covered with ice during the winter. During the summer it is thermally stratified and develops a strongly reduced anoxic hypolimnion, which disappears in November, when the autumn overturn occurs. Typical O_2, T and pH depth profiles from early spring to late autumn are given in Fig. 2 and representative concentrations of major and minor dissolved species in both the epilimnion and the hypolimnion during the summer season are respectively: Alk. (2.6/4.0 meq), sulfate (75/30 μM), *o*-phosphate (1.0/2.8 μM), nitrate (4/0.1 μM), calcium (0.9/1.5 mM), magnesium (0.3/0.3 mM) and ammonium (10/90 μM).

II.2. Methods of sampling

All water samples, and measurements *in situ*, were taken from a sampling point situated at the deepest part of the lake and at which a 16 square meter platform was permanently moored. Water samples were collected at either 1 or 0.5 meter intervals using a peristaltic pump connected to Tygon tubing lowered to the appropriate depth.

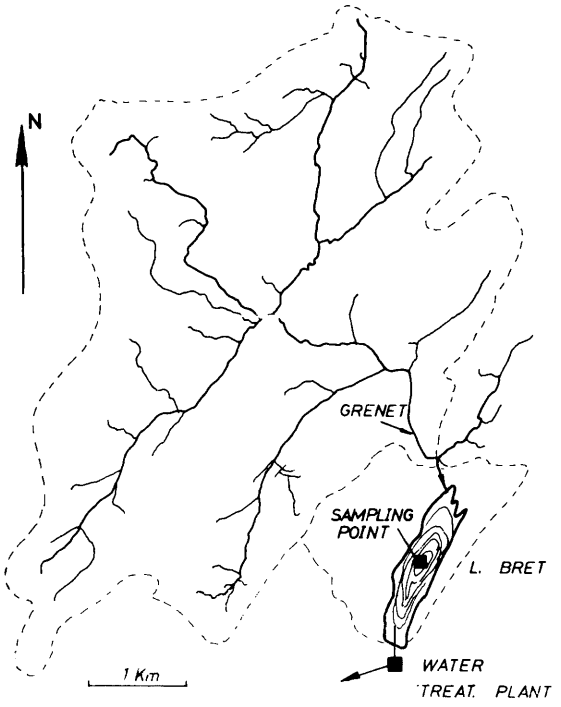

FIG. 1. Bathymetric map of Lake Bret, Vaud, Switzerland, contours at 2 m intervals. The principal features of the lake are: length 1650 m, maximum width 400 m, maximum depth 20 m, mean water residence time 1 year.

Any contamination by air is thus avoided during the collection of samples (DAVISON *et al.*, 1987). Microprofiles with a 20 cm interval at the O_2-H_2S transition layer were also performed in certain cases. All depths were normalised relative to the sediment in order to account for seasonal variations of the surface level. Absolute error in the depths for a given profile on the same date was estimated to be ±5 cm, whereas the estimated error between profiles of different dates was much larger (±50 cm). All samples for either atomic absorption or colorimetric analyses were collected in 10 ml stoppered polyethylene test-tubes and were immediately acidified to pH = 2 with 1 M HCl. Samples for polarographic analyses were pumped either directly into the polarographic cell (in the case of in the field analyses) or into sampling bottles (for laboratory analyses). Filtered samples were obtained directly in the field by pumping water through a 90 mm Plexiglass filter holder bearing a Schleicher and Schuell cellulose nitrate 0.45 μm filter, placed on-line in a side tubing close to the pump outlet. After purging the system with at least 600 ml of the water sample obtained directly from the desired depth, the filtration may be performed in the absence of air as it is necessary in the case of S(-II)- and/or Fe(II)-rich waters to avoid any change in the chemical make-up of the sample. Size distributions for particulate Mn were also obtained by filtration using syringes (Plastipack B-D in polypropylene) equipped with Swin-lok filter holders into which 25 mm Nuclepore membranes were inserted. Filtrations were performed directly in the field, less than 50 ml were filtered to avoid filter clogging and the first 15 ml were discarded to avoid contaminations. It should be underlined that in many cases filtration of natural samples only yields an operational size fraction which is dependent on the conditions used (flow rates, stirring rates), the types of filters used, the mode of filtration and the nature of the studied species. Some aspects of the above-mentioned problems have been dealt with in the literature (LAXEN and CHANDLER, 1983) and some specific results obtained for the case of Lake Bret particles has also been published (BUFFLE *et al.*, 1987; DE VITRE, 1986; DE VITRE *et al.*, 1987).

II.3. Methods of analysis

Polarographic determinations were done by using the differential pulse polarographic mode (DPP), a Metrohm polarograph (modules E506, E612 and E586) and a Metrohm stand E505.

Colorimetric analyses were done using a Beckman DBG or a Varian 634 digital spectrophotometer. Atomic absorption analyses were performed on a PYE-Unicam SP1900 spectrometer using an air/acetylene flame. For low concentrations (less than 1 μM) a Perkin Elmer 2280 Graphite Furnace spectrometer was used.

Water temperature, dissolved oxygen and pH were simultaneously measured *in situ* when sampling, using an Orbisphere 2112/2067 combined T/O_2 probe and display unit and an Ingold-503 pressure compensated combined glass electrode linked to a portable pH-meter

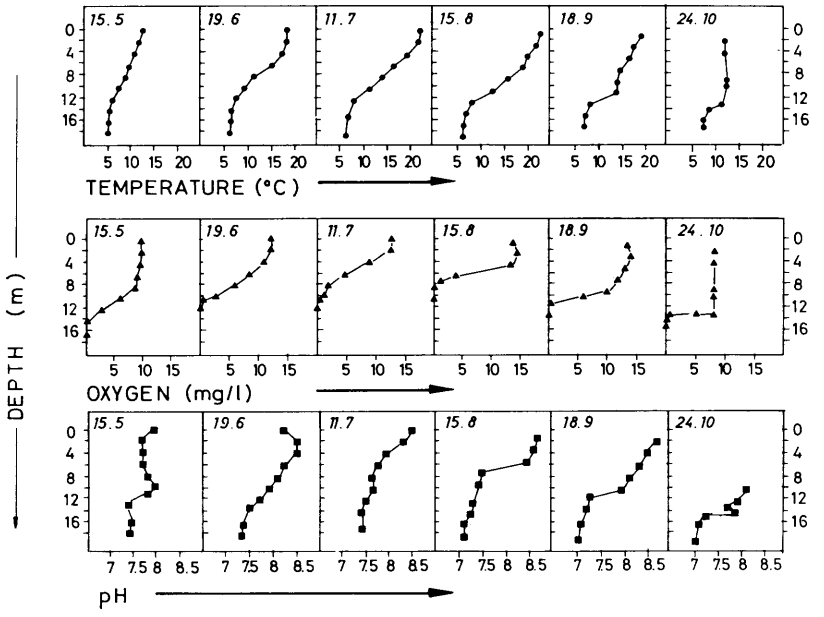

FIG. 2. Temperature, oxygen and pH profiles in Lake Bret, May to October 1985.

(Metrohm E604). The probes were attached close to the orifice of the Tygon tubing in order to ensure that the O_2, T and pH measurements were done exactly at the sampling depth.

Total orthophosphate was determined colorimetrically by the molybdenum blue method (APHA, 1971) on unfiltered samples. Bicarbonate alkalinity was determined by titration with dilute HCl and a fixed pH 4.5 for end point detection.

Total iron, manganese, calcium and magnesium in filtered and unfiltered samples were determined by flame atomic absorption.

Ferrous iron was determined colorimetrically using the orthophenantroline method (APHA, 1971), omitting however the reduction step. The use of this procedure for determining Fe(II) in the presence of Fe(III) has been criticized (FADRUS and MALY, 1975; MACALADY *et al.*, 1982) because it may lead to overestimation of Fe(II) due to the reduction of Fe(III) by orthophenantroline itself and various procedures have been suggested to overcome this problem (FADRUS and MALY, 1975). This positive interference was tested for in samples, artificially enriched in Fe(III) and it was found that for Fe(III) concentrations lower than 50 μM, no interference was found. Since the total Fe(III) concentration measured in Lake Bret never exceeded 25 μM, the *o*-phenanthroline method without the reduction step was used.

Polarographic measurements of Fe(II), Mn(II) and S(-II) were performed either directly in the field on the platform, or for comparison purposes in the laboratory after sampling and sample storage. For field measurements a portable Honda AC current generator was used. The analysis was performed by pumping a lake water sample directly into a specially designed polarographic cell (DE VITRE, 1986) through which a continuous flow of N_2 was maintained during filling. Once the cell was full, the flow of N_2 was stopped, and the sampled water allowed to overflow until at least twice the cell volume had been flushed through the system. The voltammograms were then immediately recorded. Water samples for laboratory polarographic determinations were collected using glass Winkler bottles (total capacity *ca.* 110 ml) as well as Plexiglass syringe samplers (volume *ca.* 100 ml) specially designed in our laboratory (DE VITRE, 1986) to minimize O_2 contamination of the anoxic water sample during the sampling procedure, sample storage and its transfer into the polarographic cell prior to analysis. Before sampling both types of samplers were flushed with at least 6 times their volume of the sampled lake water and then stoppered. Extreme care was taken to avoid trapping of air bubbles during sampling. The samples were stored close to their *in situ* temperature (±4°C) and the analyses were performed within 6 hours of sampling by carefully transferring a 25 ml aliquot into the polarographic cell.

MnO_x in unfiltered samples was determined using three different techniques (see Fig. 3). The complementarity of these methods with respect to MnO_x reactivity is particularly useful for data interpretation as will be seen later.

Method 1. The concentration of particulate Mn(IV) is computed by subtracting the polarographically measured concentration, $|Mn(II)|_{ea}$, from the total Mn concentration determined by AAS. In Lake Bret no particulate form of Mn(II) is present (see III.3) and all the electroactive Mn(II) species are polarographically labile having

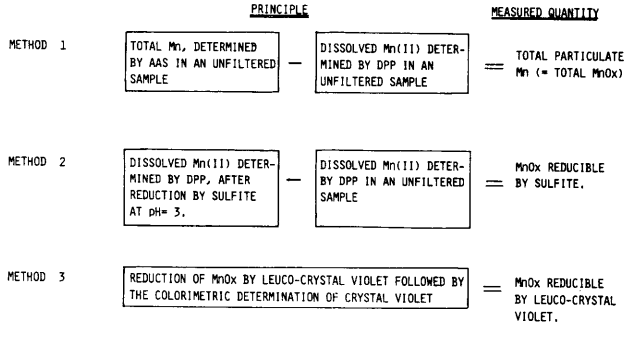

FIG. 3. Methods used to determine MnO_x concentrations in lake water samples.

TABLE 1 : Flow chart for method 2 for the determination of reducible MnOx

STEP	SAMPLE A	SAMPLE B	REMARKS
1	ADD 1 ml OF KCl 0.1 M + HCl 0.001 M		ACIDIFIES SAMPLE TO pH 3
2	ADD 0.2 ml OF Na_2SO_3 0.001 M	ADD 0.2 ml OF H_2O	EXCESS REDUCING AGENT IN SAMPLE A
3			REACTION TIME 5 MIN.
4	ADD DROPWISE $NaHCO_3$ (0.5 M)		pH ADJUSTED TO 7.5
5	DEGAS WITH N_2/CO_2 (2100 ppm)		O_2 ELIMINATED AND pH = 7.8
6	DDP SCAN FROM -1.2 TO -1.7 V (VS Ag/AgCl)		
7	REDUCIBLE MnOx + IN SITU Mn(II) DETERMINED	IN SITU Mn(II) DETERMINED	
8	REDUCIBLE MnOx = DPP PEAK OF SAMPLE A	- DPP PEAK OF SAMPLE B	

the same diffusion coefficient. Hence, they all contribute proportionately to the same polarographic Mn(II) peak and therefore the above mentioned concentration difference may be equated to the MnO_x concentration.

Method 2 (see Table 1 for details). "Total" Mn was measured polarographically after reduction of MnO_x by sodium bisulfite at pH = 3. *In situ* $|Mn(II)|_{ea}$ (see III.1) was also determined polarographically prior to the reduction. Thus, the concentration of MnO_x can be readily computed by subtraction.

Method 3. Mn(IV) is measured directly by the colorimetric determination of crystal violet resulting from the oxidation of leuco-crystal violet by MnO_x as described by KESSICK *et al.* (1972).

III. MEANING OF THE MEASURED PARAMETERS

III.1. Multi-method speciation scheme

The analytical scheme used here (see Fig. 4) is a modified version of a scheme that has already been described elsewhere (BUFFLE *et al.*, 1987; BUFFLE, 1988). This speciation scheme presents the following important features with regards to the nature and reactivity of Fe and Mn species at an O_2-H_2S transition layer in the water column of a lake:

a) Perturbation of labile equilibria is minimized, since fractionation techniques are used minimally and are replaced by direct species sensitive analytical techniques such as DPP and colorimetry. Artefacts due to sample storage are also minimized, since the latter techniques are applied directly in the field when necessary.

b) Redox state discrimination for a given species is obtained by comparing concentrations determined by oxidation state sensitive analytical techniques (colorimetry and DPP) with concentrations determined by non-discriminating techniques such as AAS.

c) The judicious combination of methods used enables one to get a size discrimination based on three fractions where the cut-off limits are operationally defined as *ca.* 0.45 μm (filtration) and 0.05 μm (DPP, see below).

As can be seen from Fig. 4, the following iron and manganese fractions may be defined using the multi-method approach.

1) *Total concentrations:* $|X|_t$, where X may represent i) the sum of all Fe(III) and Fe(II) species, denoted by $|Fe|_t$; ii) all Fe(II) species,

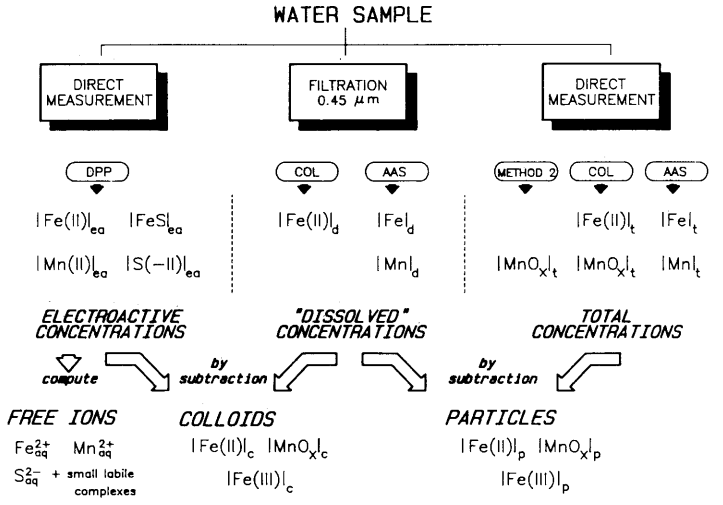

FIG. 4. Schematic representation of the multi-method analytical scheme used to determine and discriminate between Fe and Mn species (the different fractions are defined in section III.1).

denoted by $|Fe(II)|_t$; iii) the sum of all Mn(II), Mn(III) and Mn(IV) species denoted below $|Mn|_t$; and finally, the concentration of manganese oxyhydroxide (MnO_x) denoted $|MnO_x|_t$. All these concentrations were determined in unfiltered lake water samples.

2) *"Dissolved" concentrations:* $|X|_d$, where X is either Fe (*i.e.* Fe(II) + Fe(III)), Fe(II) or Mn (*i.e.* Mn(II) + Mn(III) + Mn(IV)). These were determined in 0.45 μm filtrates of lake water.

3) *Electroactive concentrations:* $|X|_{ea}$, where X is any Fe(II), Mn(II) or S(-II) species giving rise to a DPP peak. For most freshwaters having a pH of 7–8 it may be shown (DAVISON *et al.*, 1987; MOREL and MORGAN, 1972; CHISWELL and MOKHTAR, 1986) that Mn(II) is essentially aquated Mn^{2+}_{aq}, S(-II) is mostly present as H_2S and HS^- and Fe(II) exists mostly as aquated Fe^{2+}_{aq}. However, an important feature of sulfide rich waters is that a peak corresponding to a specific iron sulfide complex is also measureable by DPP (see below).

4) *True ionic and labile complex species* such as Fe^{2+}_{aq}, Mn^{2+}_{aq}, $Fe(HCO_3)^-$, $Mn(HCO_3)^-$, etc. may be computed using the appropriate equilibrium constants and conditions and mass balance equations based on the electroactive concentrations. It is worthwhile to emphasize the last point for the following reasons:

—$|X|_{ea}$ is more representative than $|X|_d$ of the sum of the concentrations of the labile complexes and the aquated M^{2+} cation, since $|X|_d$ may include colloidal sized species which should not be included in mass balance equations (BUFFLE, 1988).
—in most freshwaters only *ca.* 10% of both the $Fe(II)_{ea}$ and $Mn(II)_{ea}$ exist as simple inorganic complexes. This also holds for Lake Bret (ZALI, 1983) and the electroactive concentrations $|Mn(II)|_{ea}$ and $|Fe(II)|_{ea}$ can be considered almost equal to the concentrations of the aquated cations, Mn^{2+}_{aq} and Fe^{2+}_{aq}.

5) *"Particulate" concentrations:* $|X|_p$ where X can be either Fe, Fe(II), Fe(III) or Mn and may be computed from: $|X|_p = |X|_t - |X|_d$ Note, however that $|Fe(III)|_p$ was computed as $|Fe|_p - |Fe(II)|_p$ and that $|MnO_x|_p$ was measured directly (see III.3).

6) *"Colloidal" concentrations:* $|X|_c$, where X can be Fe, Fe(II), Fe(III) and Mn and may be computed from: $|X|_c = |X|_d - |X|_{ea}$, except for the colloidal Fe(III) concentration which was calculated from the difference between $|Fe|_d$ and $|Fe(II)|_d$ assuming that ionic or complex species of Fe(III) are not present in significant amounts under lacustrine conditions.

The distinction between particulate and colloidal species is made by the use of 0.45 μm filters. It should however be stressed that as shown by DE VITRE *et al.* (1987), DE VITRE (1986) and BUFFLE *et al.* (1987), field filtration, using syringes, yields size distributions which do not really correspond to the true particle sizes, because of retention factors other than particle diameter. However, filtration can be used as an operational tool to define two broad size classes. The distinction between colloidal and electroactive species of Fe and Mn is made by virtue of the specificity of the polarographic technique. Indeed, this method measures either the aquated forms or small labile species and, therefore, gives very different, but complementary, information compared to separation by membrane filtration followed by analysis by AAS (BUFFLE, 1988; DE VITRE, 1986; ZALI, 1983). It may be shown (BUFFLE, 1988) that for practical purposes any particle with a radius greater than 50 nm is considered as electroactively inert. This value, therefore, may be considered as an operational limit between "colloidal" and "electroactive" species, whereas 0.45 μm (defined by filtration) can be considered as the limit between "colloidal" and "particulate" species (see Fig. 4). Nevertheless, it should be borne in mind that both these limits are rough estimations, since a rigorous interpretation of polarographic results should take into account the whole size distribution of reactive species and their chemical dissociation kinetics (VAN LEEUWEN *et al.*, 1987, PAC, submitted).

III.2. Field versus laboratory polarographic analyses

Polarographic techniques have been increasingly used over the past decade for the study of anoxic natural waters (DAVISON *et al.*, 1987), in particular for the determination of Mn(II), Fe(II) and S(-II) species. However, these measurements have been generally done in the laboratory, *i.e.* after at least several hours of sample storage. To our knowledge, no systematic investigation has been published on the effect of sampling and sample storage on the nature and the concentrations determined. This is an important factor, since all of the studied species are very reactive: both Fe(II) and S(-II) species may be rapidly oxidized, losses of H_2S and CO_2 by volatilization due to equilibrium pressure changes during sampling can lead to changes in the species distribution and

in the pH and finally solid iron sulfide and Fe and Mn oxyhydroxides may easily coagulate and aggregate.

Comparative DPP voltammograms of the same samples recorded in the field and in the laboratory 6 hours later are shown in Fig. 5. The peak current at $E = -1.45$ V is proportional to the sum of the concentrations of Mn^{2+}_{aq} and its simple labile inorganic complexes, but as mentioned earlier the latter are negligible. Similarly, the peak at -1.3 V corresponds to the sum of Fe^{2+}_{aq} and its polarographically labile complexes. The origin of the Fe(II) peak at $E = -1.02$ V, is more complicated, and depends on the polarographic technique used as well as on the chemical nature of the solution investigated. A detailed study on its nature and origin (BUFFLE *et al.*, 1987) showed that the peak height at $E = -1.02$ V is a measure of the concentration of a small electroactive iron sulfide (FeS_{ea}) complex. This property was used here to follow the concentration of this species. In Fig. 5, the striking differences between field and laboratory polarographic measurements are shown. The evolution and the effect of sample storage on the sulfide peak at $E = -0.53$ V and on the two Fe(II) peaks at $E = -1.02$ and $E = -1.3$ V may be readily seen.

In Table 2, the results of a series of both field and laboratory polarographic analyses are given. In each case, five replicate samples were analysed for electroactive Mn(II), Fe(II), FeS_{ea} and S(-II). For manganese(II) no differences between field and laboratory determined values were apparent and the dispersion of the data was low: individual values always fell within 4% of the mean value. Furthermore, the type of sampler used does not seem to have a significant effect. For Fe(II) two situations must be distinguished: a) if the sample contains

TABLE 2: A comparison between Fe(II), FeS_{ea}, S(-II) and Mn(II) electroactive concentrations determined by Differential Pulse Polarography in the field and in the laboratory. Data are average concentrations (uM) computed from five replicate samples. Error interval is $\pm ts$, where t is the student factor for a 95% confidence interval and s the sample standard deviation. §-- concentrations in equivalents of Fe(II).

SPECIES	POTENTIAL (sat. Ag/AgCl)	IMMEDIATE DETERMINATION	LABORATORY DETERMINATION AFTER 6 HOURS STORAGE TIME	
	(V)	FIELD	SYRINGE-SAMPLER	WINKLER-BOTTLE
$Fe(II)_{ea}$	-1.3	27.9 ±5.4	32.9 ±7.8	33.9 ±6.2
FeS_{ea} §	-1.02	6.2 ±2.0	1.0 ±2.1	1.0 ±0.4
S(-II)	-0.53	11.4 ±1.9	1.7 ±0.3	5.0 ±4.4
$Mn(II)_{ea}$	-1.45	8.1 ±0.5	8.2 ±0.3	8.3 ±0.4

electroactive Fe(II) but no sulfide then field and laboratory determined values (peak at $E = -1.3$ V) were found to be the same (DE VITRE, 1986); b) on the other hand, in hypolimnetic lake water containing both electroactive Fe(II) and S(-II) significant differences between field and laboratory determined values were observed. Surprisingly, in the latter case field measurements yielded lower values for $|Fe(II)|_{ea}$ than the corresponding laboratory determined ones. The observed differences may be explained by changes in the speciation of Fe(II). The peak currents recorded in the field as a function of time (Fig. 6) show that in the initial water sample ($t = 0$) Fe(II) is present not only as the free aquated ion but also as a small electroactive iron sulfide complex (FeS_{ea}) mentioned above, reducible at $E = -1.02$ V. When measurements are performed in the laboratory after sample storage the FeS_{ea} peak height was diminished greatly, whereas that of Fe(II) at $E = -1.3$ V increased proportionately. The detailed evolution of the inverse relationship between the two peaks may be clearly seen in Fig. 6, where the time $t = 0$ corresponds to the sampling time. In the case of laboratory measurements $|Fe(II)|_{ea}$ concentrations were identical within analytical error, in both Winkler bottles and syringe samplers indicating that the change in Fe(II) speciation was independent of the type of sampler used.

For sulfide, laboratory determined values were much lower than the corresponding field measured concentrations and a significant difference was found between Winkler bottles and

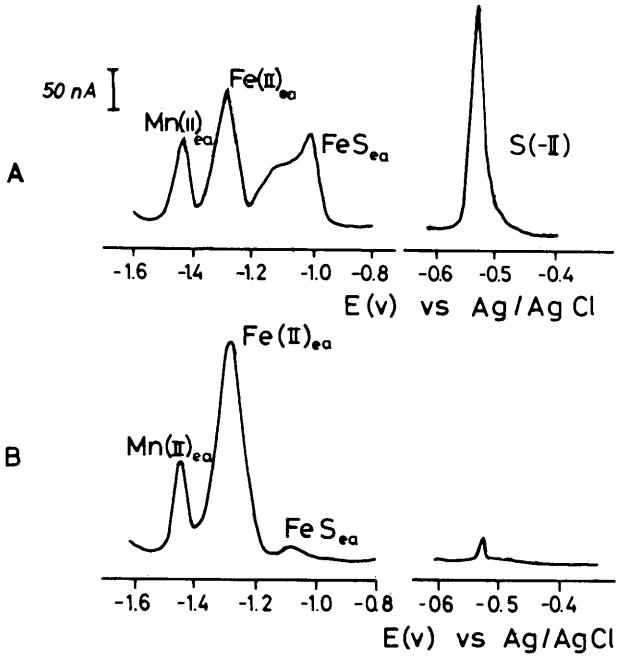

FIG. 5. Comparative differential pulse polarograms obtained in ferrous, sulfidic water sampled at a depth of 15.5 m from the hypolimnion of Lake Bret. pH = 7.2 A. Immediate measurement in the field upon sampling. B. Laboratory measurement after sample storage for 6 hours in a Winkler Bottle.

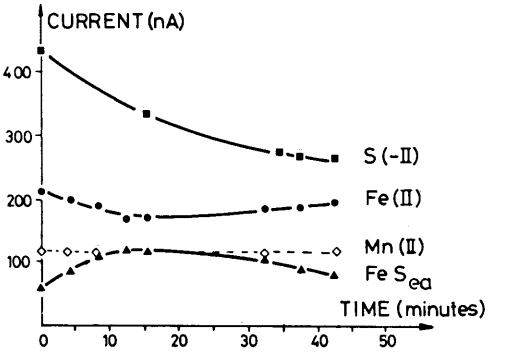

FIG. 6. Change in the DPP measurable S(-II), Fe(II), FeS_{ea} and Mn(II) currents as a function of time after sampling. The measurements were performed directly in the field, in a completely filled and air tight polarographic cell (pH = 7.1, T = 16–22°C).

syringe samplers indicating that the losses are apparently linked to the different handling sequences used in either case (DE VITRE, 1986). The lower values determined after sample storage are attributed to slow losses of H_2S by degassing. Indeed, calculations using the first dissociation constant of H_2S show that more than 25% of the total sulfide is present as H_2S at the pH of the lake water (pH = 7.2) and thus it may readily degas due to pressure changes during sampling. This was confirmed by the formation of very small bubbles in the air tight syringe samplers and Winkler bottles during the 6 hour storage period. The loss of H_2S as a function of time immediately after sampling is also apparent in Fig. 6, where *ca.* 40% of the S(-II) signal is lost within 45 minutes. This loss, together with the decrease in FeS_{ea} and the corresponding increase in $|Fe(II)|_{ea}$ with sample storage (Figs. 5 and 6), suggests that FeS_{ea} is a labile species. It should however also be pointed out that S(-II) losses might occur by the formation of colloidal and/or particulate iron sulfide (ZALI, 1983).

III.3 Determination of Mn(IV) and Mn(II)

Manganese in natural waters may occur as Mn(II), Mn(III) and Mn(IV) (STUMM and MORGAN, 1981; CHISWELL and MOKHTAR, 1986). The formation and stability of Mn(III) oxyhydroxides (MnOOH) in natural media is controversial and the latter species is thermodynamically unstable (MURRAY *et al.*, 1985). They can however under certain conditions be formed as the result of the chemical oxidation of Mn(II) in aqueous solution (STUMM and MORGAN, 1981). However, since little is known about the speciation of Mn(III) in natural Mn-oxyhydroxides, and moreover, since the analytical techniques used here are unable to distinguish between Mn(III) and Mn(IV), Mn(IV), equivalents will be used in the ensuing discussion to indicate any Mn oxidation state greater than II.

Mn(II) is generally found as a free aquated cation Mn^{2+}_{aq} or as simple inorganic complexes except in sediments or in waters containing very high concentrations of sulfide, phosphate or bicarbonate where solid Mn(II) phases may be formed. Stability of Mn(II) complexes formed with naturally occurring organics is furthermore very weak (CHISWELL and MOKHTAR, 1986) and these complexes are negligible in most natural waters. Consequently, polarographic measurements enable an unambiguous, specific determination of Mn^{2+}_{aq} and its labile inorganic complexes.

Mn(IV) is generally found as solid oxyhydroxides in natural media such as sediments and marine ferromanganese nodules. A variety of techniques ranging from redox titrations to colorimetry can be used to analytically determine the Mn(IV) concentration. Their respective advantages and drawbacks when used for the determination of Mn/O ratios have been compared by MURRAY *et al.* (1984). Colorimetric methods (MORGAN and STUMM, 1965; KESSICK *et al.*, 1972; KRUMBEIN and ALTMANN, 1973) because of their high sensitivity have often been used for the determination of Mn(IV) in Mn-oxyhydroxides (MnO_x). We have used KESSICK *et al.*'s method (method 3 in Fig. 3) because of its high sensitivity. This method, however, has three major drawbacks: a) The measured concentration is dependent on the chemical reactivity of the manganese oxyhydroxide, or, in other words, depends on the kinetics of the reduction of MnO_x by leuco-crystal violet (MURRAY *et al.*, 1984); b) analysis in natural samples requires sample turbidity corrections (which may be up to 80% of the measured signal); and, c) in anoxic waters, S(-II) strongly interferes by forming a cloudy suspension. In order to overcome the latter drawbacks and to assess the relevance of the measured signal for the characterization of natural lacustrine MnO_x we also used two other methods (methods 1 and 2 in section II.3). Methods 1 to 3 are complementary, since methods 2 and 3 measure reactive MnO_x (*i.e.* that which is reducible by sulfite or leuco-crystal violet, respectively), whereas method 1 will measure total particulate Mn.

Representative total MnO_x concentration depth profiles are shown in Fig. 7. It can be clearly seen that method 1 shows a positive bias when compared to either methods 2 or 3 at all depths. This difference is particularly noticeable in the sulfidic zone where concentrations of 1.5–3 μM are found by method 1, whereas method 2 yields a value of 0. Above the sulfidic zone, method 1 again yields a higher concentration than either methods 2 or 3, although the differences are less marked than in the anoxic water strata. Method 1's constant positive bias could be due to the measurement not only of MnO_x but also of other particulate Mn species such as Mn(II) associated to organic matter or to other particulates in suspension in the water column. However, several facts do not support this hypothesis:

—Microbeam analysis (EDS and LAMMA) of particulates in suspension in Lake Bret (BUFFLE *et al.*, 1988) at depths where no MnO_x is found but at which $|Mn(II)|_{ea}$ concentrations of up to 10 μM existed showed that no significant amounts of Mn(II) are associated to the above mentioned particles.

—Saturation index computations (ZALI, 1983) show that all likely solid Mn(II) phases (in particular $Mn(OH)_2$, $MnCO_3$ or MnS) are undersaturated.

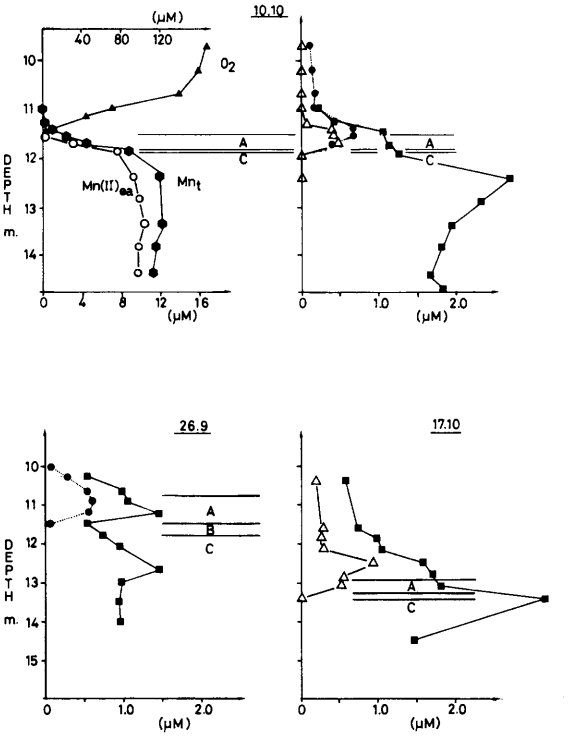

FIG. 7. Oxygen (▲) (upper scale), $|Mn|$, (●), $|Mn|_{ea}$ (○), and MnO_x concentration (lower scales) depth microprofiles in Lake Bret in 1985. All graphs except top left: MnO_x concentrations determined using method 1 (■), method 2 (△) and method 3 (●). Method 1 gives total MnO_x; Methods 2 and 3 determine reactive MnO_x. The upper limits between zones A, B and C are defined respectively by: O_2 < 2.0 mg/l, $|Fe(II)|_{ea} \leq 1$ μM and $|S(II)|_{ea} < 0.2$ μM).

—Mn(II) associated/complexed to natural organic matter is, as previously mentioned, highly unlikely.

We consider consequently that method 1 measures total MnO_x and, furthermore, that the colloidal Mn fraction is most probably MnO_x. The observed differences between methods 1–3 should be interpreted as being due to the chemical reactivity of MnO_x, *i.e.* that lacustrine MnO_x encompasses Mn(IV) (and possibly Mn(III)) in different forms and with different reactivities. Therefore, in the case where one is absolutely sure that no particulate Mn species other than MnO_x is present, method 1 should be preferred for the determination of total MnO_x, since it is independent of the chemical reactivity of MnO_x. Simultaneous use of method 1 and one of the two other methods is recommended if the goal is, as it is here, to follow the limnological cycling of Mn at a redox interface.

IV. DEPTH-TIME DISTRIBUTION OF IRON AND MANGANESE

IV.1. Overall picture

The different forms of Fe and Mn and their transformations at the O_2/H_2S interface have been studied using the multi-method speciation scheme. In Figs. 8 and 9, seasonal changes

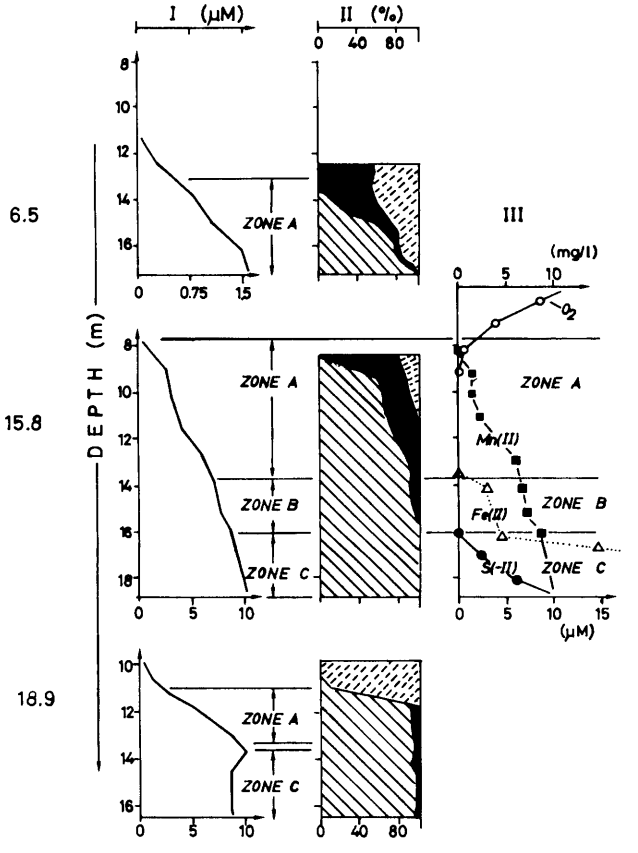

FIG. 8. Representative multi-method graphs for manganese at the O_2-H_2S transition layer in Lake Bret in 1985. I. $|Mn|_t$ II. Size fractions: □ % of $|Mn|_p$, ■ % of $|Mn|_c$ and □ % of $|Mn|_{ea}$. III. Concentration profiles of O_2 (upper concentration axis), and $|Fe(II)|_{ea}$, $|Mn(II)|_{ea}$ and $|S(-II)|_{ea}$ (lower concentration axis), the 15.8.85 for definitions of zones A, B and C.

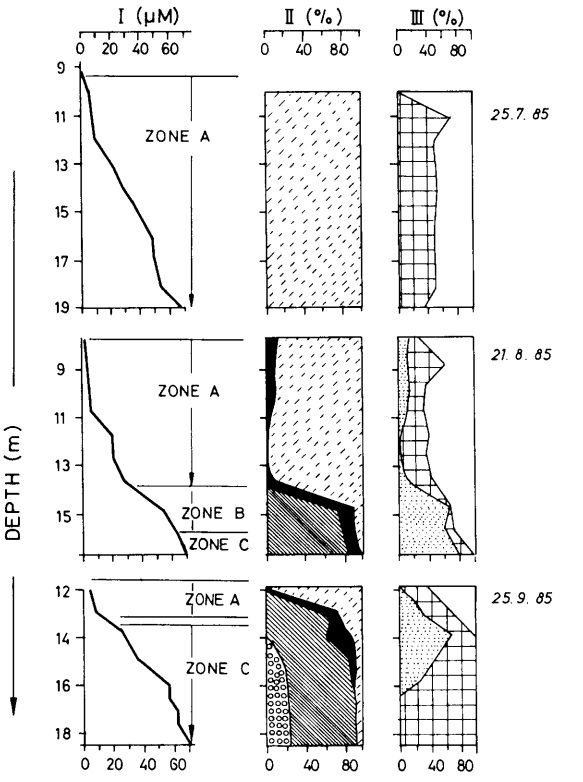

FIG. 9. Representative multi-method graphs for iron at the O_2/H_2S interface in Lake Bret (1985). I. $|Fe|_t$. II. Size fractions: ▨ % of $|Fe|_p$, ■ % of $|Fe|_c$, ▧ % of $|Fe(II)|_{ea}$ and ▩ % of $|FeS|_{ea}$. III. Redox state: □ % of $|Fe(III)|_p$, ▦ % of $|Fe(II)|_p$, ▩ % of $|Fe(III)|_c$. Note: $|Fe(II)|_c = 0$ in all cases.

in the concentration depth profiles obtained from the multi-method data are shown. In type I graphs, the total Fe or Mn concentration is plotted as a function of depth. In type II, graphs the total concentration is sub-divided into three operationally defined size classes, as defined in section II.3 namely: particulate, colloidal and electroactive. The percentage of each class relative to total Fe or Mn is then plotted as a function of depth. In the case of iron (see Fig. 9) a further type of graph, III, shows the variation of the redox state within both the particulate and colloidal fractions of iron as a function of depth. In these graphs, the fraction of a given species is expressed as a percentage relative to the sum of the concentrations of all the particulate and colloidal species.

In general and in particular in Lake Bret, the chemical transformations of both iron and manganese species at the O_2-H_2S transition layer are governed by the overall "redox potential" of a given water strata. For clarity, we have divided the transition layer into three zones A, B and C (see Figs. 7–9 and 11–13) which represent three different redox environments and which in the case of Lake Bret may be defined by the different redox couples present in a given strata of water (see Fig. 8.III).

Zone A represents the top part of the O_2-H_2S transition layer, with a high pE environment and is characterized by a low but not negligible O_2 concentration between (0.1 and 2 mg/l), low concentrations of Fe(II) ($|Fe(II)|_{ea} < 1$ μM) and no detectable sulfide ($|S(-II)|_{ea} < 0.2$ μM).

Zone B represents an intermediate pE environment characterized by high Fe(II) and Mn(II) concentrations ($|Fe(II)|_{ea} > 1\ \mu M$ and $|Mn(II)|_{ea} > 5\ \mu M$), but no detectable S(-II).

Zone C represents the lower part of the O_2-H_2S transition layer. It extends downwards to the deeper waters of the hypolimnion and is characterized by a low pE and by high Fe(II), Mn(II) and S(-II) concentrations.

The vertical position and the thickness of a given zone changes as a function of the increasingly reduced conditions which develop in the metalimnion and the hypolimnion of Lake Bret, during the summer stratification season.

IV.2 Manganese

An overview of both seasonal and spatial changes in the forms of manganese in the lake is shown in Fig. 8. Both particulate and colloidal Mn are found in zone A and only colloidal Mn and electroactive Mn(II) are found in zones B and C. A detailed study has shown (DE VITRE, 1986) that the particulate and colloidal sized Mn result from the biologically mediated autochthoneous formation of MnO_x, by the oxidation of upward diffusing Mn^{2+}_{aq}. The maximum in the concentration of reactive MnO_x within zone A (in Fig. 7), corresponds to the depth at which this process is most intense.

The successive disappearance of particulate and colloidal Mn as a function of depth (decreasing pE) in zones B and C is a notable feature of all the data shown in Figs. 10 and 11. Figure 10 shows typical size distributions obtained by filtration in zones A and C; a shift towards a small size range with increasing depth was always observed. Note also that a major portion of "dissolved" Mn is non-electroactive. The size distribution for Mn in Fig. 10b obtained by *in situ* cascade ultrafiltration (DE VITRE *et al.*, 1987) shows that this non-electroactive colloidal Mn fraction has a size range between *ca.* 0.002 and 0.4 μm.

The decrease in size of MnO_x with depth is also seen in Fig. 11 which indicates that in zones B and C, $|MnO_x|_c$ is always equal to total MnO_x ($=|MnO_x|_t = |Mn|_t - |Mn(II)|_{ea}$). This is not the case in zone A where particulate MnO_x exists in most cases. Comparison of the different forms of MnO_x in Figs. 7 and 11 suggests furthermore that the "reactive" MnO_x measured by methods 2 and 3 (Fig. 7) is mainly found in the particulate fraction. Somewhat surprisingly, colloidal MnO_x is rather inert, since it persists into the sulfidic layer.

These results can be interpreted by considering particulate MnO_x, formed in zone A, to be composed of reactive and less reactive portions. Sedimentation of the MnO_x particles into the more reducing zones leads to the elimination of the reactive fraction, with the less reactive colloidal part remained. It should be stressed that, few studies have been published on colloidal Mn in natural waters (LAXEN and CHANDLER, 1983; HOFFMAN *et al.*, 1981; LAXEN *et al.*, 1984; ZALI, 1983) and that furthermore in most cases size distributions were obtained by measuring only total Mn in filtrates. Our results combining DPP, AAS and filtration (see Figs. 8 and 10) like those of LAXEN *et al.* (1984), show that a large proportion (20–50%) of Mn which passes through a 0.4 μm filter is non-electroactive Mn and not Mn^{2+}_{aq} as it is often implicitly assumed in the literature. Furthermore, this appears to be the case even in sulfidic waters where colloidal Mn, possibly in the form of MnO_x, appears to persist. This certainly underlines the importance of distinguishing between Mn(II) and Mn(IV) equivalents when studying the Mn species present at a redox interface.

IV.3. Iron

Figure 9 gives an overview of both seasonal and spatial changes in the forms of iron in the lake. The gradual increase in reducing conditions is directly reflected in the change of the speciation of iron. A transition from only one particulate Fe species in July to several particulate, colloidal and electroactive species in the autumn represents the two extremes of this process. In addition to seasonal changes, a depth related

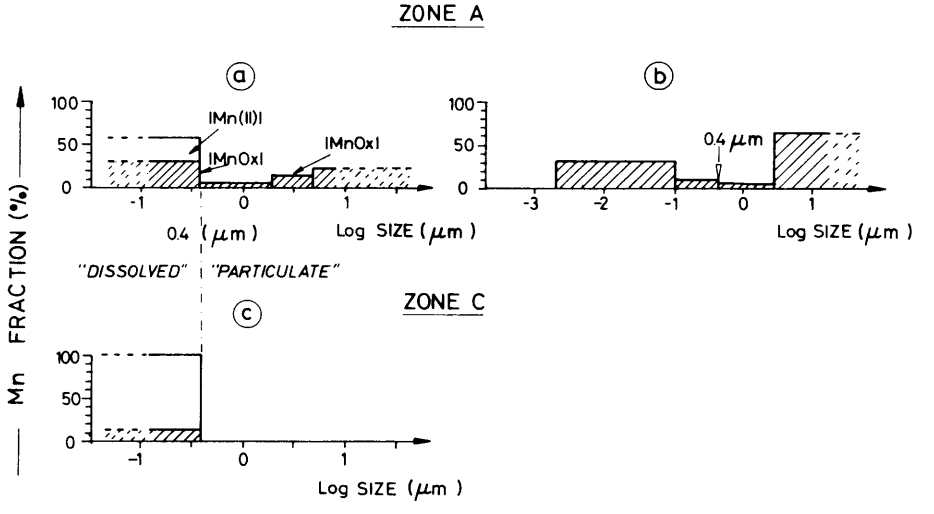

FIG. 10 (a, b). A typical size distribution for MnO_x obtained at two depths in zone A, above (b) and below (a) the redox transition layer using Nuclepore filters (8, 5, 2, 0.4 μm). ▭ electroactive Mn(II), ▭ non-electroactive Mn (MnO_x). Date: 2.9.85 Electroactive Mn(II) was obtained polarographically and MnO_x by method 1 (sect. II.3). 10. (c) *In situ* cascade ultrafiltration of non electroactive Mn in zone C. Lake Bret, 22.5.85.

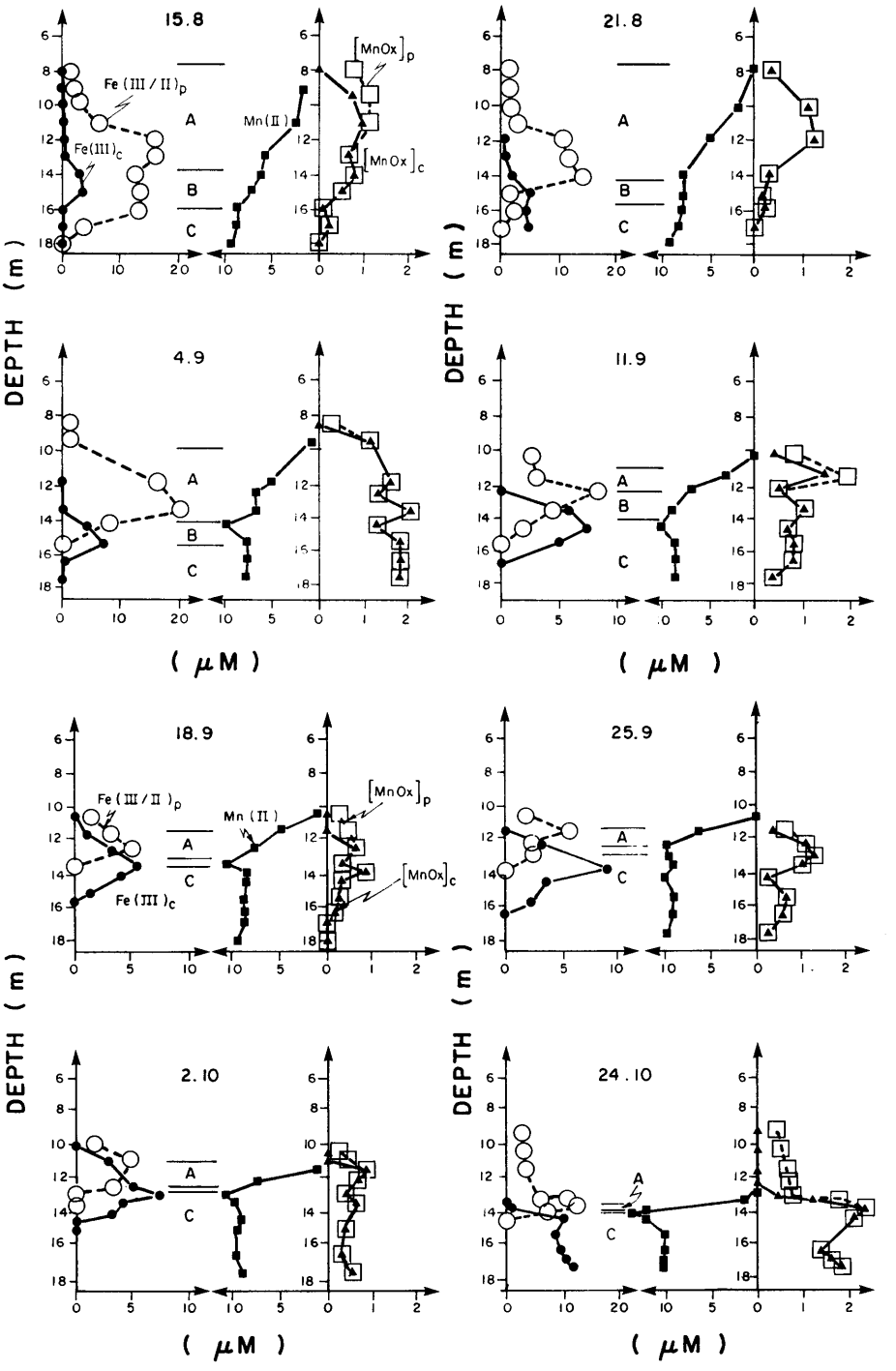

FIG. 11. Concentration depth profiles for iron and manganese species at the redox transition layer (A/B/C) from August to October 1985. ○—|Fe(III/II)|$_p$, ●—|Fe(III)|$_c$, ■—|Mn(II)|$_{ea}$, □—|MnO_x|$_p$, ▲—|MnO_x|$_c$.

redox transition can be seen in the data plotted in Figs. 9 and 11. This may be conveniently discussed as in the case of manganese by dividing the entire profile into the three redox zones: A, B and C.

In zone A and B, a particulate mixed oxidation state Fe species is formed as upwardly diffusing Fe^{2+}_{aq} (Fig. 9) is oxidised by dissolved O_2 and possibly by reactive MnO_x formed in zone A (Figs. 7 and 11). Both the physical and chemical characteristics of this particulate Fe species have been investigated using a combination of electron microscopy (STEM/EDS) and classical analytical techniques. It was found to consist of amorphous, nearly spherical globules (0.04–0.3 μm) existing either as individual entities or associated in either tightly (0.1–1 μm) or loosely (0.5 → 10 μm) packed aggregates.

The elemental composition was determined on a particle specific basis using an EDS probe combined to a STEM.

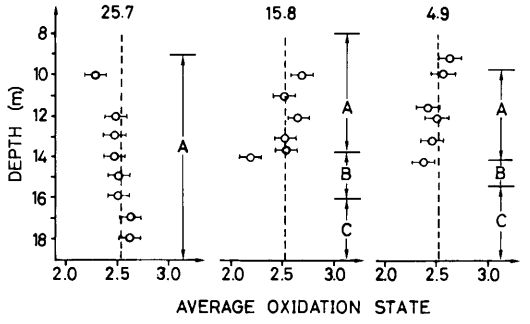

FIG. 12. Average oxidation state for the $Fe(III/II)_p$ species on three different dates as a function of depth.

Molar ratios were computed from peak intensities using a calibration procedure to account for matrix effects (BUFFLE *et al.*, 1988). The major elemental components found were Fe, Ca and P in the following atomic proportions: 4.2/1.3/1.0. Figure 9.III also shows that *ca.* 50% of the Fe in this particulate species is in the ferrous state. This can be more clearly seen in Fig. 12 and in Table 3, which show that the average oxidation state is very close to 2.5, irrespective of depth (within zone A and B) and date. The complete results are discussed in detail elsewhere (LEPPARD *et al.*, 1987; BUFFLE *et al.*, 1988).

Within zone B, the concentration of the mixed oxidation state particulate Fe species decreases whereas a colloidal Fe species containing only Fe(III) appears (see Fig. 11). The concentration depth profiles of the latter species are peak shaped and the maxima often found at the depth at which S(--II) is first detectable (interface between zones B and C). It is also useful to note that an electroactive Mn(II) concentration peak is sometimes observed at the same depth.

In zone C (low pE), two new Fe(II) species are observed (see Fig. 9): a small iron sulfide complex, FeS_{ea} and a particulate Fe(II) species containing sulfide but of ill-known stoichiometry (ZALI, 1983). These Fe sulfide species are discussed elsewhere (BUFFLE *et al.*, 1987; DE VITRE, 1986; ZALI, 1983). In this paper we deal exclusively with the particulate and colloidal Fe species formed in zones A and B and their linkage with particulate, colloidal and electroactive Mn and S(-II) species.

A summary of both the Fe and the Mn species found in zones A, B and C is given in Table 4. Concentrations given are typical for early autumn, and are based on data collected in September, 1985 (DE VITRE 1986).

TABLE 3: Average oxidation states of the $Fe(III/II)_p$ species on different sampling dates (two replicate samples were taken at each depth). Overall average equals 2.52 (± 0.12); excluding data of 11.7 since value lies outside the $\pm 2\sigma$ range.

DATE (1985)	11.7	16.7	25.7	15.8	21.8	4.9	18.9	10.10
No. of samples	10	16	16	12	10	12	8	10
Depth range (m)	12-15	11-18	10-18	10-14	9-13	9-14	9-11	10-11
$Fe(II)_p/Fe_p$ (%)	23	48	51	48	39	48	50	55
Average oxidation state	2.77	2.52	2.49	2.52	2.61	2.52	2.5	2.45
Standard deviation (σ)	0.07	0.07	0.09	0.16	0.10	0.10	0.06	0.06

Table 4: Iron and Manganese species found at the redox transition layer in Lake Bret. Values are for September 1985. *- Detection limit.

ZONE	DEFINITION	IRON SPECIES (μM)	MANGANESE SPECIES (μM)
A. HIGH pE	O_2 0.1-2 mg/l	$Fe(III/II)_p$ (0-20 μM)	$MnOx_p$, $MnOx_c$ (0-1.5 μM)
	Fe^{2+}_{aq} < 1.0 uM	$Fe(III)_c$ (1-3 μM)	Mn^{2+}_{aq} (0-3 μM)
	S(-II) <0.2* uM	Fe^{2+}_{aq} (< 1 μM)	
B. INTERMEDIATE pE	O_2 <0.1* mg/l	$Fe(III/II)_p$ (0-6 μM)	$MnOx_c$ (1-4 μM)
	Fe^{2+}_{aq} >1.0 uM	$Fe(III)_c$ (4-6 μM)	Mn^{2+}_{aq} (3-12 μM)
	S(-II) <0.2* uM	Fe^{2+}_{aq} (1-20 μM)	
C. LOW pE	O_2 = <0.1 uM	$Fe(III/II)_p$ = 0	$MnOx_c$ (0-1 μM)
	Fe^{2+}_{aq} >1.0 uM	$Fe(III)_c$ (0-5 μM)	Mn^{2+}_{aq} (7-15 μM)
	S(-II) >0.2 uM	Fe^{2+}_{aq} (20-60 μM)	
		$FeS_{complex}$ (0-15 μM)	
		$Fe(II)_p$ (0-5 μM)	

V. DISCUSSION

V.1. Interaction of Fe and Mn at the O_2-H_2S interface

The complete description of the cycling of trace metals such as Fe and Mn at a redox interface requires a detailed knowledge of all the chemical and physical processes (precipitation, oxidation, adsorption, reductive and non-reductive dissolution, etc.) that take place. Furthermore, the rates of these processes and the transport fluxes of the various species must be known and quantified. Clearly, this is not a simple task and many necessary parameters in aquatic systems are still as yet unknown. Useful detailed information may be obtained, however, from the shape of instantaneous, size and redox discriminated concentration depth profiles, as shall be seen below for Mn and Fe.

A conceptual model integrating the principal factors governing profile shapes has been recently reported by DAVISON (1985). The author has shown that peaked profile shapes are formed in the presence of a well defined redox boundary and when there is a supply of sedimenting particulate metal oxide. This particulate material is reduced on entering the anoxic water strata, releasing the reduced soluble metal cation. Upward diffusive transport of the soluble species results in its oxidation by O_2 and the formation of the insoluble metal oxide. Note that allochthonous sources of the insoluble metal oxide can in certain cases also be very important and dwarf the downward flux of metal oxide formed autochthonously. These mechanisms lead to point sources and hence to peaked profile shapes, for both particulate and soluble metal species at a redox boundary. These processes are known to occur in lakes, for instance, and peaked profiles for Mn have been reported in the literature (STAUFFER, 1986; HUTCHINSON, 1957; VERDOUW and DEKKERS, 1980; DANIELSSON *et al.*, 1980; MAYER *et al.*, 1982). However, to our knowledge, no explicit spatial and temporal comparisons of peaked profiles of particulate, colloidal and electroactive Fe and Mn have been published.

V.2. Formation of $|MnO_x|$ and $|Mn(II)|_{ea}$ profiles

The oxidation of upward diffusing soluble Mn^{2+}_{aq}, in zone A, constitutes a point source of particulate MnO_x. A point

source of electroactive Mn(II) results from the reduction of downward settling MnO_x as they encounter low pE water strata. These processes lead to the formation of peaked shaped profiles for both MnO_x and Mn^{2+}_{aq}. However, these profiles are often found as broad maxima or have multi-peaked shapes possibly due to the transient non-steady state boundary conditions. In Lake Bret such peaks (see Figs. 7 and 11) have been observed to occur every autumn (DE VITRE, 1986; ZALI, 1983) but not in the spring or summer. Their occurrence depends on the relative fluxes of sedimenting MnO_x and its reduction rate, compared to the upward or lateral transport of Mn(II) from the sediment. Earlier in the year a relatively high flux of Mn(II) comes from the sediment (as shown by the concentration gradients in Fig. 11), whereas later in the year the supply is dominated by the dissolution of sinking MnO_x particles, since the Mn(II) concentration gradients from the sediment upwards are essentially zero. The downward migration of the oxycline in September/October (see Fig. 2) leads to the formation of increasing amounts of MnO_x and, therefore, accelerates the formation of peaked $|Mn(II)|_{ea}$ profiles.

Thermodynamically, the reduction of MnO_x may be represented by the combination of Eqn. (1) with either of Eqns. (2) or (3) where the log K values are taken from STUMM and MORGAN (1981):

$$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{2+} + 2H_2O \quad \log K = 43.0 \quad (1)$$

$$2Fe^{2+}_{aq} + 6H_2O \rightleftharpoons 2 \cdot am\text{-}Fe(OH)_3 + 6H^+ + 2e \quad \log K = -34.2 \quad (2)$$

$$HS^- \rightleftharpoons S^{(0)} + H^+ + 2e \quad \log K = 2.2. \quad (3)$$

At pH 7, either of the two possible combinations are thermodynamically likely; however, complexation effects, the ill-known stoichiometry of the solid phases, and possible slow kinetic rates must also be considered when extrapolating thermodynamic considerations to environmental reactions.

Kinetic dissolution rate experiments (DE VITRE and BUFFLE, unpublished data) have shown that both of the above reactions are realistic and are not kinetically inhibited. Reductive dissolution experiments were performed directly in the field in a polarographic cell at *in situ* temperatures and pH, using natural MnO_x sampled from zone A. A 30-fold excess of either Fe(II) or S(-II) was then added to the solution in the polarographic cell and the rate of release of Mn(II) as a function of time was followed by DPP. The results show that under lacustrine conditions both reductants can reduce MnO_x and release Mn(II). Typical half-reaction times ranged from 10–20 and 20–200 minutes for Fe(II) and S(-II), respectively. Thus both reactions can play a role at the O_2-H_2S transition layer in the lake, their effective role probably being very dependent on the physical state (ageing, surface coating) of the sedimenting particles.

V.3. Iron peaked profiles

The well-defined peak-shaped profiles for both the Fe(III/II) particles and the Fe(III) colloids imply that, in both cases, a production source must exist at a given depth and elimination processes must occur above and below this depth. Before stratification, the particulate and colloidal Fe concentrations are lower than 0.5 μM (*i.e.* 10–100 times lower than during stratification), indicating that the formation of the peak profiles is directly and closely linked to the stratification and the formation of a redox interface within the water column. The formation of the particulate Fe(III/II) species along with the elimination of the colloidal Fe(III) species, since they are relatively straightforward, will be discussed first. The more speculative aspects dealing with the elimination of the particulate species and the formation of the colloidal species, which both occur in zone B, will then be discussed.

The *particulate Fe(III/II) species* is made up of amorphous, globular-shaped particles, the morphology of which is totally different from allochthonous clay particles. Its concentration peak is always precisely found in zone A, *i.e.* just in between the O_2 and Fe(II) rich water layers. Consequently, it is probable that this species results from the oxidation of Fe^{2+}_{aq} by an oxidant located in zone A. The latter may be either downward diffusing O_2 or reactive MnO_x formed in zone A. By comparing the maximum concentrations of Fe(III/II) species (*ca.* 20 μM) with those of reactive MnO_x (*ca.* 0.5 μM), it seems likely that the former oxidant plays the most important role.

The *elimination of Fe(III) colloids* is most likely due to their reaction with sulfide. Indeed, the depth corresponding to the maximum of the $Fe(III)_c$ peak often coincides to the B/C zone interface, *i.e.* the depth at which sulfide is detectable. It is, however, interesting to note that the Fe(III) colloids persist 2–3 meters down into the sulfidic layer. Now, taking into account their small size and low density, their sedimentation rate is probably very small (for particles with a diameter < 0.45 μm a sedimentation of approx. 10^{-2}–10^{-3} m · day^{-1} may be expected, LERMAN, 1979). Since they are apparently not eliminated by sedimentation but persist in the presence of S(-II), they must be only slowly reactive. Some evidence supporting this interpretation can be found in the literature: TIPPING *et al.* (1982) in a kinetic study of natural iron oxyhydroxides isolated from Esthwaite Water found that the Fe(III) oxide included an inert as well as a reactive fraction. Further evidence has been reported by DAVISON and DICKSON (1984) who found that iron oxyhydroxides isolated from the same lake persisted in sulfide-rich hypolimnetic waters, possibly due to the formation of a protective layer of iron sulfide. This behaviour put in parallel with that exhibited by MnO_x suggests that particles could have a reactive outer layer which is consumed as the particle settles downward into low pE environments, but that a smaller sized, more inert core of the initial particle can persist. Comparison of the profiles of colloidal MnO_x and Fe(III), in Fig. 11, suggests however that the Fe(III) colloids are less inert than those of MnO_x, since they frequently disappear at lesser depths.

The processes of *elimination of Fe(III/II) particles and the formation of Fe(III) colloids* are less clear. In the latter case, the directly oxidation of Fe(II) by O_2 is highly unlikely, since the O_2 concentration, although unmeasurable, should be extremely low in zone B. Furthermore, it would be difficult to understand why this reaction would produce purely Fe(III) species in zone B, whereas it produces mixed oxidation state particles in zone A. A more plausible source of colloidal Fe(III) could be the oxidation of Fe(II) by the sedimenting

MnO_x. This could be corroborated by the fact that there are peaks of Mn(II) located at the depths identical or close to those corresponding to the maxima of the $Fe(III)_c$ species. Accordingly, both peaks would result from:

$$MnO_2 + 2Fe(II) \rightleftarrows 2Fe(III)_c + Mn(II). \quad (4)$$

There are, however, several arguments against this reaction being the major source of $Fe(III)_c$:

—as already mentioned, the most reactive MnO_x is associated to particles; consequently, this component may be expected at depths where differences are observed between total and colloidal MnO_x profiles (see Fig. 11). However, often there is no coincidence between these depths and those at which the maximum concentration of $Fe(III)_c$ is observed (*e.g.* all dates before 12 Sept. and the 24 Oct.).

—the occurrence of an $Fe(III)_c$ peak is not always parralleled by that of a $|Mn(II)|_{ea}$ peak (*e.g.* 15 Aug., 21 Aug., 25 Sept.).

—the maximum $Fe(III)_c$ concentration is always 2–3 times larger than the number of redox equivalents in the corresponding Mn(II) peak.

It is, therefore, likely that the coincidences observed between the peaks of $|Mn(II)|_{ea}$ and $Fe(III)_c$, in Fig. 11, only reflects an indirect correlation, both peaks appearing at the boundary between zones B and C, because of independent reactions with S(-II).

Although the contribution of MnO_x in the formation of $Fe(III)_c$ cannot be totally excluded, it is more likely that the formation reaction is linked to the disappearance of the Fe(III/II) species. This can be clearly seen in Fig. 11, where in nearly all cases these two transformations occur concurrently. It is also striking that, as already mentioned, the chemical composition and, in particular, the ferrous to ferric iron ratio in the Fe(III/II) species is very constant and close to 1.0 even when the $|Fe(II)|_{ea}$ concentration is very low (less than 0.1 μM). This could suggest that this ratio corresponds to the stoichiometry of a particular (although as yet unknown) chemical species (BUFFLE *et al.*, 1988; LEPPARD *et al.*, 1987). Our present knowledge of iron chemistry suggests that a species containing equimolar amounts of Fe(II) and Fe(III) would not remain stable for long time periods (SCHNEIDER, 1987, pers. commun.). Therefore, a possible explanation is that during their settling process, the particles encounter chemical conditions which are different from those prevailing within zone A, leading to their transformation into Fe(III) colloids. The major factors could be:

—spontaneous dissociation into dissolved Fe(II) and colloidal Fe(III) because of the intrinsic metastability of the particles.

—reaction of the Fe(II)/Fe(III) with S(-II), destabilizing the particle because of the change in the Fe(II)/Fe(III) ratio, and leaving only slowly reactive Fe(III) colloids.

Either or both of these effects and possibly others might be operative simultaneously.

VI. CONCLUSIONS

The importance of the exact determination of colloidal Fe and Mn concentrations and the advantages of using a multi-method approach have been demonstrated. They have shown that in particular the O_2-H_2S transition layer in Lake Bret may be conveniently represented by dividing it into three spatially distinct redox zones, based on their respective chemical make-up. Peaked concentration profiles for both iron and manganese species formed at the interface have been measured and have been used to qualitatively describe the redox interactions between O_2, Fe, Mn and S(-II). Future studies of redox interfaces in aquatic systems in general should attempt to establish a dynamic description of the relevant species in terms of their size and redox state in order to gain a greater understanding of the mechanisms controlling trace element cycling. This in turn requires the development and use of either new or existing analytical techniques with a greater physicochemical selectivity. They should be used either directly in the field, or, preferably, *in situ* when studying reactive species to avoid storage artefacts which may lead to incorrect data and to erroneous interpretation.

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