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Speciation, reactivity, and cycling of Fe and Pb in a meromictic lake

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Abstract—A suite of analytical techniques were combined to study the chemical speciation of Fe and Pb in the water column of a lake characterized by a biogenic meromixis (Paul Lake, MI). Depth profiles of Fe^{2+} and "dissolved" Pb display significant concentration gradients below the chemocline, i.e., they increase from below detection limit to ca. 100 μM for Fe^{2+} and 2 nM for Pb_d. Significant correlations between particulate organic matter, hydrous iron oxides, and particulate Pb suggest that Pb is scavenged by Fe-rich particles formed at the oxic-anoxic transition. Transmission electron microscopy shows that particles of hydrous iron oxides form complex aggregates with natural organic matter at and below the oxic-anoxic transition. Experiments with batch reactors show that these organo-mineral moieties remove Pb rapidly during their formation. Thermodynamic calculations predict that FeS and PbS are respectively saturated and oversaturated in the monimolimnion, although the presence of neither FeS nor PbS was observed. This suggests that the solubilities of Fe and Pb are influenced by complexation. Voltammetric experiments on filtered samples show that Pb is weakly complexed in the mixolimnion and strongly complexed in the monimolimnion. A conditional stability constant for Pb complexation is determined using metal titration curves assuming a simple 1:1 stoichiometry and gives $\log K_{cond} = 9.4 \pm 0.8\ M^{-1}$ in the monimolimnion. These speciation results are confirmed by ion exchange chromatography, which demonstrates that more than 98% of Pb is complexed by natural organic matter.

1. INTRODUCTION

Lead is a toxic pollutant (Nriagu, 1990; Needelman, 1990; Goyer, 1993; Nriagu et al., 1996a), and its presence in aquatic systems primarily results from anthropogenic activities (Schaule and Patterson, 1981; Boyle et al., 1986; Nriagu and Pacyna, 1988; Ritson et al., 1994; Veron et al., 1994; Erel and Patterson, 1994). Lead enters lakes from rivers, atmospheric deposition, soil leachates, and groundwater seepage. The constant presence of oxygen in oligotrophic lakes and the high reactivity of lead with oxide particles ensures its uptake from the water column, resulting ultimately in its burial in the sediment (Sigg et al., 1987; Ritson et al., 1994; Nriagu et al., 1996b). In contrast, the cycling of lead in the anoxic bottom waters of eutrophic lakes is controversial (Hamilton-Taylor and Davison, 1995). Lead has been shown to be remobilized during the dissolution of redox sensitive particles (mainly hydrous iron oxides) in the water column (Balistrieri et al., 1992a) and at the sediment-water interface (SWI) (Hamilton-Taylor et al., 1984; White and Driscoll, 1985; Benoit and Hemond, 1990; Taillefert et al., 1997; Viollier, 1995). Simultaneously, it can be removed from anoxic waters by precipitation with sulfides (Sigg, 1985; Frevert, 1987; Balistrieri et al., 1994) or by adsorption onto FeS (Davison et al., 1992; Morse and Arakaki, 1993). However, lead removal was not evident in many systems where the ionic activity product (IAP) exceeds the solubility product of PbS. Benoit and Hemond (1990) summarize the possible explanations for such behavior: (i) Pb precipitates in all environments but in some waters the particles formed are too small to be retained on filters; (ii) Pb is complexed by dissolved ligands that outcompete sulfide complexation and precipitation; (iii) freshly precipitated PbS may have a higher K_{sp} than well crystallized minerals; and (iv) the precipitation may be hindered kinetically. Because of this behavior and because Pb is toxic, it is necessary to determine its chemical speciation in the dissolved phase and to assess its biogeochemical cycle in lakes.

It is generally accepted that trace elements are most efficiently removed at oxic-anoxic transitions by organic or inorganic colloidal particles, which have high specific surface areas (Tipping, 1981; Davis, 1984). It has also been shown that natural organic matter (NOM) and hydrous oxides can interact; however, the nature of this interaction has been subject to conflicting interpretations. Some authors believe that in natural systems hydrous iron oxides are coated by low molecular weight NOM, thus modifying their surface reactivity (Stumm et al., 1980; Tipping, 1981; Davis, 1984; Zhou et al., 1994; Gu et al., 1995). This idea is supported by laboratory experiments, which demonstrated that adsorptive properties are changed in the presence of dissolved NOM. In contrast, microscopic investigations (Fortin et al., 1993; Perret et al., 1994; Tessier et al., 1996; Lienemann et al., 1999) have showed that under natural conditions hydrous oxides and high molecular weight NOM form intimate structures. The aggregation of these entities leads to a more complicated structure in which trace elements may not only be scavenged at the surface, but also embedded in the mineral-organic moieties (Laxen and Sholkovitz, 1981; Laxen, 1984, 1985).

The chemical speciation of iron and lead in the water column and the scavenging of lead by hydrous iron oxides can be calculated by thermodynamic equilibrium models that use sur-

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face complexation theories (Nriagu and Gaillard, 1984). However, in Paul Lake these calculations were not successful for predicting the distribution of lead between the dissolved and particulate phases (Taillefert et al., 1997; Taillefert, 1997), probably because the adsorption and complexation of Pb by simple ligands are not the only processes controlling its chemistry in this aquatic system. Therefore, the characterization of the various physical and chemical forms under which iron and lead are present in this environment needs to be achieved analytically.

The primary goal of the present study was to determine the effect of hydrous iron oxides and NOM on the speciation of Pb in aquatic systems. Hence, the analytical speciation of Fe and Pb was determined with a combination of analytical techniques in the water column of a stratified lake that presents a permanent oxic-anoxic transition. Pb complexation was investigated by voltammetry; the fraction of dissolved Pb that was bound to NOM was quantified by ion exchange chromatography; and characterization of the particles that were scavenging Fe and Pb was performed by high-resolution transmission electron microscopy coupled to energy dispersive spectrometry (TEM-EDS). The total and total dissolved element concentrations were measured either by inductively coupled plasma mass spectrometry (ICP-MS) or Zeeman graphite furnace atomic absorption spectroscopy (Z-GFAAS). In addition, proof of concept experiments were conducted with natural samples to follow the removal of Pb by freshly formed particulate material.

2. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling was performed in the water column of Paul Lake (MI), a small stratified lake at UNDERC (University of Notre Dame Environmental Research Center), a facility located on the border of Wisconsin and the upper peninsula of Michigan (46°13′N89°32′E). This lake is small kettle lake that has been maintained in pristine conditions (Carpenter and Kitchell, 1993). Paul Lake has a surface area of about 1 ha, a mean depth of 6 m, and a maximum depth of 13 m. The lake is surrounded by trees and is well protected from dominant winds, thus experiencing little mixing. In addition, the steep conical shape of the central basin is conducive for the maintenance of a biogenic meromixis. More information on this site can be found in Carpenter and Kitchell (1993) and Lienemann et al. (1997).

2.1. Sampling

Water column samples were collected every 25 to 50 cm at the deepest location of the lake, from 0.5 m to 10.5 m, by peristaltic pumping with a portable pump (Cole Parmer) and a weighted Tygon® tubing pre-cleaned with HCl (5%) and HNO_3 (5%) and pre-rinsed with surface lake water. Samples were retrieved in line (i.e., without contact with the atmosphere) using acid washed syringes (Henke Sass Wolf, [HSW]) and subsequently filtered and stored as described in Lienemann et al. (1997). Samples for total trace metal analyses were collected in acid cleaned polypropylene tubes, which were then stored in Ziplock® bags at 4°C. It is important to note that the filtered fraction, operationally called the "dissolved" fraction, probably contains some colloidal material. Samples for total Fe analysis were preserved in HNO_3 (2%). Samples for SO_4^{2-} and Fe^{2+} analysis were conserved in syringes sealed with Luer lock valves at 4°C. The anoxic samples were analyzed within 30 min after sampling. Samples for ΣH_2S ($[H_2S] + [HS^-] + [S^{2-}]$) were preserved on board with NaOH (0.1 M) and brought to the laboratory for immediate analysis. Particulate iron was determined by two independent methods: (i) the difference between the raw and filtered sample concentrations; and (ii) in-line filtration on 0.2 μm filters (cellulose nitrate, Schleicher and Schull) and 0.45 μm filters (AcetatePlus MSI) followed by analysis of the filter residue. The in-line filtration method confirmed that particulate iron obtained by the difference method was reliable. Samples for particulate organic carbon (POC) measurements were collected by filtering 300 to 600 ml of water onto 0.7 μm glass microfiber filters (GF/F Whatman). Part of the filtrate was kept for dissolved organic carbon (DOC) analysis. It was preserved with $HgCl_2$ in glass bottles and stored in the dark until analysis. For voltammetry measurements and ion exchange chromatography experiments, samples were collected and analyzed one at a time to preserve their integrity. They were stored in the dark, in a glove box under N_2 atmosphere, and at 4°C, until analysis within 30 min after collection. Just before analysis, they were filtered through cleaned 0.45 μm Acrodisc LC-PVDE Gelman filters. Samples for TEM-EDS analysis were collected with pre-cleaned 50 ml syringes and brought immediately to the laboratory under N_2 atmosphere. They were transferred in acid-washed 50 ml centrifuge tubes and spin under N_2 atmosphere for 90 min at 55,000 rpms (ultracentrifuge Beckman Optima™ TLX) to accumulate submicron particles on TEM grids without artifacts (Perret et al., 1991).

2.2. Batch Reactor Experiments

Batch reactor experiments were conducted with natural samples to investigate the interactions between Fe and Pb during and after precipitation of hydrous iron oxides. The objective was to mimic processes occurring at the chemocline, where Fe^{2+} diffusing from the monimolimnion meets oxygen. These reactors were neither stirred nor sparged with oxygen to yield particles of similar morphology to those observed under natural conditions. Preliminary experiments established that iron particles produced in a stirred cell in the presence of synthetic polysaccharides (Xanthan Flocon, MW $> 2\ 10^6$ Dal., courtesy of Pfizer) had completely different morphologies from particles generated in the absence of stirring. TEM observation of the two types of material show that mixing leads to a rapid oxygenation of the solution and the aggregation of larger iron particles (i.e., of size greater than 1 μm). Fresh samples were obtained from 10 m, filtered through 0.45 μm filters, and stored in 14 ml tubes (Falcon) under a N_2 atmosphere. Within 15 min after sampling, the tubes were brought to the laboratory, spiked with 50 nM Pb, and left open to the atmosphere. Solutions were kept in the dark at 25°C. Fe^{2+}, $O_{2(aq)}$, and pH were monitored with time in controls. For Pb analysis, a batch reactor was sacrificed at each time step. One-half of the reactor was filtered and acidified to pH 2 ("dissolved" fraction). The other one-half was kept for total analysis by acidification to pH 2 (total fraction). Particulate Pb was calculated by the difference between the total and "dissolved" fractions in each reactor. Samples were also collected for TEM observation of the particles formed at the end of the experiments according to the method of Lienemann et al. (1998).

2.3. Analytical Techniques

Temperature and oxygen profiles in the water column were obtained using a multi-parameter probe (Hydrolab: Minisonde®) interfaced with a portable PC computer. Oxygen and pH were measured in situ in the batch reactors using respectively a Clark type microelectrode (Diamond General Corp.) with a modified picoammeter (Keithley) and a combination pH electrode (Diamond General Corp.) with a pH meter (Orion). Samples were analyzed for SO_4^{2-} by Capillary Electrophoresis (CIA, Waters) and for ΣH_2S by flow injection analysis using the methylene blue method (spectrophotometer, peristaltic pump, and autosampler from Gilson, valve from Thar Design Inc., reagent Merck Spectroquant, EM Science). DOC was determined by a high temperature combustion TOC analyzer (Shimazu). POC was analyzed using an elemental analyzer (Carlo-Erba). Fe^{2+} was analyzed colorimetrically using the ferrozine method (Stookey, 1970), Fe_t and Fe_d were measured by ICP (Thermo Jarrell), Mn_d by Z-GFAAS (Varian SpectrAA-800), and Pb_t and Pb_d by Z-GFAAS and ICP-MS (VG Plasmaquad 2+, Department of Civil Engineering and Geological Sciences, University of Notre Dame). The analytical speciation of iron was performed using the techniques presented in Table 1.

Micro-particles were observed using HRTEM (Hitachi, HF-2000 FEG, Centre Interdépartemental de Microscopie Electronique, EPFL, Lausanne, Switzerland) and their elemental composition was determined by EDS (detector Ge with a Norvar window). The sampling and analytical procedures have been described elsewhere (Perret et al.,

Table 1. Analytical speciation of Fe in the water column.

Fraction	Description	Sampling	Analysis	Concentration
Fe_{tot}	Total Fe	Raw sampled	ICP, colorimetry[1]	not shown
Fe_d	Total dissolved Fe	Filtered sample	ICP, colorimetry[1]	Fig. 2d
Fe_p	Particulate Fe	Fe_{tot}-Fe_d	Calculated	Fig. 2d
		In-line filtration	ICP	not shown
Fe^{2+}_{tot}	Total Fe^{2+}	Raw sample	Colorimetry[2]	not shown
Fe^{2+}	Dissolved Fe^{2+}	Filtered sample	Colorimetry[2]	Fig. 2d
Fe^{3+}_c	Colloidal Fe^{3+}	Fe_d-Fe^{2+}	Calculated	Fig. 2d
Fe^{2+}_p	Particulate Fe^{2+}	Fe^{2+}_{tot}-Fe^{2+}	Calculated	$<$ det. limit
Fe^{3+}_p	Particulate Fe^{3+}	Fe_p-Fe^{2+}_p	Calculated	Same as Fe_p

[1] With Ferrozine and Hydroxylamine Hydrochloride Reagent (reduction of Fe^{3+} to Fe^{2+}).
[2] With Ferrozine Only (direct measurement of Fe^{2+}). Colloidal ferric iron is ideally assumed to pass through 0.45 μm filters and contained in the filtrate.

1991; Lienemann, et al., 1997, 1998, 1999). Generally, 30 samples per depth in the water column at each sampling date were visualized and analyzed by EDS. Fibrils of polysaccharides were detected using the silver proteinate stain technique (Thiéry, 1967), a three-step reaction which binds nanometer, electron-dense, silver grains to the vic-glycol groups of neutral or acid polysaccharides. The reaction conditions were optimized with synthetic polysaccharides (i.e., alginic acid and xanthan) to stain specifically the material deposited by a whole mount procedure (Lienemann, 1997, Lienemann et al., 1998).

Differential pulse anodic stripping voltammetry (DPASV) measurements were performed with a hanging mercury drop electrode (Metrohm; reference electrode $Ag/AgCl/KCl_{sat}$ with $NaNO_3$ 0.1 M bridge; auxiliary electrode: glassy carbon rod) coupled to a potentiostat (Analytical Instrument Systems, LCP-200). Voltammograms were digitized and analyzed using Origin™ 4.0 software (Microcal Software Inc.). A constant ionic strength (i.e., I = 0.02) and a pH around 6–6.5 were maintained by adding 0.26 ml of a 0.5 M ammonium acetate (Fluka Chemika, puriss grade), 0.5 M HEPES (4(-2-hydroxyethyl)-1-piperazineethanesulfonic acid, Fisher Biotech, Enzyme grade), and 0.5 M NaOH (Fluka Chemika, puriss grade) solution to each sample (total volume 12.26 ml). Before each analysis, a blank was run to check for contaminations. Samples were collected simultaneously for pH and Pb analysis. Little pH variations occurred after addition of the buffer to samples (remaining within 0.3 pH units of in situ field measurements). No pH variations were found after the addition of Pb or after degassing with N_2. Samples were filtered, transferred to the polarographic cell under a N_2 atmosphere, and immediately analyzed. The DPASV analyses were performed by depositing Pb on Hg at -1.2 V for 8 min while stirring and 10 s without stirring. Scans were run from -1.2 V to $+0.15$ V at a scan rate of 50 mV/s and with a pulse height of 50 mV.

Metal titrations were performed in triplicate by adding known amounts of Pb^{2+} (Hart, 1981; Buffle, 1988). Samples from anoxic waters were sparged with N_2 for 10 to 90 min to remove ΣH_2S. Using these metal titration curves, ligand concentrations and equilibrium constants were estimated (Scatchard, 1949; Ruzic, 1982).

In addition, a tentacular resin bearing positively charged dimethylaminoethyl (DMAE) groups (EM Science) was used to separate anionic organic species from the filtered samples. This resin consists of an insoluble copolymerized matrix to which are grafted tentacles of acrylamide derivatives bearing an average of thirty DMAE groups each. This resin is originally employed for separating proteins. Therefore, its trapping efficiency was tested with sodium alginate as a model ligand (Taillefert, 1997; Taillefert and Gaillard, 1999). The separation method was shown to verify accurately the predicted speciation. The DMAE resin might also retain anionic inorganic species. However, the concentration of the anionic chloro and, at the pH of the water column, the anionic hydroxo and sulfo complexes of Pb are not significant. Samples were eluted through the resin with a peristaltic pump (Gilson) and Teflon™ tubing. The system was kept in a glove box under N_2 atmosphere to prevent sample oxidation. These separations were performed at UNDERC facilities within 30 min after sampling. The resin was pre-cleaned by acidification with 10 ml of 2% trace metal grade (TMG) HNO_3, rinsed with ca. 30 ml Milli-Q water until it reached a pH of 4.5, conditioned with 20 ml NaCl 1M, and rinsed again with Milli-Q water to wash out the excess NaCl. The sample (10 ml) was eluted through the resin, and the inorganic fraction collected at the output was stored in 2% TMG HNO_3. The organic fraction retained on the resin was then eluted with 5 ml of a 2% TMG HNO_3 solution. Both fractions were analyzed for Pb by Z-GFAAS.

The speciation scheme of Pb is summarized in Figure 1. Five fractions are quantitatively measurable: (1) the total "dissolved" fraction; (2) the electro-active fraction; (3) the "dissolved" organic fraction retained; (4) the "dissolved" inorganic fraction eluted; and (5) the total fraction. Two fractions are qualitatively observed by TEM to characterize the structure, morphology, and type of particles: (6) Ag stain of polysaccharides, and (7) elemental associations at the nanometer scale.

3. RESULTS

3.1. General Features in the Water Column

The water column of Paul Lake was characterized by a pronounced stratification during all sampling periods (October 1993, May 1994, June and July 1995, July and October 1996). Generally, a steep oxycline was found in the water column (i.e., 0.5 to 1 m wide). A marked conductivity gradient was observed at the chemocline, which is a characteristic feature of biogenic meromixis (Hutchinson, 1957). This results in a density gradient that slows down the transport of dissolved species from the monimolimnion to the epilimnion. Consequently, chemical species accumulate in the bottom waters, further enhancing the density gradient. Sediment porewater analysis (Taillefert et al., 1997) showed that dissolved species accumulate at the SWI and that the deep sediment is not the source of dissolved material. It was concluded that the main input of dissolved material to the monimolimnion results from the biogeochemical degradation of particulate material either at the SWI or in the water column.

Profiles of temperature, $O_{2(aq)}$, SO_4^{2-}, ΣH_2S, DOC, POC, Fe^{2+}, Fe_d, Fe^{3+}_c, and Fe_p in July 1996 are displayed in Fig. 2. A large thermocline is found between 2 and 8 m, where the temperature decreases from 22 to 5°C (Fig. 2a). Ventilation and mixing regulate the concentration of oxygen in the surface waters, but in the upper thermocline, photosynthetic activity produces an excess of oxygen (i.e., 250 μM), and below 2.5 m, oxygen is consumed during respiration by bacterial communi-

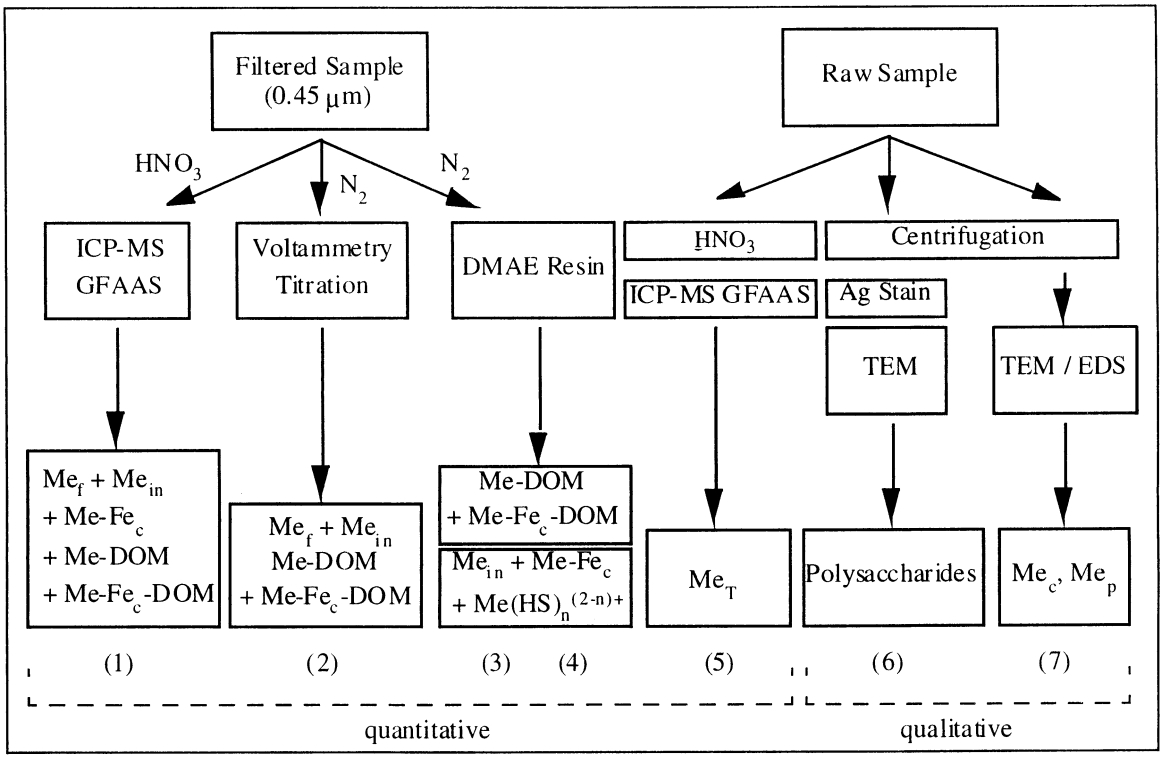

Fig. 1. Schematic diagram of the analytical procedure to determine the speciation of Pb in the water column of Paul Lake.

ties (Fig. 2a). At 6.5 m, the concentration of oxygen falls below the detection limit. The concentration of sulfides increases 50 cm below the oxic-anoxic transition (Fig. 2b) and remains constant (~17 μM) in the deep monimolimnion, suggesting that sulfide precipitation does not occur in significant amounts, or that it occurs episodically and settle rapidly to the SWI. In fact, no black deposits were observed on filters, even after the in-line filtration of about 400 ml of lake water. In addition, colloidal particles of FeS were never observed by electron microscopy. Dissolved organic matter, measured as DOC, is constant around 0.3 mM in the mixolimnion and in the chemocline (Fig. 2c). Below 7.25 m, DOC increases to reach 0.5 mM in the deep waters. Particulate organic matter, measured as POC, forms a peak below the oxic-anoxic transition (Fig. 2c) coincident with the particulate iron (Fe_p) and colloidal ferric iron (Fe_c^{3+}) maxima (Fig. 2d). This striking feature may be indicative of an interaction between colloidal iron, particulate iron, and organic matter. The concentration of Fe_c^{3+} is approximately three times higher than Fe_p at 7 m (i.e., 60 vs. 20 μM). Deeper in the monimolimnion, "dissolved" iron (Fe_d) consists essentially of ferrous iron (Fe^{2+}), which reaches a maximum concentration of ca. 120 μM.

3.2. Total Dissolved and Particulate Pb

Annual profiles of dissolved Pb (Pb_d) from 1994 to 1996 and one profile of particulate Pb (Pb_p) observed in July 1995 are displayed in Figure 3. The Pb_d profiles follow some of the typical distribution patterns observed in stratified lakes (Balistrieri et al., 1994; Viollier, 1995). In Paul Lake, the concentration of Pb increases at the oxic-anoxic transition from 200 pM to 1.8–2.0 nM depending on the season, but does not decrease in the monimolimnion. In July 1995, a summer with high primary productivity, dissolved Pb reached 3.7 nM in the bottom waters.

3.3. Fe_p–POM Association

TEM micrographs of samples collected between 6.5 and 7.5 m systematically display particles consisting of inter-connected organic fibrils that have been rendered electron dense by metal coating (Fig. 4a and b). TEM-EDS measurements (Fig. 4c) show that these entities are mainly composed of iron (6.5–7 keV) with minor contributions of P (2 keV) and Ca (3.7 keV) compared to measurements made on similar systems (Buffle et al., 1989; Fortin et al., 1993; Lienemann et al., 1999). On some occasions, a Pb signal is present on the EDS spectra (10–13 keV) of Fe-NOM moieties (Fig. 4c), establishing that Fe and Pb are associated. This NOM is primarily comprised of polysaccharides, as revealed by the presence of Ag-labeled species (Fig. 5a and b) when using the silver stain technique (Thiéry, 1967; Lienemann et al., 1998). This NOM was evidenced around bacteria (Fig. 5b) suggesting that these microorganisms play a significant role in the production of polysaccharides in the water column. Therefore, we conclude that exocellular polymeric substances (EPS) scavenge hydrous iron oxides formed at the oxic-anoxic transition. In contrast, we observed crystalline forms of iron oxides (i.e., particles of magnetite)

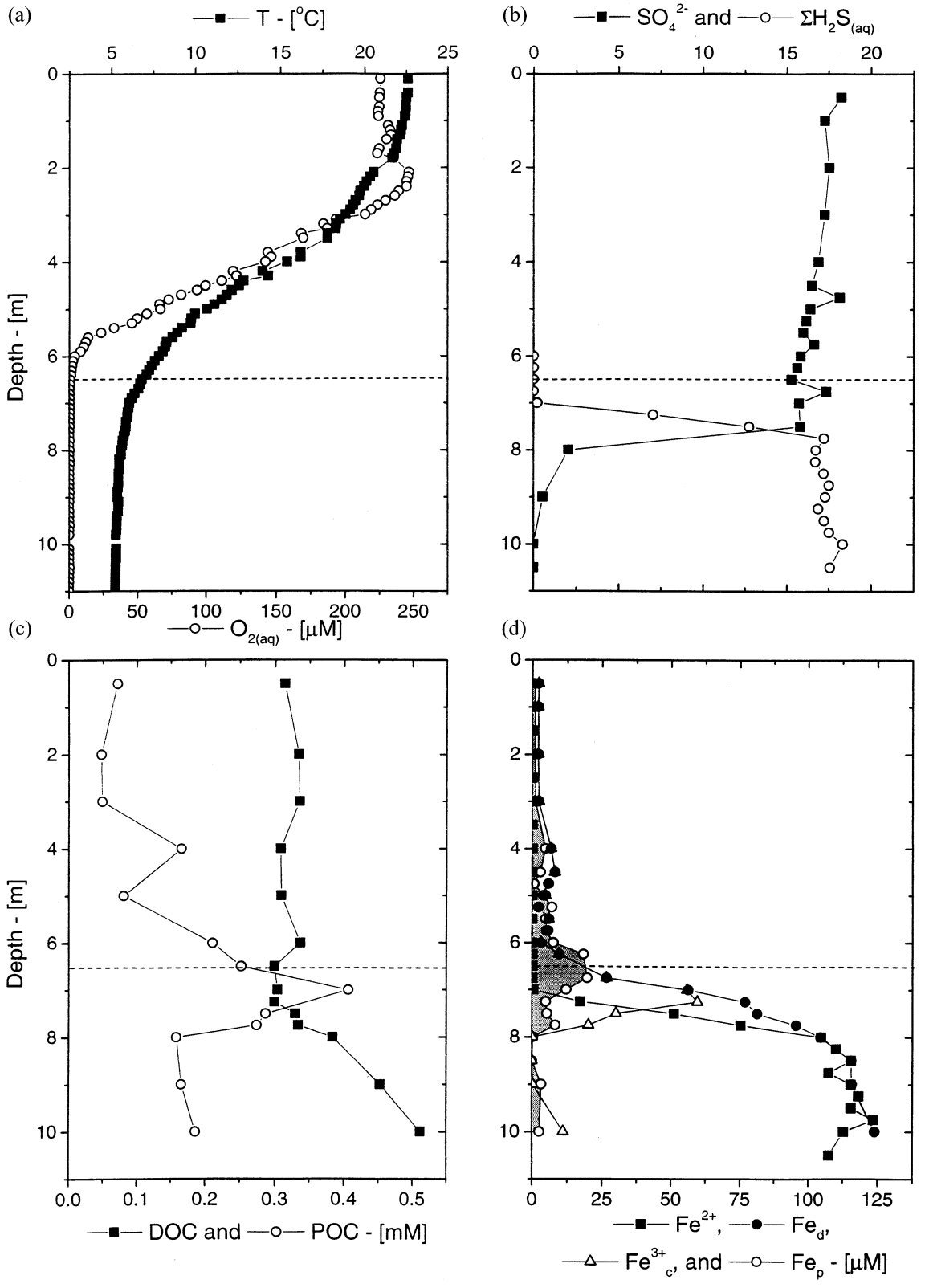

Fig. 2. Profiles of (a) temperature, $O_{2(aq)}$; (b) SO_4^{2-}, $\Sigma H_2S_{(aq)}$; (c) DOC and POC; and (d) Fe^{2+}, Fe_d, Fe_c^{3+}, and Fe_p (shaded area) in the water column of Paul Lake (July 1996).

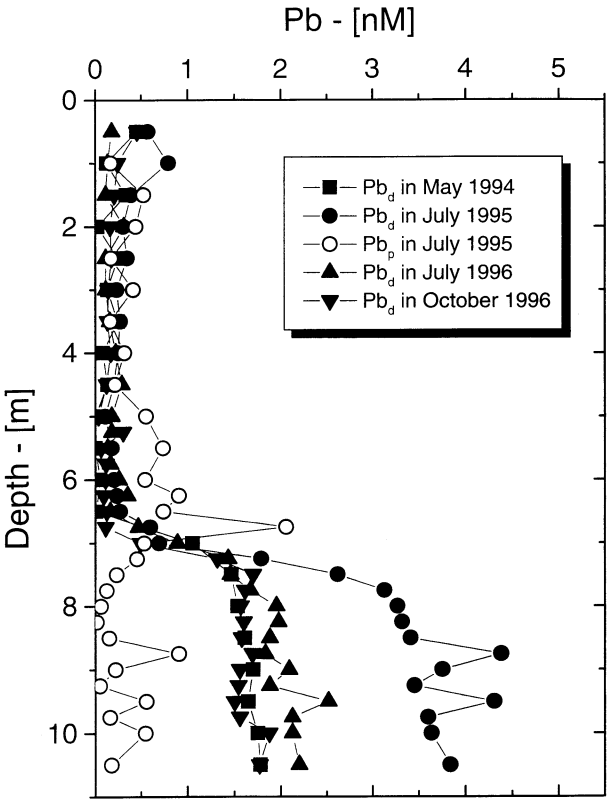

Fig. 3. Annual variations of Pb_d in the water column (data of May 1994, July 1995, July 1996, and October 1996) and profile of Pb_p in July 1995.

formed inside some bacteria that were not supported by any organic matter template and did not contain any noticeable amount of Pb.

3.4. Fe-Pb Interactions

The time evolution of the concentrations of Fe^{2+} and sorbed Pb in batch reactors exposed to the atmosphere is presented with time in Fig. 6a. Fe^{2+} is oxidized with a half-life of ca. 1.8 h. Its concentration is below detection limit within 8 to 9 h. During the first four hours of the experiment, Pb is not removed significantly from the solution. After this original phase lag, the sorption of Pb is rapid and occurs simultaneously with the formation of iron precipitates. It reaches a steady-state after all Fe^{2+} has precipitated.

Samples were collected at the end of the experiment for TEM characterization of the nature of the hydrous iron oxides formed (Fig. 6b). Long sheaths of hydrous iron oxides associated with fibrils of NOM were observed. These aggregates resemble closely the entities found in the water column, suggesting that our oxidation experiments simulate extremely well the conditions leading to the precipitation of Fe_p at the oxic-anoxic transition.

3.5. Analytical Speciation of Pb in the Dissolved Phase

In the water column, the concentration of electro-labile Pb is too low to be detected by voltammetry. Voltammograms of the monimolimnion samples display consistently a peak at a potential of -0.58 ± 0.02 V (average of all depths), which can be attributed to an electro-active sulfide species (Davison et al., 1988). This species does not influence the ligand titration (i.e., does not complex Pb or forms a labile complex), as the signal measured at -0.58 V in the anoxic samples does not decrease on addition of Pb. However, since this peak overlapped the peak of labile Pb at low concentrations of titrant, signals were deconvoluted using a multiple Gaussian fitting technique (Fig. 7a, insert). First, the baseline was subtracted from the data to suppress the offset. The number of peaks and estimates of the half-wave potentials were then used to optimize the total area under the curve, the half-wave potential ($E_{1/2}$), and the width of the peak at half-height ($\Delta E_{1/2}$) with a least squares method.

Typical titration curves obtained with samples collected at 6 m and 10 m are presented in Figure 7a. No significant complexation is evidenced in the chemocline and above 7.25 m in the monimolimnion. In contrast, high conditional stability constants ($\log K_{cond} = 9.4 \pm 0.8$ M^{-1} at pH $= 6.3 \pm 0.2$ and assuming Pb:L $=$ 1:1) are measured below the oxic-anoxic transition (Fig. 7b). The concentration of the active sites (L_T) fluctuates between 5 and 14 nM (mean: $L_T = 9.2 \pm 4$ nM) in the monimolimnion.

Results of the separation of bottom water samples with the DMAE anionic exchanger show that Pb is mostly retained by the resin (98–100%, Fig. 8) below the oxic-anoxic transition. The non-retained fraction remains insignificant (i.e., <0.1 nM) all along the monimolimnion. Our recovery (i.e., 75–99%) is within the analytical error at such low concentrations (i.e., <2 nM).

4. DISCUSSION

In the next sections, the effects of the interaction between Fe_p and particulate organic matter (POM) on the distribution of Pb in the water column are discussed. Then the complexation of Pb in the "dissolved" fraction is examined by combining the results obtained by voltammetry and ion exchange chromatography with equilibrium calculations.

4.1. Formation of the Fe-EPS Entity

Two important conclusions can be drawn from the direct observation of natural particles by TEM: (i) iron oxides do not only act as a nucleus center for the aggregation of NOM, but can also be attached onto fibrillar organic material. (ii) Their interaction is systematic and was observed consistently at every sampling date. These observations contrast with conceptual views derived from laboratory studies, which showed that organic matter is adsorbed at the surface of hydrous iron oxides (Stumm et al., 1980; Tipping, 1981; Davis, 1984; Zhou et al., 1994; Gu et al., 1995). However, in these laboratory experiments, organic material was added to already existing mineral phases. Alternatively at oxic-anoxic interfaces, the oxidation of ferrous iron is usually limited by oxygen concentration, and it is possible that organic matter catalyzes the precipitation of ferric iron. Such mechanisms have already been proposed by several authors (Degens and Ittekot, 1982; Manns, 1988; Cowen and Silver, 1984; Fortin et al., 1993).

The half-life of Fe^{2+} in the batch reactors (Fig. 6) was

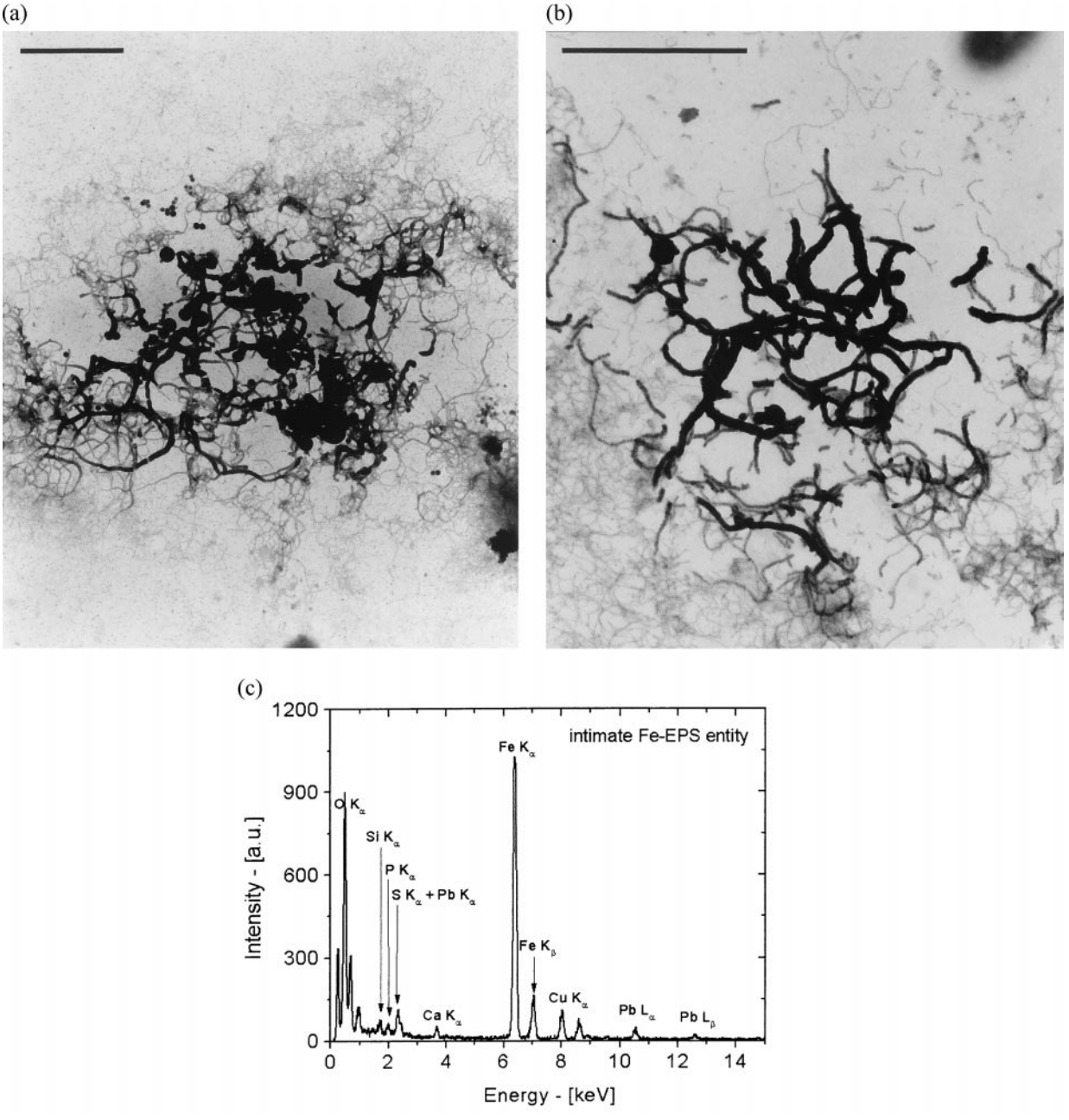

Fig. 4. (a) Natural hydrous iron oxide aggregates found between 6.5 and 7.5 m in the water column (Scale bar = 1 μm). The micrographs display intimate mixtures of organic fibrils naturally stained by iron oxides. (b) The EDS spectrum of these mixtures displays some Fe-Pb elemental association. The Cu peak originates from the TEM supporting grid.

compared to that estimated from the equation of Millero et al. (1987) in a sample from the same depth, assuming a constant pH of 6.5 and an oxygen concentration of 250 μM at 25°C. The experimental half-life is about 47 times shorter than the calculated value, even if the concentration of oxygen is maintained at saturation in the calculation. Although Fe^{2+} could be removed from the solution by adsorption onto particulate material (De Vitre et al., 1988; Buffle et al., 1989), we were unable to measure significant levels of particulate Fe^{2+} in the water column (Table 1). In addition, the autocatalytic oxidation of Fe^{2+} at the surface of iron oxides should not occur at such low pH in the water column (Sung and Morgan, 1980). This suggests that the reaction is catalyzed by another substance in these natural waters. Such observations have already been made in laboratory experiments at low oxygen content and in the presence of NOM (Liang et al., 1993). Hence, it seems reasonable to propose that exocellular polymeric substances (EPS) could act as nucleation centers during the oxidation reaction, because they are systematically found intimately linked with iron particles both in the natural setting (Fig. 4a and b) and in the batch reactors (Fig. 6b). This effect is probably even more pronounced as the ionic strength is low ($I < 10^{-4}$) in the water

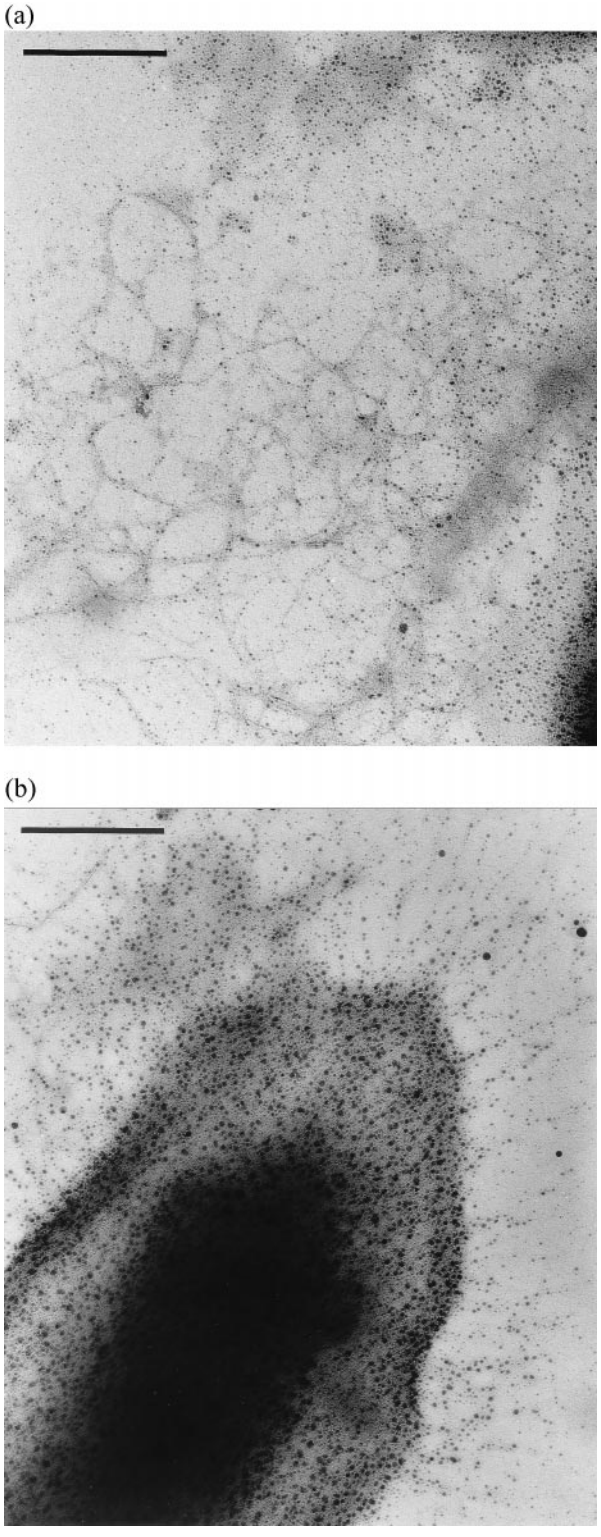

Fig. 5. (a) Silver stain techniques of Thiéry (1967) on organic fibrils found at 7 m in the water column (Scale bar = 200 nm). These fibrils consist of polysaccharides that may be naturally stained by hydrous iron oxides (see Fig. 4a and b). (b) The same fibrils are found exuding from a bacteria at 6.25 m, indicating that polysaccharides are exocellular polymeric substances (EPS). (Data from July 1995.)

column. In such conditions, the electrical screening of the sites of same charge on the fibrils, usually provided by counterions at high ionic strength, does not exist (Buffle, 1988). Electrostatic interactions between sites of same charge favor repulsion, thus extending these fibrils in the water column and increasing their interaction with iron.

4.2. Pb Removal During Fe^{2+} Oxidation

As shown by the batch reactor experiments (Fig. 6), Pb can be removed below the chemocline during the formation of the Fe-EPS entity. This suggests that the removal rate of Pb follows the kinetics of transformation of iron species according to an entrainment process rather than the adsorption mechanism usually envisioned (e.g., Sigg et al., 1987; Stumm, 1992). This has already been observed in natural systems (Laxen and Sholkovitz, 1981; Laxen, 1984, 1985). This further suggests that the recycling of trace metals at the oxic-anoxic transition in this natural system cannot be addressed using surface adsorption models (Taillefert et al., 1997). The good correlation between dissolved Pb and ferrous iron in the water column over all the seasons (Pb:Fe = 1.5 $\pm$ 0.12 10^{-5}) supports the results obtained with batch reactors. The metal could be scavenged by Fe-EPS at the oxic-anoxic transition, then released in the monimolimnion or at the SWI upon reductive dissolution of ferric iron.

4.3. Pb Complexation and the Nature of the Ligand

Two independent analytical methods (i.e., voltammetry and ion exchange chromatography) indicate that dissolved Pb is complexed in the monimolimnion. Several ligands could potentially complex the metal in the monimolimnion. Colloidal hydrous iron oxides are probably not responsible for the complexation of Pb as their concentrations remain low below 7.5 m (Fig. 2d), in the zone containing the unknown ligand determined by voltammetry (Fig. 7b). Carbonates form electrochemically labile complexes (Buffle, 1988), and hydrogen sulfide and bisulfide cannot be involved in the complexation of Pb as measured by voltammetry because they were degassed prior to the metal titrations.

Polysulfides (i.e., S_4^{2-} and S_5^{2-}) are strong ligands for trace metals in anoxic natural waters (Boulégue, 1978), but we believe they are not important in complexing Pb in the water column of Paul Lake. Although these ligands are not volatile and could complex Pb, to date, no complexation constant for lead with polysulfide has been reported. However, it has been shown (Chadwell et al., 1998) that Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} react with S_4^{2-} and S_5^{2-} to form a monodentate MS_x (where x = 4 or 5), and a bimetal-complex $M_2S_x^{2+}$ where the ligand bridges two metal ions. These complexes are electrochemically labile. Conversely, Cu^{2+} and Zn^{2+} form electrochemically non-labile complexes: $[Cu(S_x)]_2$, and the monodentate ZnS_x. Interestingly, at pH below the pK_{a2} of the polysulfides ($<$6.6 for S_4^{2-} and $<$6 for S_5^{2-}) these metal complexes tend to decompose (Chadwell et al., 1998). Thus, it is rather unlikely that such complexes are present in significant amounts in the water column of Paul Lake (pH ranging between 5.8–6.3). In addition, Chadwell et al. (1998) show that the stability constants of the polysulfide complexes are not

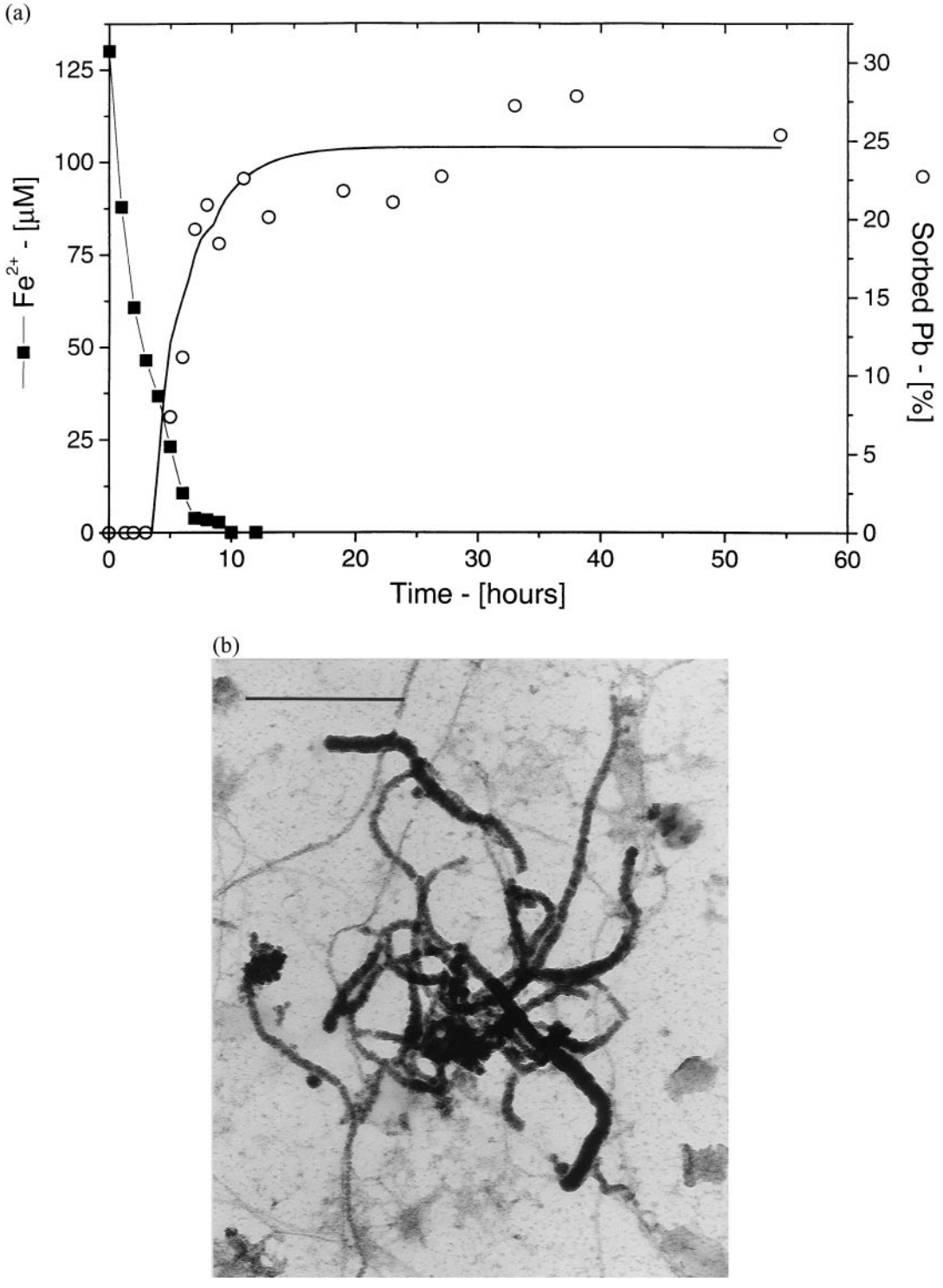

Fig. 6. (a) Fe^{2+} change and scavenged fraction of Pb with time in a filtered sample from 10 m open to the atmosphere and kept in the dark at 25°C. (b) Natural hydrous iron oxide aggregates formed during the experiment. The scale bar is 500 nm.

much larger than those of the corresponding bisulfide complexes. Since the stability constant for the lead bisulfide complex $Pb(HS)_2$ ranges between $\log B_2 = 12.5 - 13.5$ (Dyrssen, 1985; Zhang and Millero, 1994), the constants for lead polysulfide complexes should be much higher than those measured in this study.

Using molecular orbital theory (MOT), Chadwell et al. (1998) suggest that Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+} form mono-

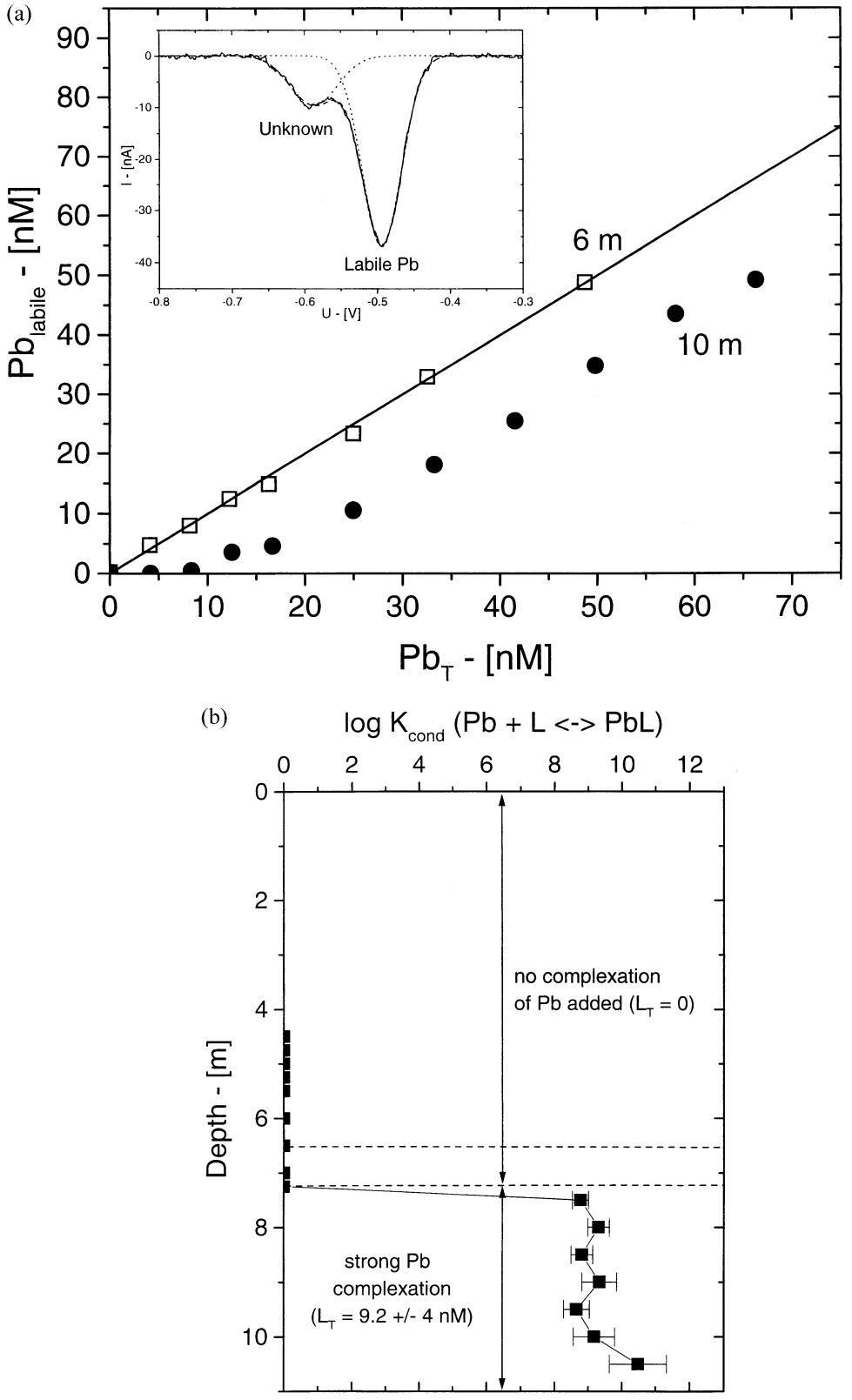

Fig. 7. (a) Labile Pb as a function of total added Pb during the titration of a sample at 6 m (mixolimnion) and 10 m (monimolimnion) in the water column. The insert displays the voltammogram of an anoxic water sample (8.5 m) spiked with 16 nM of Pb (U = −0.49 V) in presence of an unknown electro-active species (U = −0.59 V). The dash line is the fitted deconvolution of the two electroactive species (July 1996). (b) Profile of L_T and K_f in the monimolimnion (July 1996). Notice that a log K_f of zero is just indicative of the absence of any ligand for Pb at these depths.

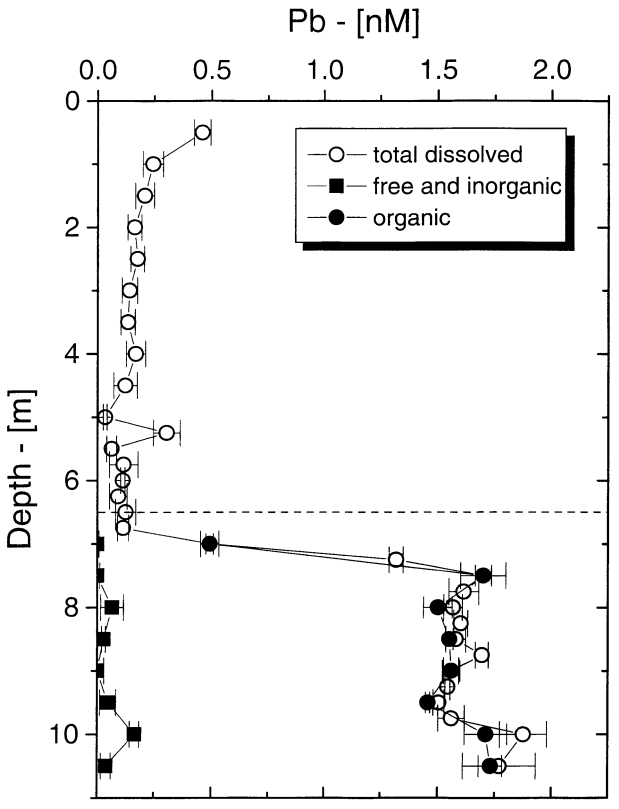

Fig. 8. DMAE speciation measurements in the monimolimnion as compared to total dissolved Pb at the same period. The dashed line represents the zero of dissolved oxygen in the water column (October 1996).

dentate octahedral complexes with S_4^{2-} and S_5^{2-}, while Cu^{2+} and Zn^{2+} prefer the more stable tetrahedral geometry. The coordination chemistry of the post-transition metals is still poorly understood because of the intricate combination of shielding and contraction of the valence orbitals, and because of the inert pair effects of the group IIIA and IVA (Cotton and Wilkinson, 1988). Thus, the following discussion is only conceptual. The electronic configuration of the valence shell of Pb^{2+} is $5d^{10}$ $6s^2$ $6p^0$ which, except being from a different series, is similar to the $3d^{10}$ $4s^0$ $4p^0$ valence shell of Zn^{2+}. If Pb^{2+} forms a bond with S_4^{2-} or S_5^{2-}, the two electrons of the $6s^2$ orbital should be added to the next antibonding orbitals, decreasing the number of bonds to three in the molecule. Thus, Pb^{2+} and S_4^{2-} or S_5^{2-} should form a trigonal monodentate complex with two water molecules and one polysulfide, $Pb(H_2O)_2S_n$ (with $n = 4$ or 5). This complex, if existing, should not be very stable, and can be expected to be electrochemically labile. Finally, Chadwell et al. (1998) show that the formation of negative complexes with several linear polysulfides binding the metal is unlikely in natural conditions. Therefore, we can conclude that the negatively charged complex retained on the DMAE ion exchanger is not likely to be a lead polysulfide complex.

The change in the complexation of Pb follows the change in the concentration of DOC below the oxic-anoxic transition (Fig. 2c). Hence we propose that Pb forms an electrochemically non-labile complex with a natural organic ligand in the monimolimnion.

4.4. Precipitation of PbS in the Deep Monimolimnion

The presence of a strong ligand in the monimolimnion has implications for the solubility of PbS. The chemical speciation of Fe and Pb with inorganic sulfides was computed using MINTEQA2 (Allison et al., 1989) by assuming that mineral solids do not precipitate. Profiles of pH, Cl^-, ΣH_2S, ΣCO_2, and of total "dissolved" lead (Pb_d) were used as input concentrations. The thermodynamic database was updated with more recent parameters obtained from the literature (Dyrssen, 1985; Balistrieri et al., 1992b; Luther and Fedelman, 1993).

The ionic activity product (IAP) and the saturation coefficient were calculated for amorphous iron sulfide (FeS) and galena (PbS). The equilibria considered for the metal sulfide species are presented in Table 2. The results, presented in Table 3, indicate that Fe^{2+} is mainly free (98–100%). In contrast, dissolved lead should prevail as aqueous PbS^0 (55–87%) and the bisulfide species (8–40%). Saturation coefficients for the precipitation of FeS and PbS in the monimolimnion indicate that these minerals are, respectively, saturated and oversaturated. Thus, FeS and PbS should be present in the bottom waters. However, sulfide rich particles were never observed during filtration of the bulk waters or by TEM. In addition, ion exchange chromatography results showed that "dissolved" inorganic Pb is minimum in this lake, suggesting that FeS does not play a significant role in the cycling of Pb and that colloidal PbS does not form. However, voltammetric results suggest that Pb remains dissolved in the monimolimnion because it is complexed. If so, the kinetics of the complexation reaction involving the ligand and the metal must be fast to compete with sulfides, because sulfide precipitation is a relatively rapid reaction (Pyzik and Sommer, 1981; Rickard and Luther, 1997).

Using the conditional stability constant of the PbL complex and the average number of sites (L_T) obtained by voltammetry, the chemical speciation of "dissolved" lead in the samples analyzed by voltammetry can be recalculated using MINTEQA2. These calculations were performed with and without hydrogen sulfide and bisulfide since volatile sulfide species were removed during degassing prior to the voltammetric analyses.

Table 2. Complexation and precipitation reactions used for the speciation of sulfides with Fe and Pb in the water column of Paul Lake in July 1996 and their respective equilibrium constants.

Reaction	Constant	Fe	Pb
$MeS_{(s)} + 2H^+ \leftrightarrow Me^{2+} + H_2S_{(aq)}$	$\log K_{SO}$	2.8[1]	−7.83*
$Me^{2+} + H_2S_{(aq)} \leftrightarrow MeS^0 + 2H^+$	$\log K_1$	—	−3.38[2]
$Me^{2+} + H_2S_{(aq)} \leftrightarrow Me(HS)^+ + H^+$	$\log K_2$	−1.48[3]	−1.65[2]
$Me^{2+} + 2H_2S_{(aq)} \leftrightarrow Me(HS)_2 + 2H^+$	$\log K_3$	−4.63[1]	−1.06[1]
$Me^{2+} + 3H_2S_{(aq)} \leftrightarrow Me(HS)_3^- + 3H^+$	$\log K_4$	−9.95[4]	−6.19[2]
$Me^{2+} + 4H_2S_{(aq)} \leftrightarrow Me(HS)_4^{2-} + 4H^+$	$\log K_5$	—	−11.62[2]
$Me^{2+} + 2H_2S_{(aq)} \leftrightarrow MeHS_2^- + 3H^+$	$\log K_6$	−10.91[1]	−7.33[1]

* At 25°C ($\log K_{SO} = -8.58 + 0.02947T + 3.57810^{-5}\,T^2 - 2.4710^{-7}\,T^3 + 2.80710^{-10}\,T^4$)

[1] Dyrssen, 1985.
[2] Balistrieri et al., 1992b.
[3] Luther and Fedelman, 1993.
[4] Allison et al., 1989.

Table 3. Computed Fe and Pb sulfide speciation with MINTEQA2 in July 1995.

Depth	Metal fraction - [%]							log(Ω)	
	Fe^{2+}	$FeHS_2^-$	$Fe(HS)_2$	Pb^{2+}	PbS^0	$PbHS_2^-$	$Pb(HS)_2$	FeS_{ppt}	PbS
7.75	100	0	0	0.1	87.4	0.0	8.1	−0.99	3.9
8	99.5	0.3	0.2	0	71.3	0.1	30.4	0.11	3.9
8.25	99.2	0.5	0.3	0	68.0	0.1	32.2	0.35	3.9
8.5	99.2	0.6	0.2	0	66.4	0.1	29.0	0.43	3.9
8.75	99	0.7	0.3	0	54.8	0.1	24.3	0.5	3.9
9	98.9	0.8	0.3	0	63.9	0.1	30.0	0.53	3.9
9.25	98.8	0.9	0.3	0	67.9	0.2	33.4	0.53	3.9
9.5	98.7	0.9	0.4	0	56.9	0.1	29.9	0.54	3.9
9.75	98.7	0.9	0.4	0	68.1	0.2	36.2	0.55	3.9
10	98.7	0.9	0.4	0	64.5	0.2	40.4	0.54	4
10.5	98.9	0.8	0.3	0	62.0	0.1	33.2	0.5	3.9

The saturation index log(Ω) is defined as:

$$log(\Omega) = Log\left(\frac{IAP}{K}\right)$$

FeS^0 is below detection limit.

Results predict that, in the decreasing order, Pb^{2+}, $Pb(CO_3)_{2(aq)}$, $PbHCO_3^+$ and $PbOH^+$ are the predominant species in samples collected from the chemocline. In samples from the monimolimnion and without considering sulfides in the calculation, Pb^{2+} decreases abruptly to no more than 100 pM (~5% of total dissolved Pb), whereas PbL and $Pb(CO_3)_{2(aq)}$ are the main complexes formed (Fig. 9). In these conditions, the organic complex fraction (~90%) prevails over the inorganic species. Considering sulfides present in the monimolimnion, Pb^{2+} decreases to less than 20 pM (~1% of total dissolved Pb), and $Pb(HS)_2$ (~76%) prevails over PbL (~20%). The concentration of the PbL complex calculated above without considering sulfides agrees well within analytical errors with the concentration of Pb species retained by the DMAE anionic exchanger. However, in the presence of sulfides, PbL calculated does not corroborate data from the anionic exchanger. $Pb(HS)_2$ is a neutral species, which should not be retained on the anionic exchanger, and this complex is probably not part of the PbL fraction retained by the resin. The disagreement between the predicted speciation in the presence of sulfides and that measured with the resin can be explained if the PbL complex formed is inert. However, this anomaly has to be considered cautiously because thermodynamic constants for lead sulfide complexes are poorly characterized and since the constant measured by voltammetry is conditional (i.e., measured in the absence of hydrogen sulfide and bisulfide). Therefore, we think that the same complex is determined by these two independent analytical methods. Since metal-inorganic sulfide complexes, which could exist in reasonable concentration in the monimolimnion, are known to be neutral or positively charged (Dyrssen and Kremling, 1990; Balistrieri et al., 1992b; Luther et al., 1996), it can be concluded that the metal complex retained by the resin is an metal-organic species.

5. SUMMARY AND IMPLICATIONS

The chemical speciation and the reactivity of Fe and Pb were assessed in a natural aquatic system (Paul Lake, MI) using a combination of analytical techniques. This study is one of a few on the speciation of Pb in anoxic freshwater systems (Davison et al., 1992; Balistrieri et al., 1994; Benoit, 1995; Jackson and Bistricki, 1995), and, to our knowledge, is the first one that combines a variety of analytical techniques to measure the speciation of Pb in freshwaters. In previous studies, it has been shown that colloidal iron oxides plays a significant role in the transfer of Pb to the particulate phase (Benoit, 1995), and that sulfides compete with hydrous iron and manganese oxides particles (Balistrieri et al., 1994) or algae (Jackson and

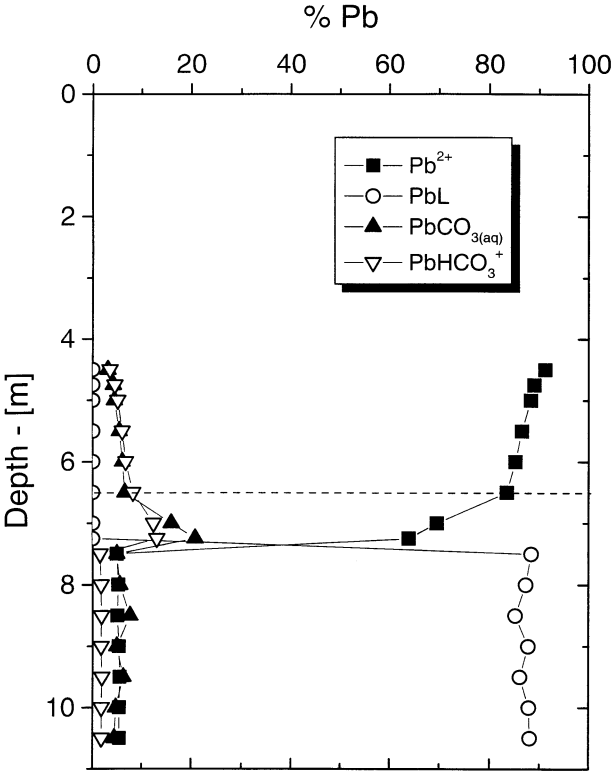

Fig. 9. Speciation calculation of Pb in the monimolimnion using MINTEQA2. The dashed line represents the zero of dissolved oxygen in the water column (July 1996).

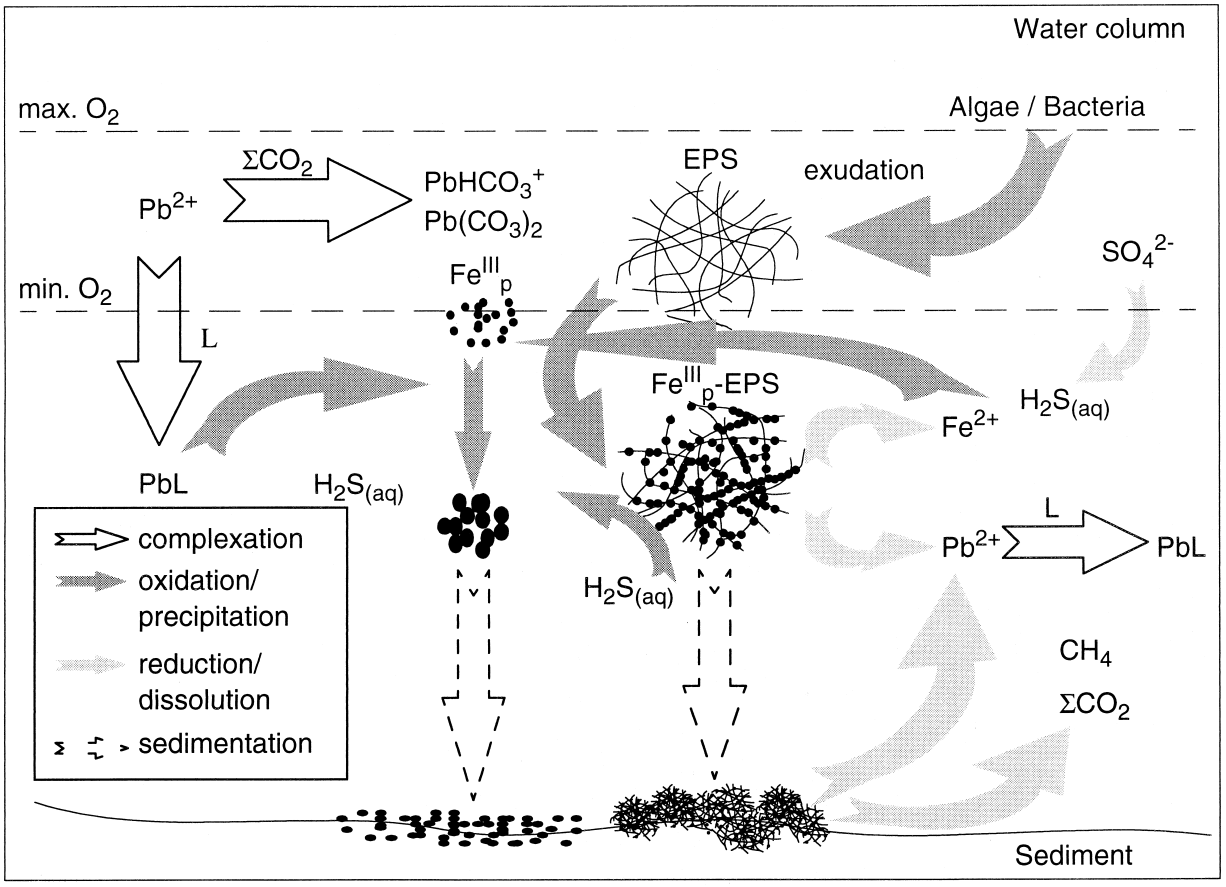

Fig. 10. Schematic diagram of the Pb cycling in Paul Lake (MI) as proposed in this study.

Bistricki, 1995) to scavenge Pb (Balistrieri et al., 1994). It has also been shown that Pb can be removed in sulfidic environments by surface adsorption onto FeS (Davison et al., 1992).

In this article, we have shown that hydrous iron oxides form complex aggregates with exocellular polymeric substances (EPS) below the oxic-anoxic transition, and that these moieties can contain significant amounts of lead. Simple experiments mimicking the physico-chemical conditions prevailing in the natural system indicate that Pb is entrained during the formation of Fe-EPS. Although it is not clear if the metal is complexed to the EPS or directly to the iron oxide, this result in itself confirms that surface adsorption models do not describe accurately processes occurring at oxic-anoxic interfaces. In contrast to the lake studied by Balistrieri et al. (1994), one of the striking feature of the water column of Paul Lake, is that sulfides present in bottom waters have no significant influence on the fate of Fe^{2+} and Pb, though saturation and oversaturation are predicted for FeS and PbS, respectively. In fact, voltammetry and ion exchange chromatography results suggest that "dissolved" Pb is completely attached to an organic ligand with a conditional stability constants of $\log K_{cond} = 9.4 \pm 0.8$ M^{-1}. This ligand seems to prevent precipitation of PbS. These speciation results have a direct implication on the cycling of Fe and Pb summarized in the schematic diagram of Fig. 10. Pb is scavenged below the oxic-anoxic transition by entrainement during the formation of the Fe-EPS moieties. These particles sink and are redissolved in the deep waters or at the SWI, releasing Fe(II) and Pb in the monimolimnion. Pb is then complexed by the organic ligand, which seems to compete directly with sulfides for metal complexation and precipitation.

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