
***In situ* adsorption of mercury, methylmercury and other elements by iron oxyhydroxides and organic matter in lake sediments**

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Abstract:

Samples of authigenic material, sediment overlying water and oxic surface sediment (0–0.5-cm depth) from a perennially oxygenated lacustrine basin were analysed to investigate which solid phases are important for binding a suite of trace elements (Ag, As, Ca, Cd, Cu, Hg, In, methylmercury (MeHg), Mg, Mo, Pb, Sb and Zn). The authigenic material, which was collected with inert Teflon sheets deployed for several years across the sediment–water interface, contained mainly poorly crystallized Fe oxyhydroxides and natural organic matter, presumably humic substances derived from the watershed. Manganese oxyhydroxides were not present in the collected authigenic material due to the slightly acidic condition (pH = 5.6) of the lake that prevents the formation and recycling of these compounds. Conditional equilibrium constants for the adsorption of cationic ($K_{\text{Fe-M}}$) and anionic ($K_{\text{Fe-A}}$) trace elements onto the authigenic Fe oxyhydroxides were estimated from their concentrations in the authigenic material and in bottom water samples. These field-derived values of $K_{\text{Fe-M}}$ and $K_{\text{Fe-A}}$ were compared with those predicted by the surface complexation model, using laboratory-derived intrinsic adsorption constants and the water composition at the study site. Equilibrium constants ($K_{\text{POM-M}}$) were also calculated for the adsorption of the cationic trace elements onto the humic substances contained in the diagenetic material. The field-derived values of $K_{\text{POM-M}}$ were compared to those predicted by the speciation code WHAM 6 for the complexation of the trace elements by dissolved humic substances in the lake. Combining the results of the present study with those on the distributions of trace elements in the porewater and solid-phase sediments reported in previous studies at the same site, it was determined whether the trace elements bind preferentially to Fe oxyhydroxides or natural organic matter in oxic sediments. The main inferences are that the anionic trace elements As, Mo and Sb, as well as the cationic metal Pb are preferentially bound to the authigenic Fe oxyhydroxides whereas the other trace elements, and especially Hg and MeHg, are preferentially bound to the humic substances.

1. Introduction

Bottom sediments comprise detrital organic and inorganic compounds as well as products derived from diagenetic reactions (e.g., Fe and Mn oxides). The diverse components that constitute the complex sediment matrix do not usually exist as separate particles but rather as aggregates (Jenne, 1968; Davis and Kent, 1990). Knowledge of how trace elements partition among these sediment components is desirable to better understand their geochemical mobility and cycling, and to estimate their bioavailability. However, the direct measurement of trace element association with a given sediment component is seldom feasible, due to the low concentrations of the trace elements involved and to the inherent complexity of sediment composition. The fact that some of the most important sedimentary phases for binding the trace elements may themselves be present at low concentrations, i.e., diluted in the sediment matrix, also adds further complication.

In this context, there is reliance on several approaches that can provide indirect information about the association of trace elements to sediment components. Methods involving extraction of sediments with reagents of various strengths have been used to partition trace elements into broad geochemical classes (Tessier et al., 1979; Chao and Zhou, 1983; Bacon and Davidson, 2008; Linge, 2008). Although such procedures can yield useful information about trace element binding to sediment components, it is generally recognized that the results obtained depend on factors such as the choice of reagents and the duration of extraction (Bacon and Davidson, 2008). Other limitations are that the reagents are generally not completely selective towards targeted sedimentary trace element forms and that the extracted trace elements can readsorb onto other sediment components (Bacon and Davidson, 2008). Search for statistical relationships between concentrations of trace elements and those of the sediment components that can bind them is another approach that has been often used to obtain information about trace element binding (Luoma and Bryan, 1981; Sigg et al., 1987; Hammerschmidt and Fitzgerald, 2006). However, statistically significant relationships are not sufficient by themselves to demonstrate the association of a trace element with a sediment component. Following the advent of synchrotrons, a most promising approach to obtain the sought information, is the application to the sediments of X-ray spectroscopy techniques such as Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES); these techniques can yield information such as the oxidation state of the elements, the number and type of their neighbours, the coordination state, and the bond distance between atoms (Murata, 1991; Parsons et al., 2002; Zhao et al., 2006; Singer et al., 2009). Main limitations of these molecular techniques are, however, their lack of sensitivity for most trace elements in environmental samples, the limited access to instruments and, in some cases, the absence of appropriate reference material (Murata, 1991; Zhao et al., 2006).

This study investigates trace element (Ag, As, Cd, Cu, Hg, In, methylmercury (MeHg), Mo, Pb, Sb and Zn) binding in an oxic lacustrine sediment by combining *in situ* techniques and thermodynamic modeling. The oxic layer of sediments is important in the overall cycling of trace elements because it is the locus of several diagenetic reactions that can profoundly influence their behaviour. The importance of adsorption of trace elements onto diagenetic Fe and Mn oxyhydroxides and organic matter has been inferred in several studies (e.g., Davis and Kent, 1990) and its theoretical treatment is emphasized here. The trace elements studied are all known regional or global atmospheric pollutants (e.g. Pacyna and Pacyna, 2001; Krachler and Shotyk, 2004; Laforte et al., 2005; Ranville and Flegal, 2005) and Mo is also a potential tracer of past fluctuations in organic C flux at the sediment–water interface and/or in bottom water O₂ concentration (e.g. Crusius et al., 1996; Adelson et al., 2001). Among these trace elements, special attention is paid to Hg and MeHg for which binding information is urgently required to better understand the Hg cycle at the sediment–water interface. The study was carried out in the perennially oxygenated lacustrine basin of Lake Tantaré (47°04'N, 71°32'W), an acidic and oligotrophic Canadian Shield lake whose watershed is uninhabited. Authigenic material (Belzile et al., 1989), surficial sediment and bottom

water samples were collected at the deepest site (15 m) of the westernmost basin of this lake, and an extensive dataset comprising the authors' own analyses, as well as results obtained in previous studies carried out by the authors' group at the same site (Alfaro-De la Torre and Tessier, 2002; Gallon et al., 2004; Quirion, 2004; Laforte, 2005; Chappaz, 2008; Couture et al., 2008; Bernatchez, 2009), were used to clarify the mode of association of trace elements in oxic lake sediments.

2. Material and methods

Clean techniques were used to avoid sample contamination during field work and subsequent chemical analysis in the laboratory. Hereafter, $[X]$ and $\{X\}$ refer to the concentrations of species X in the aqueous and solid phases, respectively, dissolved inorganic Hg concentration ($[Hg]_i$) is assumed to be the difference between total dissolved Hg ($[Hg]_T$) and dissolved MeHg ($[MeHg]$), and, similarly, sediment inorganic Hg ($\{Hg\}_i$) is assumed to be the difference between total sediment Hg ($\{Hg\}_T$) and sediment MeHg ($\{MeHg\}$).

2.1. Sampling

Twelve acrylic *in situ* dialysis samplers (peepers; 1-cm vertical resolution; two columns of 4-mL cells) similar to those described by Carignan et al. (1985) were used to sample the water within the 5-cm thick layer above the sediment–water interface for the determination of pH, $[Hg]_T$, $[MeHg]$, $[Cu]$, $[Zn]$, $[Al]$, $[Fe]$ and $[Mn]$ as well as for measuring the concentrations of major cations and anions and organic C. The acid-washed peeper cells were filled with ultrapure water ($> 18 \text{ M}\Omega \text{ cm}$) and covered with a pre-cleaned $0.2 \mu\text{m}$ nominal pore size polysulfone membrane (HT-200, Gelman). The peepers were deployed by divers in September 2006 and retrieved 3 weeks later.

Water contained in the cells of 3 peepers positioned at a given height above the sediment–water interface was obtained by piercing the polysulfone membrane with an acid-washed plastic tip fixed on a 5-mL Gilson pipette. The pooled sample (total volume of 24 mL) was put in cleaned Teflon (PFA) bottles and shaken. A 1-mL aliquot was transferred to a preacidified ($10 \mu\text{L}$ of 2 N SeaStar HNO_3) vial for the determination, after dilution, of $[Al]$, $[Ca]$, $[Cu]$, $[Fe]$, $[K]$, $[Mg]$, $[Mn]$, $[Na]$ and $[Zn]$. The remaining 23-mL sample was acidified with $115 \mu\text{L}$ of suprapur (SeaStar) 0.5% (v/v) HCl and kept for the measurements of $[Hg]_T$ and $[MeHg]$; the Teflon bottles were then sealed in double plastic bags. Nine of the peepers were sampled in this manner in order to get triplicate measurements of each metal for each of the 5 depth intervals above the sediment–water interface. The 3 peepers left were used for triplicate measurements of pH, dissolved organic C and major anions according to protocols described by Alfaro-De la Torre and Tessier (2002). Samples of water overlying the sediment had been obtained in previous studies at the same sampling site using similar methodology, and Ag, As, Cd, In, Mo, Pb and Sb were measured in these samples (Alfaro-De la Torre and Tessier, 2002; Gallon et al., 2004; Quirion, 2004; Laforte, 2005; Chappaz, 2008; Couture et al., 2008; Bernatchez, 2009).

Sheets of skived Teflon (7 cm \times 15 cm) that had been inserted by divers across the sediment–water interface at the sampling site in October 1993 were retrieved in August 2006, rinsed with lake water to remove living animals and sediment particles and stored in polyethylene containers. Iron recycling is commonly observed in oxygenated aquatic environments due to the reduction of reactive Fe(III) in the lower sediment strata, upward diffusion of porewater Fe(II), and its oxidation and precipitation as Fe(III) oxyhydroxides in the top sediment layers. The observation at the sampling site of a large excess in $\{Fe\}$ just below the sediment surface and of a sharp $[Fe]$ gradient close to the sediment–water interface indicate intense Fe redox recycling (Fig. 1). In contrast, the absence of excess $\{Mn\}$ and of $[Mn]$ gradients indicates that Mn does not recycle in the sediments of this low pH lake. The authigenic Fe oxyhydroxides that are normally deposited to sediment particles close to the sediment surface can also be collected by other material inserted in

sediments, such as Teflon sheets (Belzile et al., 1989). The diagenetic Fe-rich material collected during the 13-a deployment of the Teflon sheets appeared as a mm thick crust.

A sediment core was collected in June 2006 by a diver using a 9.5 cm internal diameter butyrate tube. The core was extruded and sectioned within 2 h, with only the top 0.5 cm retained for this study. At the sampling site, O₂ penetrates down to about 0.3 cm depth below the sediment–water interface (Couture et al., 2010b) and sulfide concentration is below detection limit in the top 2 - 3 cm of the sediments (Alfaro-De La Torre and Tessier; Chappaz et al., 2008; Gallon et al., 2004). Thus, according to the generally accepted definition, the upper part (about 3 mm) of the top 0.5-cm sediment layer was oxic and the lower part (about 2 mm) was suboxic. However, to simplify, this sediment sample is referred to as being oxic. Authigenic Fe in this sediment sample should be essentially Fe(III) oxyhydroxides since porewater over the 0 - 0.5 cm sediment depth interval is undersaturated with respect to Fe(OH)_{2(s)}, FeCO_{3(s)} and FeS_{m(s)} (mackinawite), whose saturation indices (*SI*), defined as $SI = \log IAP/K_s$, where *IAP* stands for ion activity product, were lower than -5.0, -2.0 and -3.5, respectively. This sediment sample was stored in a polyethylene container and freeze-dried upon return to the laboratory.

2.2. Analyses

The method used to measure [Hg]_T (Cossa et al., 2003) was modified from that of Bloom and Fitzgerald (1988). It is similar to EPA standard method No1631. Briefly, [Hg]_T was determined, using external calibration, by cold vapor atomic fluorescence spectrometry (CVAFS; Tekran model 2500) after successive addition of BrCl to release Hg(II) from its ligands, and SnCl₂ to reduce it to elemental Hg (Hg(0)). Detection limit (DL), defined as 3.3 times the standard deviation of 6 blank analyses (this definition is valid for all the analyses described below), was 0.4 pM for a 10-mL water sample. Precision, determined from 6 replicate measurements of 20 pM Hg samples, was better than 5%, but was reduced to 15% when sample Hg concentration decreased to 1 pM. Analytical accuracy was checked every day with the certified reference material ORMS-3 from the National Research Council of Canada (NRC).

Dissolved MeHg was converted to volatile MeHg hydride, separated by purge and cryo-trapping gas chromatography, and detected as elemental Hg vapor by atomic fluorescence spectrometry (AFS Tekran Model 2500). The hydride generation technique proposed by Stoichev et al. (2004) was optimized as described in detail by Cossa et al. (2009). The DL was 0.2 pM for a 10-mL sample. Analytical reproducibility, determined from 6 replicates, was better than 15% near the DL and 6% at a concentration of 0.5 pM. Accuracy was checked using the certified reference material (CRM) ERM-AE670 from the Institute for Reference Materials and Measurements (IRMM, European Commission).

Total sedimentary Hg concentration ($\{Hg\}_T$) was determined on freeze-dried sediment aliquots using an automatic mercury analyzer (Milestone DMA-80). This method, also known as the EPA standard method No 7473, includes a pyrolysis step that releases Hg from the sample. Mercury is then concentrated by Au amalgamation and detected by atomic absorption spectrometry (Cossa et al., 2002). The DL was 30 pmol g⁻¹. Precision, determined from replicate measurements (n = 10) of one of the sediment samples, was better than 5%. Accuracy was determined with the CRM MESS-3 from NRC and was lower than 5%.

Solid phase MeHg concentrations ($\{MeHg\}$) were determined using a method described by Cossa et al. (2002) and adapted from Leermakers et al. (2001). Methylmercury was solubilized in 4 M HNO₃ from a freeze-dried sediment aliquot, then extracted by CH₂Cl₂ and transferred into 40 mL of demineralized water (Milli-Q) by evaporation of the organic solvent. Methylmercury in the water phase was then ethylated and purged on a Tenax packed column. Ethylmethylmercury was isolated from other volatile compounds by gas chromatography and quantified by CVAFS. The DL was 0.1 pmol g⁻¹. Analytical precision, determined from replicate analyses (n = 6), was less than 15%.

Recoveries of MeHg were $91 \pm 8\%$ ($n = 6$) in the CRM 405 material from the International Atomic Energy Agency (IAEA).

As in the authors' previous studies (e.g., Gallon et al., 2004; Chappaz et al., 2008), the sediment samples collected in Lake Tantaré were completely mineralized with a mixture of HNO_3 , HClO_4 and HF; the acids were evaporated to near dryness and residues were redissolved in a 0.2 N HNO_3 solution. Methodology to measure pH and the concentrations of Al, Ca, Fe, K, Mg, Mn, Na, Cl, SO_4 , and organic and inorganic C in the water samples and those of Fe, Mn, total C and N in the sediments, are described by Laforte et al. (2005). The concentrations of dissolved and sedimentary Cu, Zn and Mo (Chappaz et al., 2008), In (Laforte, 2005), Sb (Bernatchez, 2009) and Ag (Quirion, 2004) were determined with a quadrupole ICP-MS (Thermo Instrument X7) whereas those of Cd (Alfaro-De la Torre and Tessier, 2002) and Pb (Gallon et al., 2004) were measured by graphite furnace atomic absorption spectrometry (Perkin-Elmer SIMAA 6000; Zeeman correction) and those of As, by hydride generation-atomic absorption spectrometry (HG-AAS; Couture et al., 2008).

Areas of the Teflon sheets containing the Fe-rich authigenic deposits were cut and dissolved in 50% HCl for 48 h at room temperature. The resulting solutions were filtered through 0.4- μm porosity Teflon filters and diluted 10 times. In these solutions, Al, Ca, Fe, K, Mg and Na were measured by inductively coupled plasma optical emission spectrometry (ICP-OES; VISTA AX CCD), Ag, Cd, Cu, In, Mo, Pb, Sb and Zn, by inductively coupled plasma mass spectrometry (ICP-MS; Thermo Instrument X7), As by HG-AAS, and C and N with a Shimadzu C N analyzer; Hg and MeHg were measured as described above for dissolved Hg and MeHg.

3. Results and discussion

3.1. Thermodynamic predictions of chemical speciation and saturation index

Speciation of dissolved trace elements in the oxic water overlying the sediment was calculated with the computer program "Windermere Humic Aqueous Model" (WHAM 6; Tipping, 2002) using measured pH and total concentrations of dissolved Ag, Al, As, Ca, Cd, Cu, Fe, In, inorganic Hg, MeHg, Mg, Mn, Mo, Na, K, Pb, Sb, Zn, as well as those of SO_4 , Cl, CO_3 , and humic (HA) and fulvic (FA) acids as inputs. It was assumed that all As, Sb and Mo exist in the oxic water of Lake Tantaré as As(V) (Couture et al., 2008), Sb(V) (Bernatchez, 2009) and Mo(VI) (Chappaz et al., 2008) species. The concentrations of HA and FA were estimated from measurements of dissolved organic carbon (C_{org}), assuming that dissolved organic matter contains 50% C (Buffle, 1988) and that all C_{org} is a part of humic substances (HS) with a ratio of [FA]:[HA] of 9:1 (Malcolm, 1985).

The WHAM 6.0 database was updated with the thermodynamic data given in Table 1 for Ag, As, Hg, In, MeHg, Mo and Sb; note that Ag^+ , In^{3+} , MeHg^+ , MoO_4^{2-} and $\text{Sb}(\text{OH})_6^-$ were new components added to the speciation code WHAM 6. The formation constants chosen for the complexation of Hg and MeHg with HA and FA were recently provided by Tipping (2007) who critically reviewed laboratory studies describing Hg and MeHg complexation with HA and FA; the WHAM 6 speciation code was also modified to include the values of the empirical parameter used to take into account HA and FA binding site heterogeneity (ΔLK_2) suggested by Tipping (2007), i.e., 5.1 and 3.6 for Hg and MeHg, respectively. It should be noted that the formation constants of Hg complexes with HA and FA are reasonably reliable because the experimental data available in the literature for extracting these constants cover a wide range of conditions (pH and levels of metal binding); however, the formation constants for the MeHg complexes remain uncertain due to the relatively limited experimental data basis available (Tipping, 2007). Formation constants of In complexes with HA and FA were estimated for WHAM 6, as suggested by Carbonaro and Di Toro (2007) for a previous version of the speciation code WHAM. A ΔLK_2 value of 2.2 was estimated for In, as in

equation 1 (Tipping, 1998), assuming that ΔLK_2 is related to the equilibrium constant for In complexation with NH_3 (K_{NH_3} ; value taken from Mulla et al., 1985):

$$\Delta LK_2 = 0.55 \log K_{\text{NH}_3} \quad (1)$$

The formation constants for the complexation of Cu, Pb and Zn with inorganic ligands and humic substances (HS) were those given in the WHAM 6 database. There is no formation constant for Ag, As, Sb and Mo complexes with HA and FA.

Table 2 shows the free-ion activities, major species and saturation index (S), as calculated by WHAM 6 for all elements. According to these calculations, almost 100% of $[\text{Hg}]_i$ and about 12% of $[\text{MeHg}]$ were associated with HS in the water overlying Lake Tantaré sediment. Association of the other elements with HS were predicted to be around 100% for Cu, 75% for Pb and In, 20-30% for Cd and Zn and 10-20% for Ca and Mg (Table 2). The negative S values for all elements indicate that the bottom water of Lake Tantaré was largely undersaturated with respect to their least soluble solids. Thus, the trace elements found in association with the authigenic Fe-rich material (Table 3) were presumably bound to it by adsorption.

3.2. Possible binding phases for the trace elements in the Fe-rich authigenic material

Fortin et al. (1993) reported that poorly crystallized lepidocrocite and ferrihydrite were the main Fe oxyhydroxides (Fe-ox) in the Fe-rich material collected on Teflon sheets in Lake Tantaré. The C_{org}/Fe molar ratio found for this material (2.6 ± 0.3 ; Table 3) indicates that a large amount of organic matter is associated with the authigenic Fe oxyhydroxides. The C_{org}/N molar ratio of this organic matter (15.3 ± 3.4 ; Table 3) is much higher than the C_{org}/N Redfield ratio assigned to phytoplankton (6.63; Redfield, 1934), but close to that reported for humic substances (17.5; Buffle, 1988). It is also much larger than the value ($C_{\text{org}}/\text{N} = 6.4$) reported for particles collected in sediment traps deployed from April to October in the productive lake Windermere, UK (Hamilton-Taylor et al., 1984) and the C_{org}/N values of 7.7 - 8.8 reported for the sediments of the eutrophic Gulf of Riga in the Baltic Sea (Danielsson et al., 1998). Following these observations, it is concluded that most of the organic matter in the diagenetic material collected on Teflon sheets is of terrestrial origin; such organic material is reputed to contain mainly humic substances (Buffle, 1988).

The close association of HS with metal oxyhydroxides is ubiquitous in soils and sediments; humic substances are presumed to coprecipitate with metal oxyhydroxides (Schwertmann et al., 2005) or to adsorb on their surface by a variety of mechanisms including ligand exchange, cation bridging, hydrogen bonding and van der Waals interactions (Sposito, 1984; McKnight et al., 1992; Gu et al., 1994; Schlautman and Morgan, 1994). Molar C_{org}/Fe ratios of similar magnitude to the one measured here have been reported for authigenic material collected by the same method in other lakes ($C_{\text{org}}/\text{Fe} = 1.3 - 2.3$; Tessier et al., 1996) and for Fe-rich particles formed in the water column of a seasonally anoxic lake ($C_{\text{org}}/\text{Fe} = 1.2 - 2.5$; Tipping et al., 1981).

Langmuir isotherm parameters, namely the adsorption coefficient and the maximum density of adsorption, for the adsorption of humic substances on goethite at various pHs and on fresh and aged amorphous Fe oxyhydroxides at pH values around 7 have been provided by Tipping (1981). These data show that amorphous Fe oxyhydroxides adsorb 8.5 - 24 fold more HS than goethite at pH 7. Furthermore, from the Langmuir isotherm at pH 5.5 (i.e., close to the pH 5.6 of Lake Tantaré) it can be predicted that 1 g of goethite in equilibrium with Lake Tantaré dissolved organic matter (5.1 mg HS L^{-1} ; Table 2) would adsorb 32 mg of HS. If it is assumed that ferrihydrite adsorbs 8.5 - 24 fold more HS than goethite at pH 5.5, one can then conclude that ferrihydrite would adsorb 272 - 768 mg HS g^{-1} Fe-ox (which would correspond to a C_{org}/Fe molar ratio of 1.2 - 3.4. The C_{org}/Fe molar ratio measured on the diagenetic material (2.6 ± 0.3 ; Table 3) falls within this range. Thus, based on the value of the C_{org}/N ratio and on the concordance between the measured and predicted C_{org}/Fe molar ratio, it is plausible to assume that most of the organic material associated with the diagenetic material is humic substances. Indeed, although biological material such as

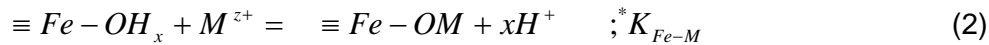
microorganisms remains and exocellular polymers can also be present in the diagenetic material (Fortin et al., 1993), these other types of organic matter likely occur in lesser amounts.

Calculations of the $\Sigma\text{TE}/\text{Fe}$ ratio (0.0075; Table 3), where ΣTE is the sum of the molar concentrations of Ag, As, Ca, Cd, Cu, Hg, In, MeHg, Mg, Mo, Sb, Pb and Zn, indicates that the $-\text{OH}$ sites on Fe oxyhydroxides would be in sufficient number to bind all of these elements. Alternatively, if it is assumed that FA and HA have a similar reactivity for Fe oxyhydroxides and that their concentrations of binding sites are 7.1×10^{-3} mol per g of FA and 4.9×10^{-3} mol per g of HA, respectively (Tipping, 1994), it is estimated that the C_{org}/Fe (2.6) measured in the authigenic material would correspond to 0.41 equivalent of adsorption sites per mole of Fe oxyhydroxide, which then is sufficient for humic substances to bind all trace metals found in the authigenic material.

Thus, the Fe-rich material deposited on the Teflon sheets contains sufficient Fe oxyhydroxides and organic matter to bind all trace elements, and, as a consequence, the following two scenarios have been examined.

3.2.1. Scenario 1: Binding of trace elements to the Fe oxyhydroxides

The framework provided by surface complexation theory can be used to examine if trace elements in the authigenic material collected on the Teflon sheets were bound to the hydroxyl groups of Fe oxyhydroxides. The following general equation, where charges on the solid species have been omitted for simplicity, can describe cation (M) adsorption on diagenetic Fe oxyhydroxides (Tessier et al., 1996):



In this equation $*K_{\text{Fe}-M}$ is an overall conditional equilibrium constant, M^{z+} is the free-metal ion, x is the apparent number of protons released per M adsorbed and " \equiv " refers to adsorption sites. If it is assumed that the proportion of sites occupied by M is low, the concentration of free adsorption sites can be related to the concentration of Fe oxyhydroxides (i.e., $\{\equiv\text{Fe}-\text{OH}\} = N_{\text{Fe}} \{\text{Fe}-\text{ox}\}$ where N_{Fe} is the number of moles of adsorption sites per mole of Fe oxyhydroxides and $\{\text{Fe}-\text{ox}\}$ is the analytical concentration of Fe oxyhydroxides). With the additional assumption that the concentration of sites occupied by M is equal to the concentration of M associated with the Fe oxyhydroxides (i.e., $\{\equiv\text{Fe}-\text{OM}\} = \{\text{Fe}-M\}$), we obtain (Tessier et al., 1989):

$$K_{\text{Fe}-M} = \frac{N_{\text{Fe}} *K_{\text{Fe}-M}}{[\text{H}^+]^x} = \frac{\{\text{Fe}-M\}}{\{\text{Fe}-\text{ox}\}[\text{M}^{z+}]} \quad (3)$$

where $K_{\text{Fe}-M}$ is a conditional equilibrium constant varying as a function of pH, and $\{\text{Fe}-M\}$ is the concentration of M associated with the Fe oxyhydroxides.

If a similar approach is adopted for anion (A), a conditional equilibrium constant ($K_{\text{Fe}-A}$) is defined as follows (Belzile and Tessier, 1990):

$$K_{\text{Fe}-A} = N_{\text{Fe}} *K_{\text{Fe}-A}[\text{H}^+]^x = \frac{\{\text{Fe}-A\}}{\{\text{Fe}-\text{ox}\}[\text{A}^{y-}]} \quad (4)$$

where $\{\text{Fe}-A\}$ is the concentration of A associated with the Fe oxyhydroxides and A^{y-} is the free-anion concentration.

Values of $K_{\text{Fe}-M}$ were obtained for $M^{z+} = \text{Ag}^+, \text{Ca}^{2+}, \text{Cd}^{2+}, \text{Cu}^{2+}, \text{Hg}^{2+}, \text{MeHg}^+, \text{Mg}^{2+}, \text{Pb}^{2+}$ and Zn^{2+} , and $K_{\text{Fe}-A}$ values for $\text{A}^{y-} = \text{AsO}_4^{3-}, \text{MoO}_4^{2-}$ and $\text{Sb}(\text{OH})_6^-$ by introducing into equation (3) or (4) the free-ion activities given in Table 2 and the molar ratios M/Fe or A/Fe given in Table 3; by doing this,

it is implicitly assumed that the measured molar ratios M/Fe and A/Fe corresponded to $\{Fe-M\}/\{Fe-ox\}$ and $\{Fe-A\}/\{Fe-ox\}$, respectively, i.e., that the trace elements in the authigenic material were entirely associated with Fe oxyhydroxides. These overall conditional equilibrium constants (hereafter called measured equilibrium constants and represented as ${}^m K_{Fe-M}$ or ${}^m K_{Fe-A}$) can be compared to the overall conditional equilibrium constants predicted (hereafter called predicted equilibrium constants and represented as ${}^p K_{Fe-M}$ or ${}^p K_{Fe-A}$) by the surface complexation model (SCM) under Lake Tantaré geochemical conditions using the intrinsic surface complexation constants (K^{int}) given in Table 4. Formulation of predicted equilibrium constants is also given by Eq. 3 and 4, but with the ratios $\{Fe-M\}/\{Fe-ox\}$ and $\{Fe-A\}/\{Fe-ox\}$ being predicted by the SCM rather than being measured. In the calculation of ${}^p K_{Fe-M}$ or ${}^p K_{Fe-A}$, a calculation with the two-layer version (DLM; e.g., Dzombak and Morel, 1990) of the surface complexation model was first run, using as input the ambient concentrations of dissolved major ions in Lake Tantaré water and assuming adsorptive equilibrium of ferrihydrite with the free-ion activities given in Table 2 at the pH of Lake Tantaré to obtain the $\{Fe-M\}/\{Fe-ox\}$ and $\{Fe-A\}/\{Fe-ox\}$ ratios predicted by the DLM. In calculating the ratio for all cations, the code MINEQL+ (Schecher and McAvoy, 1998) was used which contains in its database the surface characteristics of ferrihydrite (specific surface area of 600 $m^2 g^{-1}$; concentrations of strong and weak sites of $5 \times 10^{-3} mol mol^{-1}$ of ferrihydrite and 0.2 $mol mol^{-1}$ of ferrihydrite, respectively) used by Dzombak and Morel (1990) to extract intrinsic adsorption constants (K^{int}). The K^{int} values used in the calculations were those proposed by Dzombak and Morel (1990) for the binding of H^+ , Ca^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2+} to strong and weak adsorption sites and for the binding of Ag^+ , Mg^{2+} and Pb^{2+} to strong adsorption sites (Table 4). The K^{int} values for the adsorption of Hg were from Tiffreau et al. (1995); note that the calculations for Hg, were done with the value of 0.029 mol sites per mol of Fe used by Tiffreau et al. (1995) for extracting their intrinsic constants. The missing K^{int} values for the adsorption of $MeHg^+$ on the strong and weak adsorption sites of ferrihydrite (Table 4) and of Ag^+ , Mg^{2+} and Pb^{2+} on the weak adsorption sites were obtained from the following linear free-energy relationships (LFER; Dzombak and Morel, 1990):

$$\text{Log } K^{int} (\text{strong sites}) = 1.17 \log K_{MOH} - 4.37 \quad (5)$$

and

$$\log K^{int} (\text{weak sites}) = 1.299 \log K_{MOH} - 7.89 \quad (6)$$

where K_{MOH} is the first hydrolysis constant of the cations; the required values of K_{MOH} for Ag^+ , Mg^{2+} and Pb^{2+} are given in Dzombak and Morel (1990), whereas that for $MeHg^+$ is given in Table 1. The K^{int} value for the adsorption of Mg^{2+} on strong adsorption sites could not be determined by LFER (Dzombak and Morel, 1990), and it was assumed that its value was identical to that of Ca^{2+} . Also, no K^{int} for the adsorption of In^{3+} was available and it was not possible to estimate any value with LFER; these linear free-energy relationships seem to work well with divalent cations but there are no certainties for trivalent cations such as In^{3+} . It should be noted that the possible formation of ternary complexes ($\equiv Fe-OML$, with L being HA and FA) at the surface of Fe oxyhydroxides is ignored, since no K^{int} are available for the formation of these surface species. For the adsorption of anions, the adsorption calculations were also run with the code MINEQL+, but recent values of K^{int} determined by Gustafsson (2003) and Dixit and Hering (2003) for MoO_4^{2-} and AsO_4^{3-} , respectively, were used. The value of K^{int} for $Sb(OH)_6^-$ adsorption was that reported by Dzombak and Morel (1990), as obtained by LFER. The ratios $\{Fe-M\}/\{Fe-ox\}$ and $\{Fe-A\}/\{Fe-ox\}$ predicted by the SCM were then divided by $[M^{z+}]$ or $[A^y-]$ (Table 2) to yield the ${}^p K_{Fe-M}$ values.

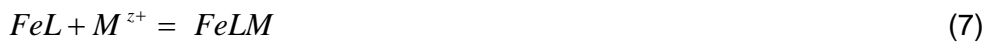
Figure 2 shows that the ${}^p K_{Fe-A}$ values are slightly higher than the ${}^m K_{Fe-A}$ values for the anions AsO_4^{3-} and MoO_4^{2-} and slightly lower for $Sb(OH)_6^-$. For the cations Ag^+ , Ca^{2+} , Cd^{2+} , Cu^{2+} , Mg^{2+} , Pb^{2+} and Zn^{2+} , the measured K_{Fe-M} (${}^m K_{Fe-M}$) values are all higher than those predicted with the DLM

(${}^p K_{Fe-M}$) (Fig. 2). The most striking feature of Fig. 2 is, however, the fact that the measured K_{Fe-M} value for Hg exceeds by nearly 20 orders of magnitude the value predicted by surface complexation theory. Another interesting feature is that ${}^m K_{Fe-M}$ is about 100-fold smaller than ${}^p K_{Fe-M}$ for MeHg, which is inconsistent with the trend that is observed for Hg and the other cations. This may be an artefact associated with the value attributed to either K^{int} for the binding of MeHg⁺ to ferrihydrite (Table 4) or to the formation constants of the MeHg complexes with HA and FA (Table 1). The K^{int} value for MeHg binding to ferrihydrite was not extracted from adsorption experiments, but obtained from a LFER, which is a source of uncertainty. However, to make ${}^p K_{Fe-M}$ smaller than ${}^m K_{Fe-M}$ in Fig. 2, a decrease of K^{int} (or of K_{MOH}) value by about 3 orders of magnitude would be required, which is unreasonable. On the other hand, as mentioned by Tipping (2007), there is some doubt about the accuracy of the formation constant for MeHg complexes with humic substances because they were extracted from laboratory experiments covering a small range of pH and MeHg levels. If, for the calculation of MeHg speciation with WHAM 6, the parameters (formation constant of $10^{3.0}$ for MeHg complexes with both HA and FA and a ΔLK_2 value of 3.6) suggested before the recent revision of Tipping (2007) are used, then the activity of MeHg⁺ becomes much smaller (4.7×10^{-24} compared to 1.68×10^{-14} reported in Table 2); as a result, the ${}^m K_{Fe-M}$ value (open triangles in Fig. 2) becomes about 7 orders of magnitude larger than ${}^p K_{Fe-M}$, a result more consistent with the behaviours of Hg and the other cations.

3.2.2. Scenario 2: Binding of trace metals to the organic matter associated with the Fe oxyhydroxides

To examine if organic matter present in the diagenetic material collected on Teflon sheets can play a dominant role in binding the trace metal, the conditional equilibrium constants for metal binding to the particulate organic matter (POM) associated with the diagenetic material (K_{POM-M}) were compared with the conditional equilibrium constants for metal binding to dissolved organic matter (DOM; K_{DOM-M}) (see Fig. 3). It was assumed that organic matter coatings in the diagenetic material behave similarly to DOM (Davis, 1984).

Reaction of the metals with the particulate organic matter coatings on the Fe oxyhydroxides can be described by the following simplified equation:



with the conditional constant

$$K_{POM-M} = \frac{\{FeLM\}}{\{FeL\}[M^{z+}]} \quad (8)$$

where $\{FeL\}$ and $\{FeLM\}$ are the concentrations of metal binding sites of the organic matter collected on Teflon sheets and of metal complexed with that organic matter, respectively. Values of K_{POM-M} were estimated by dividing the mean metal/Fe molar ratios by the HS/Fe ratio (Table 3), which provided the quotient $\{FeLM\}/\{FeL\}$ required in equation (8). The latter value was then divided by $[M^{z+}]$ (Table 2). The implicit assumption behind this treatment is that the trace metals in the authigenic material were entirely associated with the organic matter.

In a similar manner, a simplified reaction for metal binding to DOM is:



with the conditional constant

$$K_{DOM-M} = \frac{[ML^{z-r}]}{[L^{r-}][M^{z+}]} \quad (10)$$

where $[ML^{z-}]$ and $[L^r]$ are the concentration of metal complexed to DOM (assumed to be exclusively humic substances) and that of free metal binding sites of DOM, respectively. The values of $[ML^{z-}]$ and $[M^{z+}]$ (Table 2) required in equation (10) were obtained from metal speciation calculations, i.e., from the output of WHAM 6. The total concentration of metal binding sites (i.e., $[L]_T$) was estimated by assuming that the abundance of metal binding sites for FA and HA are 7.1×10^{-3} mol per g of FA and 4.9×10^{-3} mol per g of HA, respectively (Table 2); subtracting from $[L]_T$ the concentrations of metals bound to DOM, as provided by the output of WHAM 6, yielded $[L^r]$ to be used in equation (10). Calculations were not done for Ag^+ , AsO_4^{3-} , MoO_4^{2-} and $Sb(OH)_6^-$ due to the non-availability of formation constants for the complexation of these trace elements with HA and FA.

Figure 3 shows that the estimates of K_{POM-M} are reasonably similar to those of K_{DOM-M} , even though rough assumptions were made. The values of K_{POM-M} for Cd, Cu, Hg, MeHg and Zn differ from those of K_{DOM-M} by less than 0.5 log units and those of Ca by around 0.7 log units; slightly larger differences between 1.1 and 1.7 log units are only observed for In, Mg and Pb.

3.3. On the proportions of authigenic and organically-bound trace elements in surficial sediments

To support the discussion on the major binding phases for the trace elements in surficial oxic sediments of Lake Tantaré (assumed to be the top 0.5-cm layer), the concentrations of authigenic trace elements were estimated as well as the concentrations of trace elements possibly bound to the whole of the organic matter present in this sediment layer.

The concentrations of authigenic trace elements were obtained by multiplying the molar ratios TE/Fe given in Table 3 by the concentration of Fe oxyhydroxides ($\{Fe-ox\}$) in the top 0.5 cm sediment layer. For this calculation, it was assumed that $\{Fe-ox\}$ (1.55×10^{-3} mol g^{-1} ; Table 5) was given by the excess $\{Fe\}$ over the constant background Fe concentration below 15 cm depth in the sediments (Fig. 1a). According to these calculations, the sediment authigenic Fe oxyhydroxides and their associated organic matter could bind practically all As, Mo and Cd present in the top 0.5 cm layer of Lake Tantaré oxic sediments, significant proportions (15-55%) of Ag, Cu, In, Pb, Sb, and Zn and small proportions (1-5%) of MeHg and Hg (Table 5). Upon sediment burial, the reductive dissolution of Fe oxyhydroxides should release their adsorbed trace elements and organic matter; some portion of these trace elements can become associated to other adsorption sites in close proximity whereas another portion can migrate in porewater.

The organic matter present in the top 0.5-cm sediment layer has a very similar molar C_{org}/N ratio (15.5; Table 5) to that found in the diagenetic material collected on Teflon sheets (15.3 ± 3.4 ; Table 3), indicating a common source which, given the high C_{org}/N values, is probably the watershed. The molar ratio $\{C_{org}\}/\{Fe-ox\}$ is, however, much larger in the sediment top layer (13; Table 5) than in the diagenetic material (2.6 ± 0.3 ; Table 3), which indicates that only a small fraction (around 20%) of the organic matter is associated with the Fe oxyhydroxides in Lake Tantaré sediments. The remaining organic matter is likely present as organic coatings on other mineral phases than Fe oxyhydroxides and as discrete particles. Thus, the maximum concentration of cationic trace metals bound to sedimentary organic matter, was estimated by multiplying the TE/ C_{org} ratios given in Table 3 by the concentration of sedimentary organic matter given in Table 5. According to this calculation, sediment organic matter could bind all In present in the top 0.5-cm sediment layer, significant proportions (30-65%) of Hg, Cu, and Zn, small proportions (7%) of MeHg, but unrealistically high proportions (300-400%) of Cd and Pb (Table 5).

3.4. Association mode of the trace elements to Lake Tantaré oxic sediments

Results obtained from the present research combined with those of other studies reporting the vertical distributions of trace elements in sediments and sediment porewaters at the same site are used below to identify which sedimentary phases the investigated elements are likely associated with Lake Tantaré oxic sediments. For example, agreement between measured and

predicted conditional constants for the association of a given element with either Fe oxyhydroxides (Fig. 2) or organic matter (Fig. 3) in the diagenetic material is taken as an indication that this element is associated with that solid phase. Realistic predictions of the trace element concentration in the oxic layer of the sediments (Table 5) based on the TE/Fe and TE/C_{org} ratios measured in the diagenetic material can also be used to reveal the most important binding phase. Furthermore, the occurrence of an enrichment for a given element in surface sediments that is coincidental with the Fe-enriched layer (Fig. 1a) is also a strong sign that the element is bound to authigenic Fe oxyhydroxides. Lastly, a correlation between the porewater concentrations of Fe and those of a trace element over the depth interval where Fe is recycled to form authigenic Fe oxyhydroxides (-2 cm to 3 cm; Fig 1b) represents another indication that this trace element becomes associated with the authigenic Fe oxyhydroxides. This would be true even if the profile of this element in the solid-phase does not exhibit any enrichment at the sediment surface. Indeed, porewater profiles of trace elements are more sensitive indicators of reactions involving the element than are their solid phase counterpart; they thus more easily reveal reactions that otherwise would remain unperceived.

3.4.1. The anionic trace elements AsO_4^{3-} and MoO_4^{2-} and $\text{Sb}(\text{OH})_6^-$

Figure 2 shows that the $K_{\text{Fe-A}}$ values for the anions AsO_4^{3-} and MoO_4^{2-} fall close to the 1:1 line, suggesting that these two anions were bound to the Fe oxyhydroxides present in the Fe-rich diagenetic material collected on Teflon sheets. The values of ${}^p K_{\text{Fe-A}}$ ($10^{12.81}$ for AsO_4^{3-} and $10^{5.71}$ for MoO_4^{2-}) are slightly higher by a factor of 2.4 - 2.9 than those of ${}^m K_{\text{Fe-A}}$ ($10^{12.35}$ for AsO_4^{3-} and $10^{5.33}$ for MoO_4^{2-}). A strong adsorption of these two anions onto Fe oxyhydroxides in Lake Tantaré sediments is supported by the occurrence of sharp {Mo} and {As} surface maxima in the sediments of this lake which are similar in shape to that of {Fe} shown in Fig. 1a and by the close parallelism between porewater [Mo] and [As] profiles and those of [Fe] shown in Fig. 1b (Chappaz et al., 2008; Couture et al., 2008). The lower observed than predicted Mo and As adsorption in Lake Tantaré sediments has been attributed to the fact that Mo and As adsorption equilibrium is not reached because natural organic matter inhibits the rate of adsorption of these two anions onto Fe oxyhydroxides (Chappaz et al., 2008; Couture et al., 2010a). This assertion is supported by laboratory experiments showing that the addition of natural organic matter decreased the rate of As adsorption onto hematite by several orders of magnitude (Redman et al., 2002). Table 5 indicates that most of the As and Mo in the surficial sediment should be authigenic.

For the anion $\text{Sb}(\text{OH})_6^-$, the ${}^m K_{\text{Fe-A}}$ value ($10^{4.31}$) is about 4 times higher than that of ${}^p K_{\text{Fe-A}}$ ($10^{3.66}$). The difference between measured and predicted adsorption of $\text{Sb}(\text{OH})_6^-$ may be due to the fact that the K^{int} values used in the calculations with the DLM were not measured but derived from LFER; relatively large errors can result from such interpolations. Bernatchez (2009) reported that the porewater [Sb] profiles at the same sampling site in Lake Tantaré paralleled those of [Fe] over the depth interval where Fe oxyhydroxides are recycled, thus supporting the association of Sb with authigenic Fe oxyhydroxides. However, there is no Sb enrichment in the sediment surface layer as observed for the other anions and for Fe, likely due to the lower “mobility” of Sb in the sediments (Bernatchez, 2009). Thus, Sb appears to be associated with the authigenic Fe oxyhydroxides but in lesser proportions than As and Mo. Consistently, Fig. 2 indicates that, adsorption of Sb to Fe oxyhydroxides is weaker than that of Mo or As and Table 5 reveals that only about 30% of total Sb in surficial sediment should be authigenic.

3.4.2. The cationic trace elements Ag^+ , Ca^{2+} , Cd^{2+} , Cu^{2+} , Hg^{2+} , In^{3+} , MeHg^+ , Mg^{2+} , Pb^{2+} and Zn^{2+}

Interestingly, the ratio between measured and predicted $K_{\text{Fe-M}}$ values increases inversely with affinity of the cations Ca^{2+} , Cd^{2+} , Cu^{2+} , Mg^{2+} , Pb^{2+} and Zn^{2+} for the Fe oxyhydroxides collected on

Teflon sheets (Fig. 2). For example, the ${}^m K_{Fe-M} / {}^p K_{Fe-M}$ ratio is 8 for Pb^{2+} , but reaches values of 3×10^4 and 6×10^4 for Ca^{2+} and Mg^{2+} , respectively. Similar behaviour has been reported for diagenetic material collected in the low pH Lake Clearwater (pH = 4.8) and has been ascribed to complexation of these metals with organic matter adsorbed at the surface of the Fe oxyhydroxides rather than to the hydroxyl groups of the Fe oxyhydroxides (Tessier et al., 1996). The latter interpretation also applies to the diagenetic material collected in Lake Tantaré, and it is supported by the close agreement between K_{POM-M} and K_{DOM-M} for Ca^{2+} , Cd^{2+} , Cu^{2+} , Mg^{2+} and Zn^{2+} (Fig. 3). The inference of preferential binding of these cations to natural organic matter (NOM) in the diagenetic material is also valid for oxic sediments, where the ratio $\{C_{org}\}/\{Fe-ox\}$ is much larger (Tables 3 and 5). This is supported by the absence of surface maxima corresponding to that of $\{Fe\}$ (Fig. 1a) in the solid-phase profiles of Cd, Ca or Mg (Alfaro-De la Torre and Tessier, 2002) and Zn (Carignan and Tessier, 1985), and by the absence of any significant correlation between porewater $[Fe]$ and $[Cd]$ (Alfaro-De la Torre and Tessier, 2002) or $[Zn]$ (Carignan and Tessier, 1985). However, it should be noted that Pb^{2+} is an exception among these cations, given that it shows a slightly better agreement between ${}^m K_{Fe-M}$ and ${}^p K_{Fe-M}$ (Fig. 2) than between K_{POM-M} and K_{DOM-M} (Fig. 3) and that the $[Pb]$ porewater profiles parallel those of $[Fe]$ (Gallon et al., 2004). Furthermore, concentrations of organically-bound Pb in the surficial sediment, predicted from the Pb/C_{org} measured in the diagenetic material collected on Teflon sheets, are unrealistic, being much larger than total $\{Pb\}$ (Table 5). Thus, collectively, the observations point consistently to the preferential binding of Ca^{2+} , Cd^{2+} , Cu^{2+} , Mg^{2+} and Zn^{2+} to organic matter and Pb^{2+} to the authigenic Fe oxyhydroxides. The mode of association of Ag^+ to Lake Tantaré sediment is more difficult to ascertain. The ${}^m K_{Fe-M} / {}^p K_{Fe-M}$ ratio larger than 1 found for this metal (Fig. 2) can be interpreted as a sign of preferential binding to humic substances in the authigenic material, like for other cations. Also, no correlations were observed between porewater $[Ag]$ and $[Fe]$ profiles (Quirion, 2004), suggesting that Ag^+ is not bound to Fe oxyhydroxides in the oxic sediment. However, to the best of the authors' knowledge, there is no available binding constant for this metal with humic substances that can be used to verify its binding to NOM. For In^{3+} , the similarities in values between K_{POM-M} and K_{DOM-M} (Fig. 3) and between measured and organically-bound $\{In\}$ (Table 5) indicate that this metal is mostly bound to humic substances in both the authigenic material and the sediment. Regarding Hg^{2+} , the close agreement between K_{POM-M} and K_{DOM-M} (Fig. 3) as well as the much larger ${}^m K_{Fe-M}$ than ${}^p K_{Fe-M}$ values (Fig. 2) indicate clearly that this metal is bound to the functional groups of organic matter and not to the hydroxyl groups of the Fe oxyhydroxides in the material collected with Teflon sheets. It is inferred that this preference of Hg^{2+} for NOM is also valid for the oxic sediment, and this interpretation is consistent with the absence of both a sharp $\{Hg\}$ maximum at the sediment surface and correlation between $[Hg]$ and $[Fe]$ depth profiles at the same site (Feyte et al., 2010). The interpretation of Hg being preferentially bound to humic substances is also supported by the correlations found in several studies between the sedimentary concentrations of Hg and organic matter (e.g., Hollweg et al., 2009; Hammerschmidt and Fitzgerald, 2004). Table 5 indicates that, despite the strong affinity of Hg for organic matter (Fig. 3), only about 30% of total sediment Hg should be organically-bound. The remaining sediment Hg should be present in refractory forms or as elemental Hg (Bouffard and Amyot, 2009). Lastly, the relatively good agreement between K_{POM-M} and K_{DOM-M} for MeHg (Fig. 3), despite the large uncertainties in its binding constants with HA and FA, suggests that this toxic compound has a greater affinity for the organic matter associated with Fe oxyhydroxides in the authigenic material than for the hydroxyl groups of these compounds. A similar interpretation for the oxic sediments is supported by the absence of any correlation between porewater $[MeHg]$ and $[Fe]$ (Feyte et al., 2010). Furthermore, the interpretation that MeHg is bound to organic matter is consistent with observations in marine and estuarine sediments suggesting that organic matter exerts a major

control on the MeHg distribution in surface deposits (e.g., Lambertsson and Nilsson, 2006; Sunderland et al., 2006).

4. Conclusions

The analyses of Lake Tantaré diagenetic material, sediment and bottom water, combined with previous results on porewater and solid phases at the same site, clarify whether Fe oxyhydroxides or natural organic matter bind a number of trace elements in oxic sediments. Collectively, these data are coherent with the scenario that in the oxic sediments of this lake: i) the oxyanions AsO_4^{3-} , MoO_4^{2-} and $\text{Sb}(\text{OH})_6^-$ are essentially associated with Fe oxyhydroxides; and ii) the cations Ca^{2+} , Cd^{2+} , Cu^{2+} , Mg^{2+} , Hg^{2+} , MeHg^+ , Mg^{2+} , In^{3+} , Zn^{2+} , and probably Ag^+ , are preferentially bound to the organic matter and Pb^{2+} to the Fe oxyhydroxides.

However, further investigations need to be carried out in environments exhibiting a larger range of geochemical conditions before generalizations can be made about the relative binding affinity of trace elements to Fe oxyhydroxides and natural organic matter. For example, Tessier et al. (1996) have shown that at higher lake pH values, the affinity of Cd^{2+} , Cu^{2+} , Ni^{2+} and Zn^{2+} for Fe oxyhydroxides can overcome that for organic matter.

The data (Fig. 3) also confirm the affinity of Hg^{2+} for natural organic matter, which has been suggested in field studies on the basis of significant linear correlations between $\{\text{Hg}\}$ and $\{\text{C}_{\text{org}}\}$. In agreement with the present observations, the generally low determination coefficients (r^2) found for these correlations could be due to the fact that, despite the strong affinity of Hg for organic matter, only a small proportion (~30% in Lake Tantaré oxic sediments) of total Hg is effectively organically-bound, most of the Hg being present in the sediments in refractory forms. As a last point, it should be noted that the excellent agreement found between $K_{\text{POM-M}}$ and $K_{\text{DOM-M}}$ for Hg^{2+} (Fig. 3) lends support to the revised formation constants of Hg complexes with humic substances provided by Tipping (2007); however, a similar conclusion cannot be drawn for MeHg^+ .

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References

- Adelson, J.M., Helz, G.R., Miller, C.V., 2001. Reconstructing the rise of recent coastal anoxia; molybdenum in Chesapeake Bay sediments. *Geochim. Cosmochim. Acta* 65, 237-252.
- Alfaro-De La Torre, C., Tessier, A., 2002. Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. *Geochim. Cosmochim. Acta* 66, 3549-3562.
- Bacon, J.R., Davidson, C.M., 2008. Is there a future for sequential chemical extraction? *Analyst* 133, 25-46.
- Belzile, N., Tessier, A., 1990. Interactions between arsenic and iron oxyhydroxides in lacustrine sediments. *Geochim. Cosmochim. Acta* 54, 103-109.

Belzile, N., De Vitre, R.R., Tessier, A., 1989. In situ collection of diagenetic iron and manganese oxhydroxides from natural sediments. *Nature* 340, 376-377.

Bernatchez, M.-N., 2009. Dépôt et mobilité de l'antimoine dans les sédiments de lacs du Bouclier canadien. MSc thesis No 1163, INRS-ETE, Université du Québec.

Bloom, N.S., Fitzgerald, W.F., 1988. Determination of volatile mercury species at picogram level by low temperature gas chromatography with cold-vapour atomic fluorescence detection. *Anal. Chim. Acta* 28, 151-161.

Bothe, J.V., Brown, P.W., 1999. The stabilities of calcium arsenates at 23±1 degrees C. *J. Hazard. Mater.* 69, 197-207.

Bouffard, A., Amyot, M., 2009. Importance of elemental mercury in lake sediments. *Chemosphere* 74, 1098-1103.

Buffle, J., 1988. *Complexation Reactions in Aquatic Systems*. Ellis Horwood Ltd, Chichester.

Carbonaro, R.F., Di Toro, D.M., 2007. Linear free energy relationships for metal-ligand complexation: Monodentate binding to negatively-charged oxygen donor atoms. *Geochim. Cosmochim. Acta* 71, 3958-3968.

Carignan, R., Tessier, A., 1985. Zinc deposition in acid lakes: the role of diffusion. *Science* 228, 1524-1526.

Carignan, R., Rapin, F., Tessier, A., 1985. Sediment porewater sampling for metal analysis: a comparison of techniques. *Geochim. Cosmochim. Acta* 49, 2493-2497.

Chao, T.T., Zhou, L., 1983. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Sci. Soc. Am. J.* 47, 225-232.

Chappaz, A., 2008. *Géochimie du molybdène, du rhénium et de l'uranium dans les sédiments de lacs du Bouclier canadien et des Appalaches*. PhD thesis No 424, INRS-ETE, Université du Québec.

Chappaz, A., Gobeil, C., Tessier, A., 2008. Geochemical and anthropogenic enrichments of Mo in sediments from perennially oxic and seasonally anoxic lakes in Eastern Canada. *Geochim. Cosmochim. Acta* 72, 170-184.

Cossa, D., Averty, B., Breteau, J., Senard, A.-S., 2003. *Spéciation du mercure dissous dans les eaux marines. Méthodes d'analyse en milieu marin*. Co-édition Ifremer et Ministère de l'Ecologie et du Développement Durable. ISBN 2-84433-125-4.

Cossa, D., Averty, B., Pirrone, N., 2009. The origin of methylmercury in open Mediterranean waters. *Limnol. Oceanog.* 54, 837-844.

Cossa, D., Coquery, M., Nakhlé, K., Claisse, D., 2002. *Dosage du mercure total et du monométhylmercure dans les organismes et les sédiments marins. Méthodes d'analyse en milieu marin*. Editions Ifremer. ISBN 2-84433-105-X.

Couture, R.M., Gobeil, C., Tessier, A., 2008. Chronology of atmospheric deposition of arsenic inferred from reconstructed sedimentary records. *Environ. Sci. Technol.* 42, 6508-6513.

Couture, R.M., Gobeil, C., Tessier, A., 2010a. Arsenic, iron and sulfur co-diagenesis in lake sediments. *Geochim. Cosmochim. Acta* 74, 1238-1255.

Couture, R.M., Shafei, B., Van Cappellen, P., Tessier, A., Gobeil, C., 2010b. Non-steady state modeling of arsenic diagenesis in lake sediments. *Environ. Sci. Technol.* 44, 197-203.

Crusius, J., Calvert, S.E., Pedersen, T.F., Sage, D., 1996. Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth Planet. Sci. Lett.* 145, 65-78.

Danielsson, A., Carman, R., Rahm, L., Aigars, J., 1998. Spatial estimation of nutrient distributions in the Gulf of Riga sediments using cokriging. *Estuar. Coast. Shelf Sci.* 46, 713-722.

Davis, J.A., 1984. Adsorption of natural organic matter at the oxide/water interface. *Geochim. Cosmochim. Acta* 46, 2381-2393.

Davis, J.A., Kent D.B., 1990. Surface complexation modeling in aqueous geochemistry. *Rev. Mineral.* 23, 177-260.

De Robertis, A., Foti, C., Patane, G., Sammartano, S., 1998. Hydrolysis of (CH₃)Hg⁺ in different ionic media: Salt effects and complex formation. *J. Chem. Eng. Data* 43, 957-960.

Dixit, S., Hering, J.G., 2003. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* 37, 4182-4189.

Dzombak, D., Morel, F.M.M., 1990. *Surface Complexation Modeling: Hydrous Ferric Oxide*. Wiley, New York.

Essington, M.E., 1992. Formation of calcium and magnesium molybdate complexes in dilute aqueous solutions. *Soil Sci. Soc. Am. J.* 56, 1124-1127.

Feyte, S., Gobeil, C., Tessier, A., Cossa, D., 2010. History of atmospheric deposition of mercury reconstructed from sedimentary records corrected for diagenesis, in prep.

Filella, M., May P.M., 2003. Computer simulation of the low-molecular-weight inorganic species distribution of antimony(III) and antimony(V) in natural waters. *Geochim. Cosmochim. Acta* 67, 4013-4031.

Fortin, D., Leppard, G.G., Tessier, A., 1993. Characteristics of lacustrine diagenetic iron oxyhydroxides. *Geochim. Cosmochim. Acta* 57, 4391-4404.

Gallon, C., Tessier, A., Gobeil, C., Alfaro-De La Torre, M.C., 2004. Modeling diagenesis of lead in sediments of a Canadian Shield lake. *Geochim. Cosmochim. Acta* 68, 3531-3545.

Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J.F., 1994. Adsorption and desorption of natural organic matter on iron oxide: Mechanisms and models. *Environ. Sci. Technol.* 28, 38-46.

Gustafsson, J.P., 2003. Modelling molybdate and tungstate adsorption to ferrihydrite. *Chem. Geol.* 200, 105-115.

Hamilton-Taylor, J., Willis, M., Reynold, C. S., 1984. Depositional fluxes of metals and phytoplankton in Windermere as measured by sediment traps. *Limnol. Oceanog.* 29, 695-710.

Hammerschmidt, C.R., Fitzgerald, W.F., 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* 38, 1487-1495.

Hammerschmidt, C.R., Fitzgerald, W.F., 2006. Methylmercury cycling in sediments on the continental shelf of southern New England. *Geochim. Cosmochim. Acta* 70, 918-930.

Hollweg, T.A., Gilmour, C.C., Mason, R.P., 2009. Methylmercury production in sediments of Chesapeake Bay and the mid-Atlantic continental margin. *Mar. Chem.* 114, 86-101.

International Union of Pure and Applied Chemistry (Ed.), 2001. *The IUPAC Stability constants database*, Sourby Old Farm, Timble, Otley, Yorks, UK: Academic Software.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: The significant role of hydrous Mn and Fe oxides. In: Gould, R. F. (Ed.), *Trace Inorganics in Water*. Adv. Chem. Ser. No 73. Am. Chem. Soc. Washington, D.C., 337-387.

Krachler, M., Shotyk, W., 2004. Natural and anthropogenic enrichments of molybdenum, thorium, and uranium in a complete peat bog profile, Jura Mountains, Switzerland. *J. Environ. Monitor.* 6, 418-426.

Laforte, L., 2005. Thallium et Indium dans les sédiments de deux lacs du Bouclier Canadien : sources, géochimie et potentiel comme traceurs. MSc thesis No 910, INRS-ETE, Université du Québec.

Laforte, L., Tessier, A., Gobeil, C., Carignan, R., 2005. Thallium diagenesis in lake sediments. *Geochim. Cosmochim. Acta* 69, 5295-5306.

Lambertsson, L., Nilsson, M., 2006. Organic material: the primary control on mercury methylation and ambient methylmercury concentrations in estuarine sediments. *Environ. Sci. Technol.* 40, 1822-1829.

Leermakers, M., Galletti, S., De Galan, S., Brion, N., Baeyens, W., 2001. Mercury in the Southern North Sea and Scheldt estuary. *Mar. Chem.* 75, 229-248.

Linge, K.L., 2008. Methods for investigating trace element binding in sediments. *Crit. Rev. Environ. Sci. Technol.* 38, 165-196.

Loux, N.T., 2007. An assessment of thermodynamic reaction constants for simulating aqueous environmental monomethylmercury speciation. *Chem. Speciation Bioavail.* 19, 183-196.

Luoma, S.N., Bryan, G.W., 1981. A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *Sci. Total Environ.* 17, 165-196.

Malcolm, R.L., 1985. Geochemistry of stream fulvic and humic substances. In: Aiken, G.R., McKnight, D.M., Wershaw, R. L., MacCarthy, P. (Eds.), *Humic Substances in Soil, Sediment and Water. Geochemistry, Isolation and Characterization.* Wiley-Interscience, New York, 181-209.

Martell, A.E., Smith, R.M., 2001. NIST Critically Selected Stability Constants of Metal Complexes, version 6 Gaithersburg, Maryland: National Institute of Standards and Technology.

McKnight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L., Thorn, K.A., 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. *Environ. Sci. Technol.* 26, 1388-1396.

Mulla, F., Marsicano, F., Nakani, B.S., Hancock, R.D., 1985. Stability of ammonia complexes that are unstable to hydrolysis in water. *Inorg. Chem.* 24, 3076-3080.

Murata, T., 1991. Synchrotron radiation for structure analysis - EXAFS and XANES. *Microchim. Acta* 104, 435-444.

Nordstrom, D.K., Archer, D.G., 2003. Arsenic thermodynamic data and environmental geochemistry. In: Welch, A.H., Stollenwerk, K.G. (Eds), *Arsenic in Ground Water, Geochemistry and Occurrence.* Kluwer Academic Publications, Norwell, MA., 1-25.

Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* 9, 269-298.

Parsons, J.G., Aldrich, M.V., Gardea-Torresdey, J.L., 2002. Environmental and biological applications of extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) spectroscopies. *Appl. Spectrosc. Rev.* 37, 187-222.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Sjöberg, S., Wanner, H., 2005. Chemical speciation of environmentally significant heavy metals with inorganic ligands. Part 1: The Hg^{2+} – Cl^- , OH^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{2-} aqueous systems. *Pure Appl. Chem.* 77, 739-800.

Quirion, R., 2004. Déposition et mobilité de Ag dans les sédiments de lacs du Bouclier Canadien. MSc thesis No 869, INRS-ETE, Université du Québec.

Rabenstein, D.L., Touranqueau, M.C., Evans, C.A., 1976. Proton magnetic resonance and Raman spectroscopic studies of methylmercury(II) complexes of inorganic anions. *Can. J. Chem.* 54, 2517-2525.

Ranville, M.A., Flegal, A.R., 2005. Silver in the North Pacific. *Geochem. Geophys. Geosyst.*, 6, Q03M01, doi:10.1029/2004GC000770.

Redfield, A.C., 1934. On the proportions of organic derivatives in seawater and their relation to the composition of plankton. In: Daniel, R.J. (Ed.), *James Johnson Memorial Volume.* Liverpool University Press, Liverpool.

Redman, A.D., Macalady, D.L., Ahmann, D., 2002. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* 36, 2889-2896.

Schecher, M.E., McAvoy, D., 1998. MINEQL+. Environmental Research Software.

Schlautman, M.A., Morgan, J.J., 1994. Adsorption of aquatic humic substances on colloidal-size aluminium oxide particles: Influence of solution chemistry. *Geochim. Cosmochim. Acta* 58, 4293-4303.

Schwertmann, U., Wagner, F., Knicker, H., 2005. Ferrihydrite-humic associations: Magnetic hyperfine interactions. *Soil Sci. Soc. Am. J.* 69, 1009-1015.

Sigg, L., Sturm, M., Kistler, D., 1987. Vertical transport of heavy metals by settling particles. *Limnol. Oceanog.* 32, 112-130.

Singer, D. M., Zachara, J.M., Brown, G.E., 2009. Uranium speciation as a function of depth in contaminated Hanford sediments - A micro-XRF, micro-XRD, and micro- and bulk-XAFS study. *Environ. Sci. Technol.* 43, 630-636.

Smith, R.M., Martell, A.E., 1976. Critical Stability Constants: Inorganic Complexes. Vol 4. Plenum Press, New York.

Sposito, G., 1984. The Surface Chemistry of Soils. Oxford University Press, New York.

Stoichev, T., Rodriguez M.-D., R.C., Tessier, E., Amouroux, D., Donard, O.F.X., 2004. Improvement of analytical performances for mercury speciation by on-line derivatization, cryofocussing and atomic fluorescence spectrometry. *Talanta* 62, 433-438.

Sunderland, E.M., Gobas, F.A.P.C., Branfireun, B.A., Heyes, A., 2006. Environmental controls on the speciation and distribution of mercury in coastal sediments. *Mar. Chem.* 102, 111-123.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem.* 51, 844-851.

Tessier, A., Carignan, R., Dubreuil, B., Rapin, F., 1989. Partitioning of zinc between the water column and the oxic sediments in lakes. *Geochim. Cosmochim. Acta* 53, 1511-1522.

Tessier, A., Fortin, D., Belzile, N., DeVitre, R.R., Leppard, G.G., 1996. Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: Narrowing the gap between field and laboratory measurements. *Geochim. Cosmochim. Acta* 60, 387-404.

Tiffreau, C., Lützenkirchen, J., Behra, P., 1995. Modeling the adsorption of mercury(II) on (hydr)oxides. 1. Amorphous iron oxides and α -quartz. *J. Colloid Interface Sci.* 172, 82-93.

Tipping, E., 1981. The adsorption of aquatic humic substances by iron oxides. *Geochim. Cosmochim. Acta* 45, 191-199.

Tipping, E., 1994. WHAM- A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comp. Geosci.* 20, 973-1023.

Tipping, E., 1998. Humic ion-binding model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquat. Geochem.* 4, 3-48.

Tipping, E., 2002. Cation Binding by Humic Substances. Cambridge University Press, Cambridge.

Tipping, E., 2007. Modelling the interactions of Hg(II) and methylmercury with humic substances using WHAM/Model VI. *Appl. Geochem.* 22, 1624-1635.

Tipping, E., Woof, C., Cooke, D., 1981. Iron oxide from a seasonally anoxic lake. *Geochim. Cosmochim. Acta* 45, 1411-1419.

Whiting, K.S., 1992. The thermodynamics and geochemistry of arsenic with application to subsurface waters at the Sharon Steel superfund site at Midvale, Utah. MSc Thesis T-4128, Colorado School of Mines, Golden, CO.

Yagasaki, A., Andersson, I., Pettersson, L., 1987. Multicomponent polyanions. 41. Potentiometric and ^{31}P NMR study of equilibria in the molybdophenylphosphonate system in 0.6 M Na(Cl) medium. *Inorg. Chem.* 26, 3926-3933.

Zhao, F.J., Lehmann, J., Solomon, D., Fox, M.A., McGrath, S.P., 2006. Sulphur speciation and turnover in soils: Evidence from sulphur K-edge XANES spectroscopy and isotope dilution studies. *Soil Biol. Biochem.* 38, 1000-1007.

Table 1. Formation constants (25°C and I = 0) used to update the WHAM 6 database for Hg, MeHg, Ag, In, As, Mo and Sb speciation calculations. The symbols R_{HA}^Z and R_{FA}^Z represent the molecules of humic and fulvic acids, respectively.

Reaction	Log K	References
Hg		
$Hg^{2+} + OH^- = HgOH^+$	10.6	Powell et al. (2005)
$Hg^{2+} + 2OH^- = Hg(OH)_2$	22.02	Powell et al. (2005)
$Hg^{2+} + 3OH^- = Hg(OH)_3^-$	20.9	Powell et al. (2005)
$Hg^{2+} + OH^- + Cl^- = HgOHCl$	18.27	Powell et al. (2005)
$Hg^{2+} + Cl^- = HgCl^+$	7.3	Powell et al. (2005)
$Hg^{2+} + 2Cl^- = HgCl_2$	14.0	Powell et al. (2005)
$Hg^{2+} + 3Cl^- = HgCl_3^-$	14.93	Powell et al. (2005)
$Hg^{2+} + 4Cl^- = HgCl_4^{2-}$	15.5	Powell et al. (2005)
$Hg^{2+} + SO_4^{2-} = HgSO_4$	2.6	Powell et al. (2005)
$Hg^{2+} + CO_3^{2-} = HgCO_3$	11.51	Powell et al. (2005)
$Hg^{2+} + OH^- + CO_3^{2-} = Hg(OH)CO_3^-$	19.34	Powell et al. (2005)
$Hg^{2+} + H^+ + CO_3^{2-} = HgHCO_3^+$	15.84	Powell et al. (2005)
$Hg^{2+} + R_{HA}^Z = RHg_{HA}^{Z+2}$	3.6	Tipping (2007)
$Hg^{2+} + R_{FA}^Z = RHg_{FA}^{Z+2}$	3.1	Tipping (2007)
MeHg		
$MeHg^+ + OH^- = MeHgOH$	9.47	De Robertis et al. (1998)
$2MeHg^+ + OH^- = (MeHg)_2OH^+$	11.85	De Robertis et al. (1998)
$MeHg^+ + CO_3^{2-} = MeHgCO_3^-$	6.1	Rabenstein et al. (1976)
$MeHg^+ + H^+ + CO_3^{2-} = MeHgHCO_3$	12.95	Loux (2007)
$MeHg^+ + Cl^- = MeHgCl$	5.45	De Robertis et al. (1998)
$MeHg^+ + SO_4^{2-} = MeHgSO_4^-$	2.64	De Robertis et al. (1998)
$MeHg^+ + R_{HA}^Z = RMeHg_{HA}^{Z+1}$	0.3	Tipping (2007)
$MeHg^+ + R_{FA}^Z = RMeHg_{FA}^{Z+1}$	0.3	Tipping (2007)
Ag		
$Ag^+ + OH^- = AgOH$	2.0	Smith and Martell (1976)
$Ag^+ + 2OH^- = Ag(OH)_2^-$	3.99	Smith and Martell (1976)
$Ag^+ + SO_4^{2-} = AgSO_4^-$	1.3	Smith and Martell (1976)
$Ag^+ + Cl^- = AgCl$	3.31	Smith and Martell (1976)
$Ag^+ + 2Cl^- = AgCl_2^-$	5.25	Smith and Martell (1976)
In		
$In^{3+} + Cl^- = InCl^{2+}$	2.4	IUPAC (2001)
$In^{3+} + 2Cl^- = InCl_2^+$	3.44	IUPAC (2001)
$In^{3+} + 3Cl^- = InCl_3$	4.3	IUPAC (2001)
$In^{3+} + NO_3^- = InNO_3^{2+}$	0.18	IUPAC (2001)
$In^{3+} + 2NO_3^- = In(NO_3)_2^+$	-0.31	IUPAC (2001)
$In^{3+} + SO_4^{2-} = InSO_4^+$	1.74	IUPAC (2001)
$In^{3+} + 2SO_4^{2-} = In(SO_4)_2^-$	2.6	IUPAC (2001)
$In^{3+} + 3SO_4^{2-} = In(SO_4)_3^{3-}$	3	IUPAC (2001)
Table 1 (Continue)		
$In^{3+} + OH^- = InOH^{2+}$	9.47	Martell and Smith (2001)
$In^{3+} + 2OH^- = In(OH)_2^+$	20.2	Martell and Smith (2001)

$\text{In}^{3+} + 3\text{OH}^- = \text{In}(\text{OH})_3$	29.6	Martell and Smith (2001)
$\text{In}^{3+} + 4\text{OH}^- = \text{In}(\text{OH})_4^-$	33.9	Martell and Smith (2001)
$2\text{In}^{3+} + 2\text{OH}^- = \text{In}_2(\text{OH})_2^{4+}$	-4.8	Martell and Smith (2001)
$4\text{In}^{3+} + 4\text{OH}^- = \text{In}_4(\text{OH})_4^{8+}$	-8.2	Martell and Smith (2001)
$4\text{In}^{3+} + 6\text{OH}^- = \text{In}_4(\text{OH})_6^{6+}$	-12.9	Martell and Smith (2001)
$\text{In}^{3+} + \text{R}_{\text{HA}}^z = \text{RIn}_{\text{HA}}^{z+3}$	2.6	Estimated
$\text{In}^{3+} + \text{R}_{\text{FA}}^z = \text{RIn}_{\text{FA}}^{z+3}$	2.5	Estimated
As		
$\text{AsO}_4^{3-} + \text{H}^+ = \text{HAsO}_4^{2-}$	11.80	Nordstrom and Archer (2003)
$\text{AsO}_4^{3-} + 2\text{H}^+ = \text{H}_2\text{AsO}_4^-$	18.79	Nordstrom and Archer (2003)
$\text{AsO}_4^{3-} + 3\text{H}^+ = \text{H}_3\text{AsO}_4$	21.09	Nordstrom and Archer (2003)
$\text{AsO}_4^{3-} + 2\text{H}^+ + \text{Fe}^{2+} = \text{FeH}_2\text{AsO}_4^+$	5.15	Whiting (1992)
$\text{AsO}_4^{3-} + \text{H}^+ + \text{Fe}^{2+} = \text{FeHAsO}_4$	6.1	Whiting (1992)
$\text{AsO}_4^{3-} + \text{Fe}^{2+} = \text{FeAsO}_4^-$	-13.60	Whiting (1992)
$\text{AsO}_4^{3-} + \text{H}^+ + \text{Mn}^{2+} = \text{MnHAsO}_4$	15.54	Whiting (1992)
$\text{AsO}_4^{3-} + \text{Mn}^{2+} = \text{MnAsO}_4^-$	6.1	Whiting (1992)
$\text{AsO}_4^{3-} + \text{H}^+ + \text{Mg}^{2+} = \text{MgHAsO}_4$	14.7	Whiting (1992)
$\text{AsO}_4^{3-} + \text{Mg}^{2+} = \text{MgAsO}_4^-$	6.3	Whiting (1992)
$\text{AsO}_4^{3-} + 2\text{H}^+ + \text{Ca}^{2+} = \text{CaH}_2\text{AsO}_4^+$	20.09	Bothe and Brown (1999)
$\text{AsO}_4^{3-} + \text{H}^+ + \text{Ca}^{2+} = \text{CaHAsO}_4$	14.46	Bothe and Brown (1999)
$\text{AsO}_4^{3-} + \text{Ca}^{2+} = \text{CaAsO}_4^-$	4.36	Bothe and Brown (1999)
Mo		
$\text{MoO}_4^{2-} + \text{H}^+ = \text{HMoO}_4^-$	4.299	Schecher and McAvoy (1998)
$\text{MoO}_4^{2-} + 2\text{H}^+ = \text{H}_2\text{MoO}_4$	8.164	Schecher and McAvoy (1998)
$7\text{MoO}_4^{2-} + 8\text{H}^+ = \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O}$	52.99	Schecher and McAvoy (1998)
$7\text{MoO}_4^{2-} + 9\text{H}^+ = \text{HMo}_7\text{O}_{24}^{5-} + 4\text{H}_2\text{O}$	59.377	Schecher and McAvoy (1998)
$7\text{MoO}_4^{2-} + 10\text{H}^+ = \text{H}_2\text{Mo}_7\text{O}_{24}^{4-} + 4\text{H}_2\text{O}$	64.169	Schecher and McAvoy (1998)
$7\text{MoO}_4^{2-} + 11\text{H}^+ = \text{H}_3\text{Mo}_7\text{O}_{24}^{3-} + 4\text{H}_2\text{O}$	67.405	Schecher and McAvoy (1998)
$8\text{MoO}_4^{2-} + 12\text{H}^+ = \text{Mo}_8\text{O}_{26}^{4-} + 6\text{H}_2\text{O}$	71.62	Yagasaki et al. (1987)
$8\text{MoO}_4^{2-} + 13\text{H}^+ = \text{HMo}_8\text{O}_{26}^{3-} + 6\text{H}_2\text{O}$	73.38	Yagasaki et al. (1987)
$8\text{MoO}_4^{2-} + 15\text{H}^+ = \text{H}_3\text{Mo}_8\text{O}_{26}^- + 6\text{H}_2\text{O}$	76.34	Yagasaki et al. (1987)
$\text{MoO}_4^{2-} + \text{Ca}^{2+} = \text{CaMoO}_4$	2.57	Essington (1992)
$\text{MoO}_4^{2-} + \text{Mg}^{2+} = \text{MgMoO}_4$	2.958	Essington (1992)
$\text{MoO}_4^{2-} + \text{K}^+ = \text{KMoO}_4^-$	1.29	Essington (1992)
$\text{MoO}_4^{2-} + \text{Na}^+ = \text{NaMoO}_4^-$	1.66	Essington (1992)
Sb		
$\text{Sb}(\text{OH})_6^- + \text{H}^+ = \text{Sb}(\text{OH})_5 + \text{H}_2\text{O}$	2.82	Filella and May (2003)
$\text{Sb}(\text{OH})_6^- + 2\text{H}^+ = \text{Sb}(\text{OH})_4^+ + 2\text{H}_2\text{O}$	0.54	Filella and May (2003)

Table 2. Mean concentrations (\pm SD) of total dissolved solutes including fulvic and humic acids in water overlying Lake Tantaré sediments, as well as free-ion activity, major trace element species and saturation index ($SI = \log IAP/K_s$) predicted by WHAM 6 (see section 3.1 for details on the thermodynamic calculations).

Solute	Total concentration ^a	Free-ion activity ^d	Major species ^e (%)	SI ^f
Ag	$6.3 \pm 3.6 \times 10^{-12}$ M	(Ag ⁺) = 5.94×10^{-12}	Ag ⁺ (94%)	≤ -11.9
As	$1.9 \pm 1.0 \times 10^{-9}$ M	(AsO ₄ ³⁻) = 1.25×10^{-16}	H ₂ AsO ₄ ⁻ (96%)	= -64.3
Ca	$2.0 \pm 0.2 \times 10^{-5}$ M	(Ca ²⁺) = 1.65×10^{-5}	Ca ²⁺ (83%)	≤ -5.3
Cd	$2.8 \pm 0.4 \times 10^{-10}$ M	(Cd ²⁺) = 1.83×10^{-10}	Cd ²⁺ (65%)	≤ -4.9
Cu	$2.7 \pm 1.3 \times 10^{-9}$ M	(Cu ²⁺) = 1.7×10^{-11}	Cu-HS (99.3%)	≤ -7.2
Hg	$3.7 \pm 1.0 \times 10^{-12}$ M	(Hg ²⁺) = 1.45×10^{-34}	Hg-HS (99.9%)	= -24.3
In	$5.0 \pm 2.0 \times 10^{-13}$ M	(In ³⁺) = 3.98×10^{-18}	In-HS (78%)	≤ -5.7
MeHg	$2.6 \pm 1.0 \times 10^{-13}$ M	(MeHg ⁺) = 1.68×10^{-14}	MeHgOH (79%)	
Mg	$8.7 \pm 0.3 \times 10^{-6}$ M	(Mg ²⁺) = 7.75×10^{-6}	Mg ²⁺ (84%)	≤ -6.6
Mo	$3.1 \pm 0.8 \times 10^{-10}$ M	(MoO ₄ ²⁻) = 2.91×10^{-10}	MoO ₄ ²⁻ (94%)	≤ -8.7
Pb	$0.4 \pm 0.2 \times 10^{-9}$ M	(Pb ²⁺) = 8.49×10^{-11}	Pb-HS (77%)	≤ -5.9
Sb	$1.5 \pm 0.1 \times 10^{-10}$ M	(Sb(OH) ₆ ⁻) = 1.5×10^{-10}	Sb(OH) ₆ ⁻ (100%)	
Zn	$6.0 \pm 1.0 \times 10^{-8}$ M	(Zn ²⁺) = 4.19×10^{-8}	Zn ²⁺ (70%)	≤ -6.3
C _{org}	$2.5 \pm 0.4 \times 10^{-3}$ g L ⁻¹			
HA ^b	$5.1 \pm 0.8 \times 10^{-4}$ g L ⁻¹			
FA ^b	$4.6 \pm 0.8 \times 10^{-3}$ g L ⁻¹			
[L] _T ^c	3.5×10^{-5} mol sites L ⁻¹			

^a: Average of between 19 and 80 measurements; [Ag], [As], [Cd], [In], [Mo], [Pb] and [Sb] were from previous studies at the same site (see text).

^b: To estimate [FA] and [HA] it was assumed that all C_{org} is humic substances comprising 50% C with a molar ratio [FA]:[HA] of 9.

^c: $[L]_T = [HA] \times n_{HA} + [FA] \times n_{FA}$ where n_{HA} is 4.9×10^{-3} mol site per g of HA and n_{FA} is 7.1×10^{-3} mol site per g of FA

^d: (X) is for the activity of species X.

^e: HS is for humic substances.

^f: (hydr)oxide and carbonate solid phases were considered.

Table 3. Mean (\pm SD) trace element/Fe (TE/Fe), trace element/organic C (TE/C_{org}) and C_{org}/N molar ratios in the diagenetic material collected on Teflon sheets in Lake Tantaré sediment.

TE/Fe	Mean (\pm SD)	TE/C _{org}	Mean (\pm SD)
Ag/Fe	$2.8 \pm 1.0 \times 10^{-7}$	Ag/C _{org}	$1.1 \pm 0.5 \times 10^{-7}$
As/Fe	$2.8 \pm 0.2 \times 10^{-4}$	As/C _{org}	$1.1 \pm 0.2 \times 10^{-4}$
Ca/Fe	$5.6 \pm 1.1 \times 10^{-3}$	Ca/C _{org}	$2.2 \pm 0.5 \times 10^{-3}$
Cd/Fe	$9.8 \pm 1.0 \times 10^{-7}$	Cd/C _{org}	$3.9 \pm 0.5 \times 10^{-7}$
Cu/Fe	$2.8 \pm 0.7 \times 10^{-5}$	Cu/C _{org}	$1.1 \pm 0.2 \times 10^{-5}$
Hg/Fe	$1.3 \pm 0.3 \times 10^{-7}$	Hg/C _{org}	$4.9 \pm 0.7 \times 10^{-8}$
In/Fe	$1.4 \pm 0.4 \times 10^{-7}$	In/C _{org}	$5.4 \pm 2.0 \times 10^{-8}$
MeHg/Fe	$6.5 \pm 1.9 \times 10^{-10}$	MeHg/C _{org}	$2.5 \pm 0.6 \times 10^{-10}$
Mg/Fe	$1.2 \pm 0.2 \times 10^{-3}$	Mg/C _{org}	$4.6 \pm 0.8 \times 10^{-4}$
Mo/Fe	$6.3 \pm 0.3 \times 10^{-5}$	Mo/C _{org}	$2.5 \pm 0.3 \times 10^{-5}$
Pb/Fe	$1.9 \pm 0.2 \times 10^{-4}$	Pb/C _{org}	$7.4 \pm 1.0 \times 10^{-5}$
Sb/Fe	$3.1 \pm 0.6 \times 10^{-6}$	Sb/C _{org}	$1.2 \pm 0.3 \times 10^{-6}$
Zn/Fe	$9.0 \pm 2.9 \times 10^{-5}$	Zn/C _{org}	$3.6 \pm 1.4 \times 10^{-5}$
C _{org} /N	15.3 ± 3.4		
C _{org} /Fe	2.6 ± 0.3		
HS/Fe ^a	0.41		
Σ TE/Fe	0.0075		

^a: Units are moles of metal binding sites per mole of Fe oxyhydroxides. Calculated from the C_{org}/Fe molar ratio, with the assumptions that the abundance of metal binding sites for FA and HA are 7.1×10^{-3} mol per g of FA and 4.9×10^{-3} mol per g of HA, respectively (Tipping, 1994), and that all C_{org} is humic substances comprising 50% C with a molar ratio [FA]:[HA] of 9.

Table 4. Intrinsic surface complexation constants K^{int} at $I = 0$ used for the calculation of *in situ* adsorption of the elements by Fe oxyhydroxides^a.

Reaction	$\log K^{int}$	Reference
$\equiv\text{FeOH}_2^+ = \equiv\text{FeOH} + \text{H}^+$	-7.29	Dzombak and Morel (1990)
$\equiv\text{FeOH} = \equiv\text{FeO}^- + \text{H}^+$	-8.93	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Ag}^+ = \equiv\text{FeOAg} + \text{H}^+$	-1.72	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Ag}^+ = \equiv\text{FeOAg} + \text{H}^+$	-5.3	Estimated from LFER ^b
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Ca}^{2+} = \equiv\text{FeOHCa}^{2+}$	4.97	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Ca}^{2+} = \equiv\text{FeOCa}^+ + \text{H}^+$	-5.85	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Cd}^{2+} = \equiv\text{FeOCd}^+ + \text{H}^+$	0.47	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Cd}^{2+} = \equiv\text{FeOCd}^+ + \text{H}^+$	-2.90	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Cu}^{2+} = \equiv\text{FeOCu}^+ + \text{H}^+$	2.89	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Cu}^{2+} = \equiv\text{FeOCu}^+ + \text{H}^+$	0.6	Dzombak and Morel (1990)
$\equiv\text{FeOH} + \text{Hg}^{2+} = \equiv\text{FeOHg}^+ + \text{H}^+$	6.9	Tiffreau et al. (1995)
$\equiv\text{FeOH} + \text{Hg}^{2+} + \text{H}_2\text{O} = \equiv\text{FeOHgOH} + 2\text{H}^+$	-0.9	Tiffreau et al. (1995)
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{MeHg}^+ = \equiv\text{FeOMeHg} + \text{H}^+$	6.67	Estimated from LFER ^b
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{MeHg}^+ = \equiv\text{FeOMeHg} + \text{H}^+$	4.41	Estimated from LFER ^b
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Mg}^{2+} = \equiv\text{FeOHMg}^{2+}$	4.97	Assumed identical to Ca ^c
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Mg}^{2+} = \equiv\text{FeOMg}^+ + \text{H}^+$	-4.6	Estimated from LFER ^b
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Pb}^{2+} = \equiv\text{FeOPb}^+ + \text{H}^+$	-3.5	Estimated from LFER ^b
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Pb}^{2+} = \equiv\text{FeOPb}^+ + \text{H}^+$	0.3	Estimated from LFER ^b
$\equiv\text{Fe}^{\text{s}}\text{OH} + \text{Zn}^{2+} = \equiv\text{FeOZn}^+ + \text{H}^+$	0.99	Dzombak and Morel (1990)
$\equiv\text{Fe}^{\text{w}}\text{OH} + \text{Zn}^{2+} = \equiv\text{FeOZn}^+ + \text{H}^+$	-1.99	Dzombak and Morel (1990)
$\equiv\text{FeOH} + \text{SbO}(\text{OH})_4^- + \text{H}^+ = \equiv\text{FeSbO}(\text{OH})_4 + \text{H}_2\text{O}$	8.4	Dzombak and Morel (1990)
$\equiv\text{FeOH} + \text{SbO}(\text{OH})_4^- = \equiv\text{FeOHSbO}(\text{OH})_4^-$	1.3	Dzombak and Morel (1990)
$\equiv\text{FeOH} + \text{AsO}_4^{3-} + 3\text{H}^+ = \equiv\text{FeH}_2\text{AsO}_4 + \text{H}_2\text{O}$	29.88	Dixit and Hering (2003)
$\equiv\text{FeOH} + \text{AsO}_4^{3-} + 2\text{H}^+ = \equiv\text{FeHAsO}_4^- + \text{H}_2\text{O}$	24.43	Dixit and Hering (2003)
$\equiv\text{FeOH} + \text{MoO}_4^{2-} = \equiv\text{FeOHMoO}_4^{2-} + \text{H}_2\text{O}$	3.14	Gustaffson (2003)
$\equiv\text{FeOH} + \text{MoO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O} = \equiv\text{FeOMo}(\text{OH})_5$	17.96	Gustaffson (2003)

^a: “ \equiv ” refers to adsorption sites; “s” and “w” refer to strong and weak adsorption sites, respectively, in the two-layer surface complexation model.

^b: Estimated from linear free energy relationship (LFER) as described in Dzombak and Morel (1990).

^c: K^{int} for adsorption of Mg on strong adsorption sites is assumed to be identical to that of Ca.

Table 5. Total measured concentrations of the elements in the top 0.5-cm layer of Lake Tantaré sediments compared to those predicted to be associated with diagenetic material or to organic matter in this sediment layer. Also given are the Fe oxyhydroxide (Fe-ox) and organic C concentrations and the C_{org}/N molar ratio in this sediment layer.

	Measured concentration or molar ratio	Predicted concentration	
		Authigenic ^a	Organically-bound ^b
{C _{org} } (mol C g ⁻¹)	2.02 ± 0.08 × 10 ⁻²		
{Fe-ox} (mol g ⁻¹)	1.55 ± 0.05 × 10 ⁻³		
C _{org} /N	15.5		
{C _{org} }/{Fe-ox}	13		
{Hg} _T (mol g ⁻¹)	3.0 ± 0.1 × 10 ⁻⁹	1.9 ± 0.5 × 10 ⁻¹⁰	1.0 ± 0.2 × 10 ⁻⁹
{MeHg} (mol g ⁻¹)	7.6 ± 1.1 × 10 ⁻¹¹	1.0 ± 0.3 × 10 ⁻¹²	5.0 ± 1.2 × 10 ⁻¹²
{Ag} (mol g ⁻¹)	2.8 × 10 ⁻⁹	4.3 ± 1.4 × 10 ⁻¹⁰	
{As} (mol g ⁻¹)	2.3 ± 0.1 × 10 ⁻⁷	4.3 ± 0.3 × 10 ⁻⁷	
{Cd} (mol g ⁻¹)	1.8 × 10 ⁻⁹	1.5 ± 0.2 × 10 ⁻⁹	7.8 ± 1.1 × 10 ⁻⁹
{Cu} (mol g ⁻¹)	3.7 × 10 ⁻⁷	4.4 ± 1.1 × 10 ⁻⁸	2.2 ± 0.4 × 10 ⁻⁷
{In} (mol g ⁻¹)	1.1 × 10 ⁻⁹	2.1 ± 0.6 × 10 ⁻¹⁰	1.1 ± 0.4 × 10 ⁻⁹
{Mo} (mol g ⁻¹)	1.2 ± 0.01 × 10 ⁻⁷	1.0 ± 0.1 × 10 ⁻⁷	
{Pb} (mol g ⁻¹)	5.4 ± 0.2 × 10 ⁻⁷	2.9 ± 0.3 × 10 ⁻⁷	1.5 ± 0.2 × 10 ⁻⁶
{Sb} (mol g ⁻¹)	1.6 × 10 ⁻⁸	4.7 ± 0.9 × 10 ⁻⁹	
{Zn} (mol g ⁻¹)	1.1 × 10 ⁻⁶	1.4 ± 0.5 × 10 ⁻⁷	7.2 ± 2.8 × 10 ⁻⁷

^a: obtained by multiplying the TE/Fe ratios given in Table 2 by the sedimentary Fe oxyhydroxide concentration in the top 0.5-cm sediment layer.

^b: obtained by multiplying the TE/C_{org} ratios given in Table 2 by the sedimentary C_{org} concentration in the top 0.5-cm sediment layer.

Figures

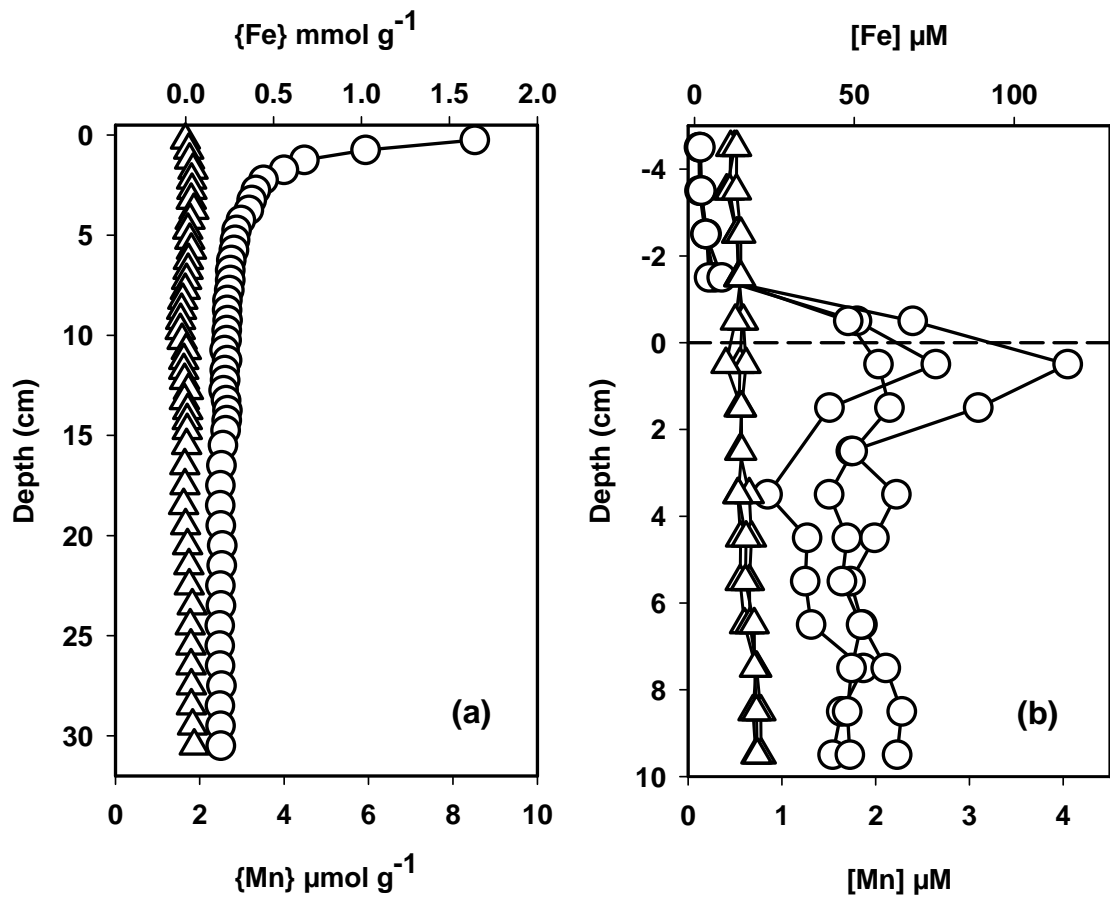


Fig. 1

Figure 1. Depth distributions of Fe (\circ) and Mn (Δ) in sediments (a) and sediment porewaters (b) at the sampling site.

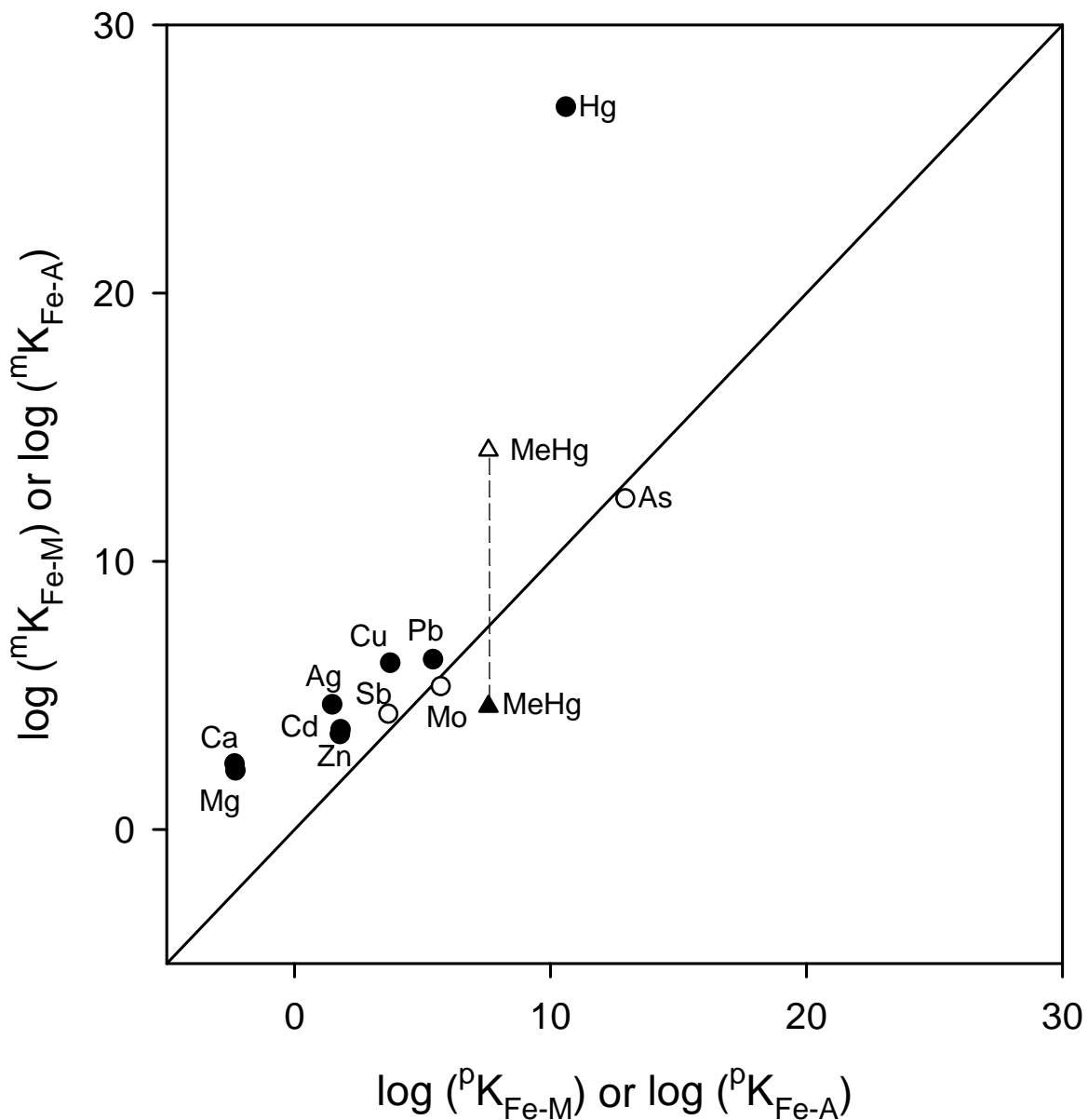


Fig. 2

Figure 2. Comparison between values of the conditional equilibrium constant obtained from *in situ* measurements (${}^m K_{Fe-M}$ and ${}^m K_{Fe-A}$) with those predicted by the two-layer version of the surface complexation model (${}^P K_{Fe-M}$ and ${}^P K_{Fe-A}$). The 1:1 line is shown. Open and filled circles are used for anions and cations (except MeHg), respectively. Triangles represent ${}^P K_{Fe-M}$ values obtained when the $MeHg^+$ activity was calculated with WHAM 6 using either default (open triangle) or revised (filled triangle) formation constants for MeHg complexes with both HA and FA.

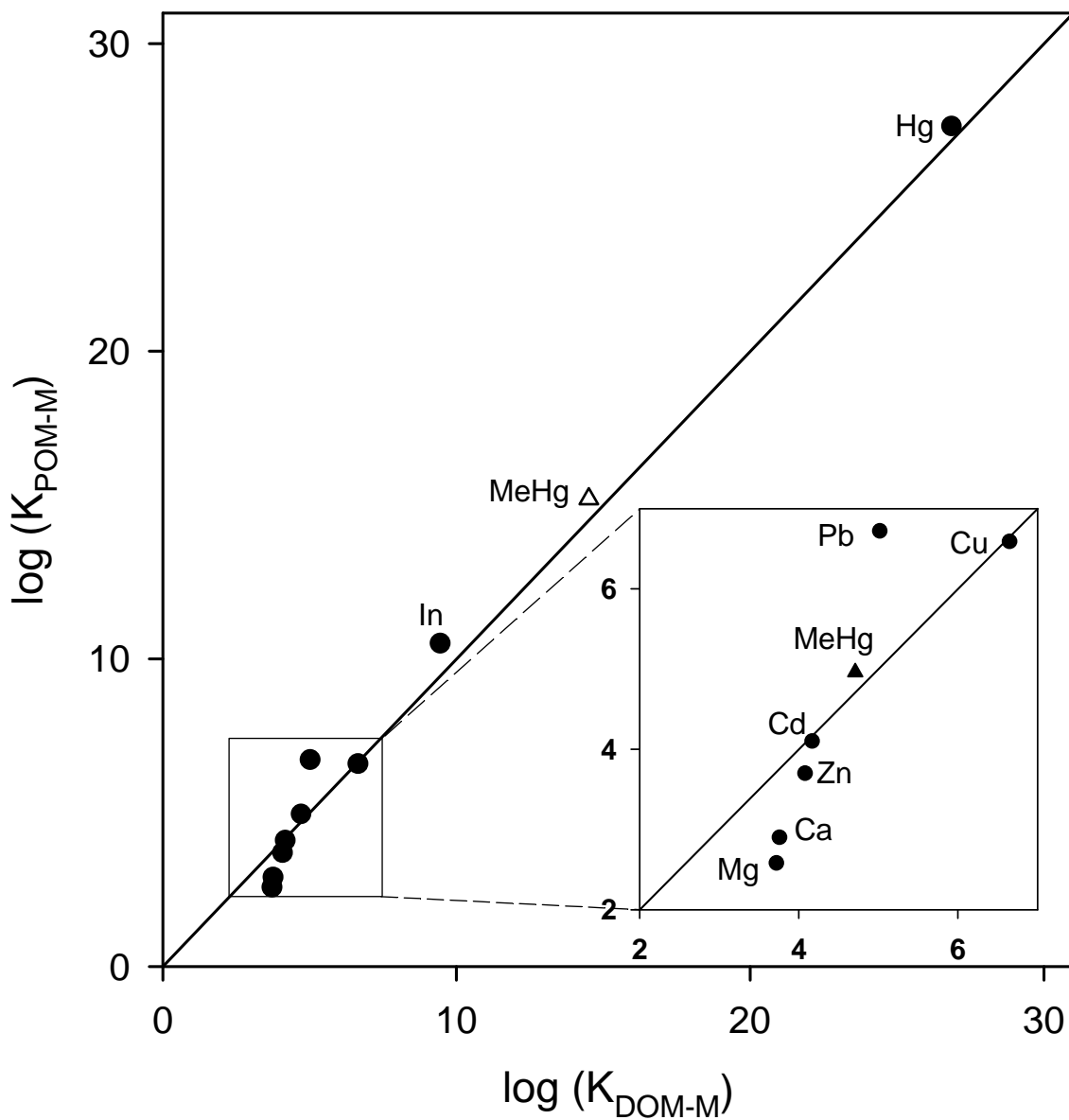


Fig. 3

Figure 3. Comparison between the conditional constants for trace metal binding with dissolved (K_{DOM-M}) and adsorbed (K_{POM-M}) natural organic matter assumed to be humic substances. The 1:1 line is shown. Triangles represent values obtained when the $MeHg^+$ activity was calculated with WHAM 6 using either default (open triangle) or revised (filled triangle) formation constants for MeHg complexes with both HA and FA.