

Arsenic, iron and sulfur co-diagenesis in lake sediments

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Abstract

Profiles of porewater pH and dissolved As, Fe, Mn, sulfate, total sulfide (ΣS^{-II}), total zero-valent sulfur (ΣS^0), organic carbon and major ion concentrations, as well as those of solid As, acid-volatile sulfide (AVS), total S, Fe, Mn, Al, organic C, ^{210}Pb and ^{137}Cs were determined in the sediment of four lakes spanning a range of redox and geochemical conditions. An inverse modeling approach, based on a one-dimensional transport-reaction equation assuming steady-state, was applied to the porewater As profiles and used to constrain the net rates of reactions involving As ($R_{\text{net}}^{\text{As}}$). The model defines depth intervals where As is either released to (positive $R_{\text{net}}^{\text{As}}$) or removed from (negative $R_{\text{net}}^{\text{As}}$) the porewaters.

At two of the sites, whose bottom water were oxygenated at sampling time, a production zone ($R_{\text{net}}^{\text{As}} = 12 \times 10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$ – $71 \times 10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$) is inferred a few cm below the sediment–water interface, coincident with sharp porewater As and Fe peaks that indicate an intense coupled recycling of As and Fe. This process is confirmed by solid As and Fe maxima just below the sediment surface. In these two lakes a zone of As consumption ($R_{\text{net}}^{\text{As}} = -5 \times 10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$ to $-53 \times 10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$), attributed to the slow adsorption of As to authigenic Fe oxyhydroxides, occurs just above the production zone. A second-order rate constant $k_{\text{ads}}^{\text{As}}$ of $0.12 \pm 0.03 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ is estimated for this adsorption reaction.

Such features in the porewater and solid profiles were absent from the two other lakes that develop a seasonally anoxic hypolimnion. Thermodynamic calculations indicate that the porewaters of the four lakes, when sulfidic (i.e., $\Sigma S^{-II} \geq 0.1 \mu\text{M}$), were undersaturated with respect to all known solid As sulfides; the calculation also predicts the presence of As^{V} oxythioanions in the sulfidic waters, as suggested by a recent study. In the sulfidic waters, the removal of As ($R_{\text{net}}^{\text{As}} = -1 \times 10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$ to $-23 \times 10^{-18} \text{ mol cm}^{-3} \text{ s}^{-1}$) consistently occurred when saturation, with respect to $\text{FeS}_{(\text{s})}$, was reached and when As^{V} oxythioanions were predicted to be significant components of total dissolved As. This finding has potential implications for As transport in other anoxic waters and should be tested in a wider variety of natural environments.

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1. INTRODUCTION

Sediment-bound arsenic represents a worldwide public health concern because it can contaminate water used for drinking and irrigation (Smedley and Kinniburgh, 2002; Polizzotto et al., 2008). Although it is generally recognized that the biogeochemical cycling of arsenic (As) in aquatic sediments is closely coupled to that of iron (Fe), sulfur (S) and organic carbon (C_{ORG}) (e.g., Harvey et al., 2002; O'Day et al., 2004; Wilkin and Ford, 2006), the reactions

driving arsenic release and sequestration by sediments are not fully characterized (e.g., Harvey et al., 2002, 2003).

In aquatic environments where bottom water is oxygenated, it is well established that As is recycled with Fe oxyhydroxides during early diagenesis of sediments (e.g., Belzile and Tessier, 1990; Root et al., 2007), but the kinetics of As–Fe interactions are not well known. In modeling adsorption of As onto authigenic Fe oxyhydroxides, it is commonly assumed that it is a fast process compared to transport processes such as diffusion (e.g., Raven et al., 1998; Postma et al., 2007). However, several field studies have reported that porewater As is able to diffuse through a thick layer of authigenic Fe oxyhydroxides in lake sediments (Martin and Pedersen, 2002; Senn et al., 2007),

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suggesting that As adsorption may instead be a rate-limited process. This latter hypothesis is strengthened by laboratory experiments showing that dissolved natural organic matter can slow down or impede As adsorption onto synthetic Fe oxyhydroxides (Redman et al., 2002; Bauer and Blodau, 2009).

Reducing conditions within the sediments, or at the sediment–water interface if anoxia has developed in the bottom waters, drive the dissolution of the Fe oxyhydroxides and the release of both As and Fe to the (pore)waters (e.g., Root et al., 2007). As the Fe^{II} produced consumes the available aqueous $\text{S}^{-\text{II}}$ (Morse and Rickard, 2004), dissolved As may be sequestered by co-precipitation with (Aggett and O'Brien, 1984), or adsorption onto authigenic Fe sulfide minerals (Farquhar et al., 2002; Bostick and Fendorf, 2003; Bostick et al., 2004; Wolthers et al., 2005). If all of the Fe^{II} is fixed as solid Fe sulfides, the remaining aqueous $\text{S}^{-\text{II}}$ becomes available to complex As (e.g., Wilkin et al., 2003) and to form solid As sulfide minerals, provided that As concentrations are sufficiently high to exceed the solubility of such minerals (O'Day et al., 2004; Hollibaugh et al., 2005). However, a major difficulty in interpreting As geochemistry in sulfidic waters is that there is no consensus in the literature on the thermodynamically stable species of As under these conditions. Until very recently, only reduced As^{III} was thought to be stable in sulfidic waters in the form of thioarsenites. However, laboratory experiments (Wallschläger and Staley, 2007) and *ab initio* theoretical calculations (Helz and Tossell, 2008) have highlighted the existence of As^{V} species in sulfidic waters and the role of zero-valent sulfur (S^0) in oxidizing As^{III} . The implication of these findings for As mobility in sediment have yet to be explored.

We report on the distribution of As and of a suite of geochemical parameters in porewaters and sediments of four lakes spanning a range of sedimentary and dissolved sulfur concentrations. Our extensive dataset is used to discuss the speciation of dissolved As in the porewaters as calculated using two relevant, yet contradictory, thermodynamic models. Using inverse transport-reaction modeling and surface complexation modeling we infer reactions involving As during early diagenesis and estimate their *in situ* rates. Lastly, we quantify the authigenic and anthropogenic contributions to sedimentary As enrichments at the study sites.

2. METHODS

2.1. Study sites

This study took place in four oligotrophic headwater lakes located in the Province of Québec, Eastern Canada (Fig. 1; Table 1). The Canadian Shield Lakes Tantaré and Bédard are located at 39 and 51 km, respectively, from Québec, a city of about 500,000 inhabitants; Lake Tantaré is acidic, whereas Lake Bédard is circumneutral. Lakes Du Syndicat and Holland belong to the Appalachian Region, have slightly alkaline waters, and are found 33 and 8 km, respectively, from Murdochville, a small town on the Gaspé Peninsula where a copper smelter was in operation from 1951 to 2002. The uninhabited watersheds of these lakes have been negligibly impacted by wood harvesting (with

the exception of Lake Bédard) or wildfires; thus, their As contamination arises from atmospheric transport only. Lake Tantaré was sampled in July 2003, September 2003 and August 2004, Lake Bédard in September 2004 and Lakes Du Syndicat and Holland in August 2005. At sampling time, the hypolimnetic waters were oxygenated ($>3.75 \text{ mg O}_2 \text{ L}^{-1}$) in Lakes Tantaré and Du Syndicat and anoxic in Lakes Bédard and Holland ($<0.01 \text{ mg O}_2 \text{ L}^{-1}$). Sediment dating, sediment mass accumulation rates (ω ; $\text{mg cm}^{-2} \text{ yr}^{-1}$) and sedimentation rates (v_s ; mm yr^{-1}) were obtained from the depth profiles of excess ^{210}Pb , according to Appleby (2001); details on the procedure used are given in the Electronic Annex whereas the ranges of ω and v_s are shown in Table 1.

2.2. Sampling

Two sediment cores, collected at the deepest site of each lake (Table 1) by divers using butyrate tubes (internal diameter of 9.5 cm), were extruded within 2 h and sectioned at 0.5-cm intervals from the sediment surface to 15 cm depth and then at 1-cm intervals to 30 cm depth. Sediment samples from one core were stored in polyethylene containers, while those of the other core, dedicated to acid-volatile sulfide (AVS) measurements, were individually sealed in plastic bags that were put into a larger bag filled with anoxic sediment to prevent their oxidation.

Samples of water overlying the sediment and of pore-water were collected using diffusion samplers (Plexiglas peepers with two columns of horizontal cells) at 1-cm intervals from 5 cm above the sediment–water interface to 10 cm below, or at 0.5-cm intervals from 2.5 cm above the sediment–water interface to 2.5 cm below, and then at 1-cm intervals down to 10 cm depth. Prior to their deployment, the peepers were immersed in an acidic solution for 7 d, rinsed thoroughly with ultrapure water ($>18 \text{ M}\Omega \text{ cm}$) and kept for 14 d under a N_2 atmosphere renewed daily. The peeper cells were then filled with ultrapure water, covered by a Gelman HT-200 polysulfone membrane (0.2 μm nominal pore size), and by a thin Plexiglas sheet with holes fitting the cell apertures. The assembled peepers were stored again until their deployment (for at least 7 d) under N_2 to ensure complete removal of oxygen (Carignan et al., 1994). At each sampling date and coring site, six peepers were inserted into the sediments by divers and left in place for 21 days. Upon retrieval, the peepers were sampled as described in Alfaro-De la Torre and Tessier (2002) in order to determine three independent profiles of pH and of As, Fe, Mn, Ca, K, Mg, Na, total sulfide ($\Sigma\text{S}^{-\text{II}}$), total dissolved zero-valent sulfur (ΣS^0), sulfate, Cl, dissolved organic C (DOC) and dissolved inorganic C (DIC) concentrations.

Thin Teflon sheets (7 $\times$ 15 cm) that had been vertically inserted in the sediments by divers in October 1993, leaving 5 cm of the sheets above the sediment–water interface, were retrieved in August 2006, rinsed with lake water and stored in polyethylene containers. During this 13-year deployment, the sheets collected Fe oxyhydroxides precipitating close to the sediment surface (Belzile et al., 1989). Fe oxyhydroxides particles previously collected in this lake by the same technique were identified as poorly crystalline fer-

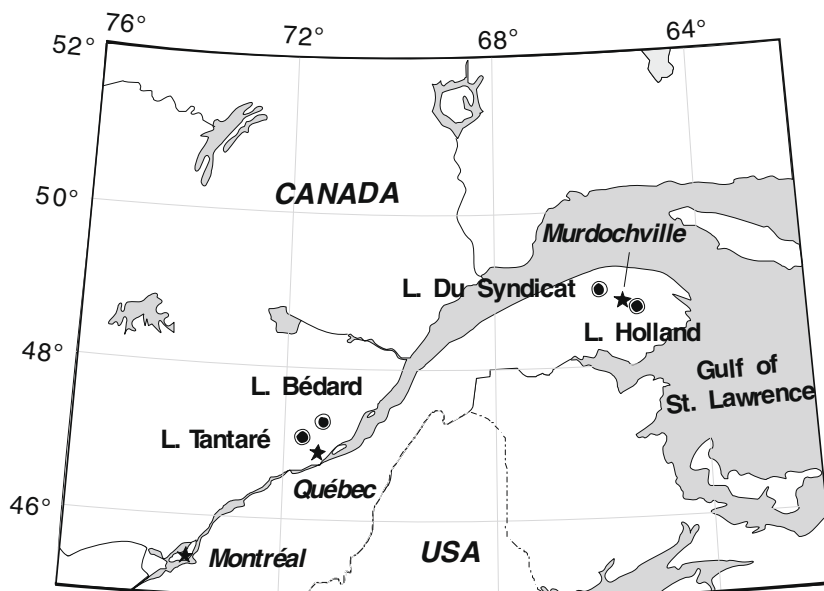


Fig. 1. Map showing the location of Lakes Tantaré, Du Syndicat, Bédard, and Holland.

Table 1
Location and characteristics of the study sites.

	L. Tantaré ^a	L. Du Syndicat	L. Bédard	L. Holland
Location	47°04'N 71°33'W	49°05'N 65°57'W	47°16'N 71°07'W	48°56'N 65°23'W
Geological region	Can. Shield	Appalachian	Can. Shield	Appalachian
Altitude (m)	450	676	680	475
Sampling depth (m)	15	13	10	11
pH (water column)	5.4–6.0	7.2–7.6	6.9–7.0	7.5–7.6
Sediment mass accumulation rate ^b (ω ; mg cm ⁻² yr ⁻¹)	4.0–7.3		2.4–46.8	4.5–15.7
Sedimentation rate (v_s ; mm yr ⁻¹)	0.9–1.3		0.5–2.6	0.5–4.4
Inventory of unsupported ²¹⁰ Pb (²¹⁰ Pb _{sed} ; Bq cm ⁻²)	0.37	1.65	0.62	0.61
Hypolimnion at sampling time	Oxygenated	Oxygenated	Anoxic	Anoxic

^a Westernmost basin.

^b Details on the calculations are given in the [Electronic Annex](#).

rihydrite and lepidocrocite by Fortin et al. (1993), using electron microscopy and X-ray diffraction.

2.3. Analyses

Freeze-dried sediment aliquots were ground, homogenized and digested on a hot plate with ultrapure HNO₃, HClO₄ and HF. After complete digestion, the acids were evaporated to near dryness and the residues were re-dissolved in 0.2 N HNO₃ (McLaren et al., 1995). Arsenic concentrations in the final solutions were determined by hydride generation-atomic absorption spectrometry (HG-AAS, Perkin-Elmer 2100 spectrometer) according to Nielsen and Hansen (1997), using a volume-based flow injection procedure (FI, Perkin-Elmer Model FIAS 400 flow injection unit with a five port FI-valve). The detection limit (3 SD of blank solutions) was 0.18 nM. The analytical precision, determined from the replicate analysis ($n = 6$) of the reference sediments MESS-3 and PACS-2 (National Re-

search Council of Canada), whose certified As concentrations (283 ± 15 and 349 ± 20 nmol g⁻¹, respectively) are of the same order of magnitude as those measured in our sediment samples (75 – 1100 nmol g⁻¹), was $\pm 2\%$ and $\pm 4\%$, respectively. Our average measured values were 5% and 2% larger than those certified for MESS-3 and PACS-2, respectively. The analytical protocols used to measure Mn, Fe and radio-isotopes (²¹⁰Pb, ²¹⁴Pb and ¹³⁷Cs) in the solid phase are given in Chappaz et al. (2008). Acid-volatile sulfide (AVS) was determined on wet samples according to the protocol described by Allen et al. (1993). A 6 N HCl solution was added to the sediments and the resulting sulfide gas was trapped in a NaOH solution and measured by colourimetry (Cline, 1969). Sediment organic C (C_{ORG}) and total sulfur (S_{TOT}) were both determined using a CNS Carbo Erba analyzer. The dry bulk density (DBD; g cm⁻³ of whole sediment) was calculated from our measured sediment C_{ORG} and water content, as described by Couture et al. (2008).

Total porewater As concentrations were also determined by a flow injection HG–AAS system which involves the simultaneous addition of HCl and NaBH₄ in the reaction vessel (Nielsen and Hansen, 1997). According to Planer-Friedrich and Wallschläger (2009), this setup prevents the precipitation of arsenic sulfides when analyzing As in sulfidic waters. Furthermore, thermodynamic calculation indicates that our As samples, once acidified by HCl at the pH required for the analysis, were undersaturated by more than two orders of magnitude with respect to As sulfide solids. The relative analytical standard deviation (RSD), as determined from the replicate analysis ($n = 10$) of the reference solution SLRS-4 (National Research Council of Canada), whose certified As concentration (9.1 ± 0.8 nM) is of the same order of magnitude as those measured in porewaters (1–16 nM), was $\pm 2\%$. Our average measured As value of SLRS-4 was 3% lower than the certified value. We measured porewater ΣS^{-II} , major cations and anions, DIC and DOC as described by Laforte et al. (2005) and ΣS^0 by square-wave cathodic stripping voltammetry as described by Wang et al. (1998). It should be noted that ΣS^{-II} and ΣS^0 are defined as (Wang and Tessier, 2009):

$$\Sigma S^{-II} = [H_2S] + [HS^-] + \Sigma [H_xS_nS^{x-2}] \quad (1)$$

$$\Sigma S^0 = [S^0_{(aq)}] + \Sigma n[H_xS_nS^{x-2}] \quad (2)$$

where x (0–2) and n (1–7) are the numbers of H and zero-valent S atoms in the polysulfide species $H_xS_nS^{x-2}$, respectively, and $S^0_{(aq)}$ is dissolved zero-valent sulfur.

Areas of the Teflon sheets showing diagenetic Fe-rich deposits were cut and the material was extracted with 5 mL of a 6 N HCl solution for 48 h at room temperature. The extracted solutions were diluted to 50 mL and filtered through 0.4 μ m Teflon filters. Arsenic, Fe and C_{ORG} concentrations in the extracted solutions were measured as described above for porewaters.

2.4. Thermodynamic modeling

Porewater As speciation was calculated with the computer code MINEQL+ version 4.6 (Schecher and McAvoy, 1992) using pH, ΣS^0 , ΣS^{-II} , and total dissolved concentrations of SO₄, CO₃, Cl, Fe, Mn, Ca, Mg, Na, K and As as input parameters. The MINEQL+ thermodynamic database was updated with the equilibrium constants given in Table 2. It should be noted that in our calculations of As speciation, we used two sets of reactions involving As, hereafter called models. The two models use the same sub-set of reactions for the ionization of As oxyacids and for the complexation of cations with oxyarsenates (reactions 3–18 in Table 2), but they differ in their treatment of As^V/As^{III} redox transformation and of As behavior in sulfidic waters. Several studies demonstrated that As thioanions dominate As speciation in sulfidic waters (Webster, 1990; Eary, 1992; Wilkin et al., 2003), but disagreements still remain on the oxidation state of As present in these thioanions (Wilkin et al., 2003; Hollibaugh et al., 2005; Stauder et al., 2005; Wallschläger and Stadey, 2007).

The reactions describing the formation of thioanions in Model 1 (reactions 19–24 in Table 2) are derived from

Wilkin et al. (2003); these authors assumed that As thioanions contain only As^{III}. Model 1 has been used in many studies to calculate As speciation in sulfidic waters and it is assumed in all of them that redox processes are controlled by the couple SO₄²⁻/HS⁻. (O'Day et al., 2004; Bostick et al., 2005; Haque and Johannesson, 2006; Lee et al., 2006; Keimowitz et al., 2007; Beak et al., 2008; Gallegos et al., 2008). The sub-set of reactions describing As sulfidation in Model 2 (reactions 19–45) was provided by Helz and Tossell (2008); these authors critically reviewed As speciation in previous laboratory studies and used an *ab initio* quantum chemical method to derive a provisional model of As speciation in sulfidic waters. A main feature of Model 2 is that it allows for the formation of both As^{III} and As^V thioanions in sulfidic waters. In their study, Helz and Tossell (2008) provided two explanations for the production of As^V in sulfidic waters: (i) the redox disproportionation of As^{III} into As^V and As⁰ or (ii) the oxidation of As^{III} by zero-valent sulfur. Since we measured porewater ΣS^0 , our study allows testing the latter hypothesis; dissolved elemental sulfur has been shown to be common in various sulfidic aquatic environments (Wang and Tessier, 2009).

In our calculations using Models 1 and 2, the redox state of As was allowed to vary (reaction 1 in Table 2). We assumed that the redox potential was controlled by the redox couples O₂/H₂O in the oxygenated overlying waters of Lakes Tantaré and Du Syndicat and Fe(II)/Fe(OH)_{3(s)} in porewater samples with ΣS^{-II} concentrations <0.1 μ M. In all sulfidic samples, hereafter defined as those with ΣS^{-II} concentrations ≥ 0.1 μ M, the redox potential was fixed by the redox couples SO₄²⁻/HS⁻ and S⁰_(aq)/HS⁻ for Models 1 and 2, respectively. The two different redox couples were chosen for consistency with the proposed models. It has been shown by Berner (1963) that the polysulfide/sulfide couple can control redox processes in sulfidic sediments. The use of Model 2 required the description of the formation of polysulfide species ($H_xS_nS^{x-2}$; reactions 46–66 in Table 2). It should be noted that all reactions expressed in terms of solid rhombic sulfur (S(α)_{8(s)}) in the literature were transformed and expressed in terms of S⁰_(aq), by adding the reaction $1/8 S(\alpha)_{8(s)} = S^0_{(aq)}$ (Wang and Tessier, 2009); this step is required for the treatment of these reactions by speciation codes.

3. RESULTS

3.1. Solid phase

In Lakes Tantaré and Du Syndicat, whose hypolimnion was oxygenated, sedimentary As concentrations ({As}) show a decrease from the sediment–water interface to 2–3 cm depth (Fig. 2a and b). Below this horizon, {As} increases with depth, reaches a maximum at 5.5 and 11.5 cm depth in Lake Tantaré and Du Syndicat, respectively, and then decreases to low and nearly constant values. Similarly to {As}, Fe concentration in the solid phase ({Fe}) falls sharply in the first 2 cm below the sediment surface in Lake Tantaré and the thickness of its enriched layer is similar to that of As (Fig. 2e). A surface enrichment is not observed for Mn, because the low pH val-

Table 2

Reactions for the formation of the various As and polysulfide species and their corresponding equilibrium constants added to the MINEQL+ database to calculate As speciation. The left-hand side of the reactions is expressed in terms of the MINEQL+ components $\text{As}^{\text{V}}\text{O}_4^{3-}$, $\text{As}^{\text{III}}\text{O}_3^{3-}$, $\text{S}_{(\text{aq})}^0$, H^+ and HS^- . When required, the reactions were expressed in terms of S_{aq}^0 using $1/8 \text{S}(\alpha)_{8(\text{s})} = \text{S}_{(\text{aq})}^0$; $\log K = -6.68$ (Wang and Tessier, 2009).

#	Reactions	Model 1		Model 2	
		Log K	Ref.	Log K	Ref.
<i>Electron transfer</i>					
1	$\text{As}^{\text{V}}\text{O}_4^{3-} + 2\text{e}^- + 2\text{H}^+ \leftrightarrow \text{As}^{\text{III}}\text{O}_3^{-3} + \text{H}_2\text{O}$	2.17	a	2.17	a
2	$\text{S}_{(\text{aq})}^0 + \text{H}^+ + 2\text{e}^- \leftrightarrow \text{HS}^-$			4.57	a
<i>Ionization</i>					
3	$\text{AsO}_3^{3-} + \text{H}^+ \leftrightarrow \text{HASO}_3^{2-}$	15.0	a	15.0	a
4	$\text{AsO}_3^{3-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{AsO}_3^-$	29.2	a	29.2	a
5	$\text{AsO}_3^{3-} + 3\text{H}^+ \leftrightarrow \text{H}_3\text{AsO}_3^0$	38.3	a	38.3	a
6	$\text{AsO}_4^{3-} + \text{H}^+ \leftrightarrow \text{HASO}_4^{2-}$	11.80	a	11.80	a
7	$\text{AsO}_4^{3-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{AsO}_4^-$	18.79	a	18.79	a
8	$\text{AsO}_4^{3-} + 3\text{H}^+ \leftrightarrow \text{H}_3\text{AsO}_4^0$	21.09	a	21.09	a
<i>Complexation</i>					
9	$\text{AsO}_4^{3-} + 2\text{H}^+ + \text{Fe}^{+2} \leftrightarrow \text{FeH}_2\text{AsO}_4^+$	5.15	b	5.15	b
10	$\text{AsO}_4^{3-} + \text{H}^+ + \text{Fe}^{+2} \leftrightarrow \text{FeHASO}_4^0$	6.1	b	6.1	b
11	$\text{AsO}_4^{3-} + \text{Fe}^{+2} \leftrightarrow \text{FeAsO}_4^-$	-13.6	b	-13.6	b
12	$\text{AsO}_4^{3-} + \text{H}^+ + \text{Mn}^{+2} \leftrightarrow \text{MnHASO}_4^0$	15.54	b	15.54	b
13	$\text{AsO}_4^{3-} + \text{Mn}^{+2} \leftrightarrow \text{MnAsO}_4^-$	6.1	b	6.1	b
14	$\text{AsO}_4^{3-} + \text{Mg}^{+2} \leftrightarrow \text{MgAsO}_4^-$	6.3	b	6.3	b
15	$\text{AsO}_4^{3-} + \text{H}^+ + \text{Mg}^{+2} \leftrightarrow \text{MgHASO}_4^0$	14.7	b	14.7	b
16	$\text{AsO}_4^{3-} + 2\text{H}^+ + \text{Ca}^{+2} \leftrightarrow \text{CaH}_2\text{AsO}_4^+$	20.09	c	20.09	c
17	$\text{AsO}_4^{3-} + \text{H}^+ + \text{Ca}^{+2} \leftrightarrow \text{CaHASO}_4^0$	14.46	c	14.46	c
18	$\text{AsO}_4^{3-} + \text{Ca}^{+2} \leftrightarrow \text{CaAsO}_4^-$	4.36	c	4.36	c
<i>Sulfidation</i>					
19	$\text{AsO}_3^{3-} + \text{HS}^- + 4\text{H}^+ \leftrightarrow \text{H}_3\text{AsSO}_2^0 + \text{H}_2\text{O}$	47.0	d	45.7	e
20	$\text{AsO}_3^{3-} + \text{HS}^- + 3\text{H}^+ \leftrightarrow \text{H}_2\text{AsSO}_2^- + \text{H}_2\text{O}$	41.8	d	42.0	e
21	$\text{AsO}_3^{3-} + 2\text{HS}^- + 3\text{H}^+ \leftrightarrow \text{HAS}_2\text{O}_2^{2-} + 2\text{H}_2\text{O}$	46.9	d	44.2	e
22	$\text{AsO}_3^{3-} + 3\text{HS}^- + 4\text{H}^+ \leftrightarrow \text{HAS}_3^{2-} + 3\text{H}_2\text{O}$	58.7	d	56.7	e
23	$\text{AsO}_3^{3-} + 3\text{HS}^- + 3\text{H}^+ \leftrightarrow \text{AsS}_3^{3-} + 3\text{H}_2\text{O}$	50.8	d		
24	$\text{AsO}_3^{3-} + 4\text{HS}^- + 6\text{H}^+ \leftrightarrow \text{As}(\text{SH})_4^- + 3\text{H}_2\text{O}$	74.8	d		
25	$\text{AsO}_3^{3-} + 2\text{HS}^- + 5\text{H}^+ \leftrightarrow \text{H}_3\text{AsS}_2\text{O}^0 + 2\text{H}_2\text{O}$			56.5	e
26	$\text{AsO}_3^{3-} + 3\text{HS}^- + 6\text{H}^+ \leftrightarrow \text{H}_3\text{AsS}_3^0 + 3\text{H}_2\text{O}$			69.0	e
27	$\text{AsO}_3^{3-} + \text{HS}^- + 4\text{H}^+ \leftrightarrow \text{H}_3\text{AsSO}_3^0 + \text{H}_2\text{O}$			39.1	e
28	$\text{AsO}_3^{3-} + 2\text{HS}^- + 5\text{H}^+ \leftrightarrow \text{H}_3\text{AsS}_2\text{O}_2^0 + 2\text{H}_2\text{O}$			46.2	e
29	$\text{AsO}_4^{3-} + 3\text{HS}^- + 6\text{H}^+ \leftrightarrow \text{H}_3\text{AsS}_3\text{O}^0 + 3\text{H}_2\text{O}$			56.7	e
30	$\text{AsO}_4^{3-} + 4\text{HS}^- + 7\text{H}^+ \leftrightarrow \text{H}_3\text{AsS}_4^0 + 4\text{H}_2\text{O}$			66.3	e
31	$\text{AsO}_3^{3-} + \text{HS}^- + 2\text{H}^+ \leftrightarrow \text{HAS}_2\text{O}_2^{2-} + \text{H}_2\text{O}$			27.9	e
32	$\text{AsO}_3^{3-} + 2\text{HS}^- + 4\text{H}^+ \leftrightarrow \text{H}_2\text{AsS}_2\text{O}^- + 2\text{H}_2\text{O}$			52.8	e
33	$\text{AsO}_3^{3-} + 3\text{HS}^- + 5\text{H}^+ \leftrightarrow \text{H}_2\text{AsS}_3^- + 3\text{H}_2\text{O}$			65.3	e
34	$\text{AsO}_4^{3-} + \text{HS}^- + 3\text{H}^+ \leftrightarrow \text{H}_2\text{AsSO}_3^- + \text{H}_2\text{O}$			35.8	e
35	$\text{AsO}_4^{3-} + \text{HS}^- + 2\text{H}^+ \leftrightarrow \text{HAS}_2\text{O}_3^{2-} + \text{H}_2\text{O}$			25.6	e
36	$\text{AsO}_4^{3-} + \text{HS}^- + \text{H}^+ \leftrightarrow \text{AsSO}_3^{3-} + \text{H}_2\text{O}$			17.6	e
37	$\text{AsO}_4^{3-} + 2\text{HS}^- + 4\text{H}^+ \leftrightarrow \text{H}_2\text{AsS}_2\text{O}_2^- + 2\text{H}_2\text{O}$			48.6	e
38	$\text{AsO}_4^{3-} + 2\text{HS}^- + 3\text{H}^+ \leftrightarrow \text{HAS}_2\text{O}_2^{2-} + 2\text{H}_2\text{O}$			41.5	e
39	$\text{AsO}_4^{3-} + 2\text{HS}^- + 2\text{H}^+ \leftrightarrow \text{AsS}_2\text{O}_2^{3-} + 2\text{H}_2\text{O}$			30.7	e
40	$\text{AsO}_4^{3-} + 3\text{HS}^- + 5\text{H}^+ \leftrightarrow \text{H}_2\text{AsS}_3\text{O}^- + 3\text{H}_2\text{O}$			58.3	e
41	$\text{AsO}_4^{3-} + 3\text{HS}^- + 4\text{H}^+ \leftrightarrow \text{HAS}_3\text{O}^{2-} + 3\text{H}_2\text{O}$			56.9	e
42	$\text{AsO}_4^{3-} + 3\text{HS}^- + 3\text{H}^+ \leftrightarrow \text{AsS}_3\text{O}^{3-} + 3\text{H}_2\text{O}$			46.1	e
43	$\text{AsO}_4^{3-} + 4\text{HS}^- + 6\text{H}^+ \leftrightarrow \text{H}_2\text{AsS}_4^- + 4\text{H}_2\text{O}$			68.6	e
44	$\text{AsO}_4^{3-} + 4\text{HS}^- + 5\text{H}^+ \leftrightarrow \text{HAS}_4^{2-} + 4\text{H}_2\text{O}$			67.1	e
45	$\text{AsO}_4^{3-} + 4\text{HS}^- + 4\text{H}^+ \leftrightarrow \text{AsS}_4^{3-} + 4\text{H}_2\text{O}$			61.9	e
<i>Formation of polysulfide species</i>					
46	$\text{S}_{(\text{aq})}^0 + \text{HS}^- \leftrightarrow \text{S}_2^{2-} + \text{H}^+$			-4.78	f
47	$2\text{S}_{(\text{aq})}^0 + \text{HS}^- \leftrightarrow \text{S}_3^{2-} + \text{H}^+$			2.92	f
48	$3\text{S}_{(\text{aq})}^0 + \text{HS}^- \leftrightarrow \text{S}_4^{2-} + \text{H}^+$			10.34	f
49	$4\text{S}_{(\text{aq})}^0 + \text{HS}^- \leftrightarrow \text{S}_5^{2-} + \text{H}^+$			17.25	f
50	$5\text{S}_{(\text{aq})}^0 + \text{HS}^- \leftrightarrow \text{S}_6^{2-} + \text{H}^+$			23.74	f
51	$6\text{S}_{(\text{aq})}^0 + \text{HS}^- \leftrightarrow \text{S}_7^{2-} + \text{H}^+$			29.84	f

Table 2 (continued)

#	Reactions	Model 1		Model 2	
		Log <i>K</i>	Ref.	Log <i>K</i>	Ref.
52	$7S_{(aq)}^0 + HS^- \leftrightarrow S_8^{2-} + H^+$			35.97	f
53	$S_{(aq)}^0 + HS^- \leftrightarrow HS_2^-$			5.25	f
54	$2S_{(aq)}^0 + HS^- \leftrightarrow HS_3^-$			10.75	f
55	$3S_{(aq)}^0 + HS^- \leftrightarrow HS_4^-$			16.97	f
56	$4S_{(aq)}^0 + HS^- \leftrightarrow HS_5^-$			23.28	f
57	$5S_{(aq)}^0 + HS^- \leftrightarrow HS_6^-$			29.25	f
58	$6S_{(aq)}^0 + HS^- \leftrightarrow HS_7^-$			35.02	f
59	$7S_{(aq)}^0 + HS^- \leftrightarrow HS_8^-$			40.91	f
60	$S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_2^0$			10.36	f
61	$2S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_3^0$			15.06	f
62	$3S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_4^0$			20.88	f
63	$4S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_5^0$			26.89	f
64	$5S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_6^0$			32.89	f
65	$6S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_7^0$			38.50	f
66	$7S_{(aq)}^0 + HS^- + H^+ \leftrightarrow H_2S_8^0$			44.31	f

References: a, Nordstrom and Archer (2003); b, Whiting (1992); c, Bothe and Brown (1999); d, Wilkin et al. (2003); e, Helz and Tossell (2008); f, Kamyshtny et al. (2004).

ues close to the sediment–water interface (pH 5.4–6.0) preclude the formation of Mn oxyhydroxides in the sediments of this lake (Laforte et al., 2005). Conversely, in the slightly alkaline Lake Du Syndicat (pH 7.2–7.9), the enriched As layer just below the sediment surface coincides with both a small Fe and a marked Mn enrichment (Fig. 2f). The mean ($\pm$ SD) {As}:{Fe} and {C_{ORG}}:{Fe} molar ratios for the Fe-rich deposits collected by the Teflon sheets in Lake Tantaré were $2.8 \pm 0.1 \times 10^{-4}$ ($n = 7$) and 2.6 ± 0.3 ($n = 7$), respectively. In Lake Du Syndicat, where diagenetic material was not collected, the {As}:{Fe} ratio in surface sediments (0–1 cm) was 6.2×10^{-4} . Aluminum ({Al}) and organic C ({C_{ORG}}) concentrations vary little with depth in Lake Tantaré while {C_{ORG}} increases slightly between 10 and 15 cm depth in Lake Du Syndicat.

In contrast to Lakes Tantaré and Du Syndicat, the two lakes whose hypolimnion was anoxic display no As, Fe or Mn enrichment close to the sediment surface (Fig. 2c, d, g, and h) but show maxima of these elements at greater depths. In both lakes, the {Al} and {C_{ORG}} concentrations varied with depth.

Both lakes with oxic bottom water show a subsurface maximum in AVS concentrations at about 5 cm depth, with values much lower in Lake Tantaré than in Lake Du Syndicat (Fig. 2i and j). The {S_{TOT}} profiles also exhibit subsurface maxima in both lakes but the position of these maxima occur deeper than those of AVS. In the two anoxic lakes, the highest AVS concentrations are found a few cm below the sediment–water interface, at the same depth as a {S_{TOT}} maximum (Fig. 2k and l). In Lake Holland, the AVS and {S_{TOT}} subsurface concentration maximum found at 4-cm depth coincide with those of {As} and {Fe}. For the sediment interval sampled, the inventories of AVS (^{AVS}*I*) in Lakes Tantaré, Bédard and Du Syndicat represent small proportions (0.5%, 3%, and 7%, respectively) of those of S_{TOT} (^{S_{TOT}}*I*), whereas in Lake Holland,

this proportion reaches 26%. The remaining fractions of ^{S_{TOT}}*I* could include organically-bound S (Luther, 2005; Russell and Werne, 2009) or inorganic sulfides that are refractory to the AVS extractions, such as pyrite (Morse and Rickard, 2004). It is likely that a large proportion of S_{TOT} occurs as organically-bound S in Lakes Tantaré, Bédard and Du Syndicat sediments, given their low ^{AVS}*I*:^{S_{TOT}}*I* values and the fact that the {C}:{S} ratios of their sediments (50–200) are typical of those of the organic matter in soils (~125; Buffle, 1988). In contrast, the larger ^{AVS}*I*:^{S_{TOT}}*I* value, combined to lower {C}:{S} ratios (5–20) found in Lake Holland suggest that inorganic S represents a larger proportion of ^{S_{TOT}}*I* in this lake.

3.2. Porewaters

Similarity among the triplicate porewater As profiles obtained at a given sampling date and site (Figs. 3 and 4) suggests that they are not artifacts related to our sampling and handling procedures. In the two lakes whose hypolimnion was oxygenated, the lowest concentrations of dissolved As ([As]) and Fe ([Fe]) were found in the overlying water while both elements reached much higher concentrations below the sediment–water interface (Fig. 3a–h). In Lake Tantaré, the featureless Mn concentration profiles ([Mn]; Fig. 3e–g) are in agreement with the absence of Mn oxyhydroxide formation (Fig. 2e). In contrast, [Mn] profiles in Lake Du Syndicat display sharp peaks just below the sediment–water interface, at a slightly shallower depth than the [Fe] peaks. The simultaneous release of both As and Fe in the porewaters of Lake Du Syndicat (Fig. 3d and h) suggests, consistently with observations from other studies (Peterson and Carpenter, 1986; Müller et al., 2002), that Fe oxyhydroxides are more important than Mn oxyhydroxides in As cycling during the early stages of diagenesis. In both lakes, porewater SO₄²⁻ concentrations ([SO₄²⁻]) decreased with

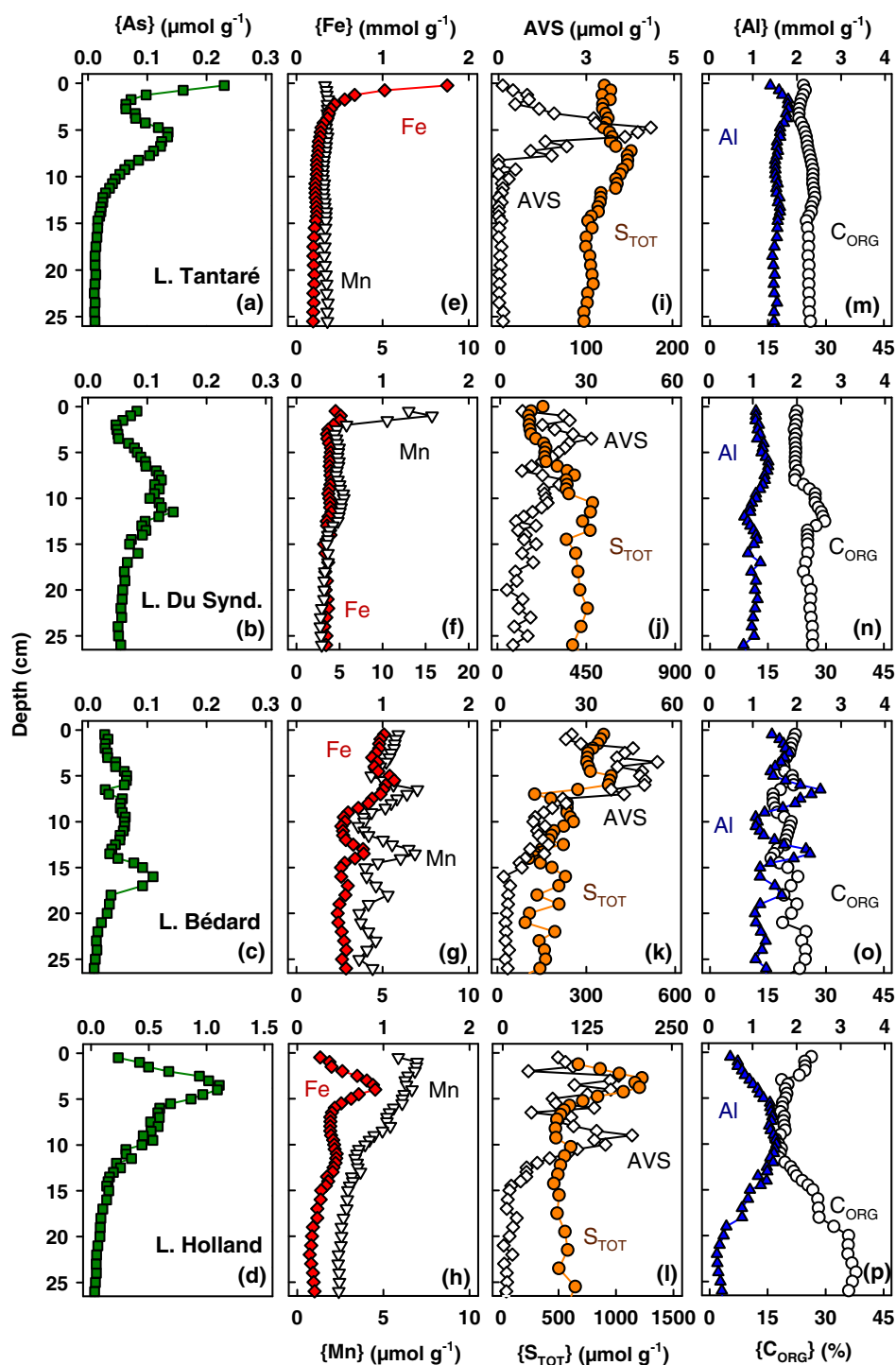


Fig. 2. Depth profiles of sedimentary As (a–d), Fe and Mn (e–h), AVS and S_{TOT} (i–l), and Al and C_{ORG} (m–p).

depth below the sediment–water interface, whereas $\Sigma\text{S}^{-\text{II}}$ and ΣS^0 , which were close to detection limits in the sediment overlying water, progressively increased below 2–6 cm sediment depth (Fig. 3i–p).

The porewater concentration profiles in the lakes with anoxic hypolimnions differ somewhat among the two lakes

and are, for some solutes, in sharp contrast to those of the perennially oxic lakes (Figs. 3 and 4). Both Lakes Bédard and Holland show a consumption of dissolved As at or just below the sediment–water interface (Fig. 4a and b) at approximately the same depth where a production of As was observed in the oxygenated lakes (Fig. 3a–d). Judging

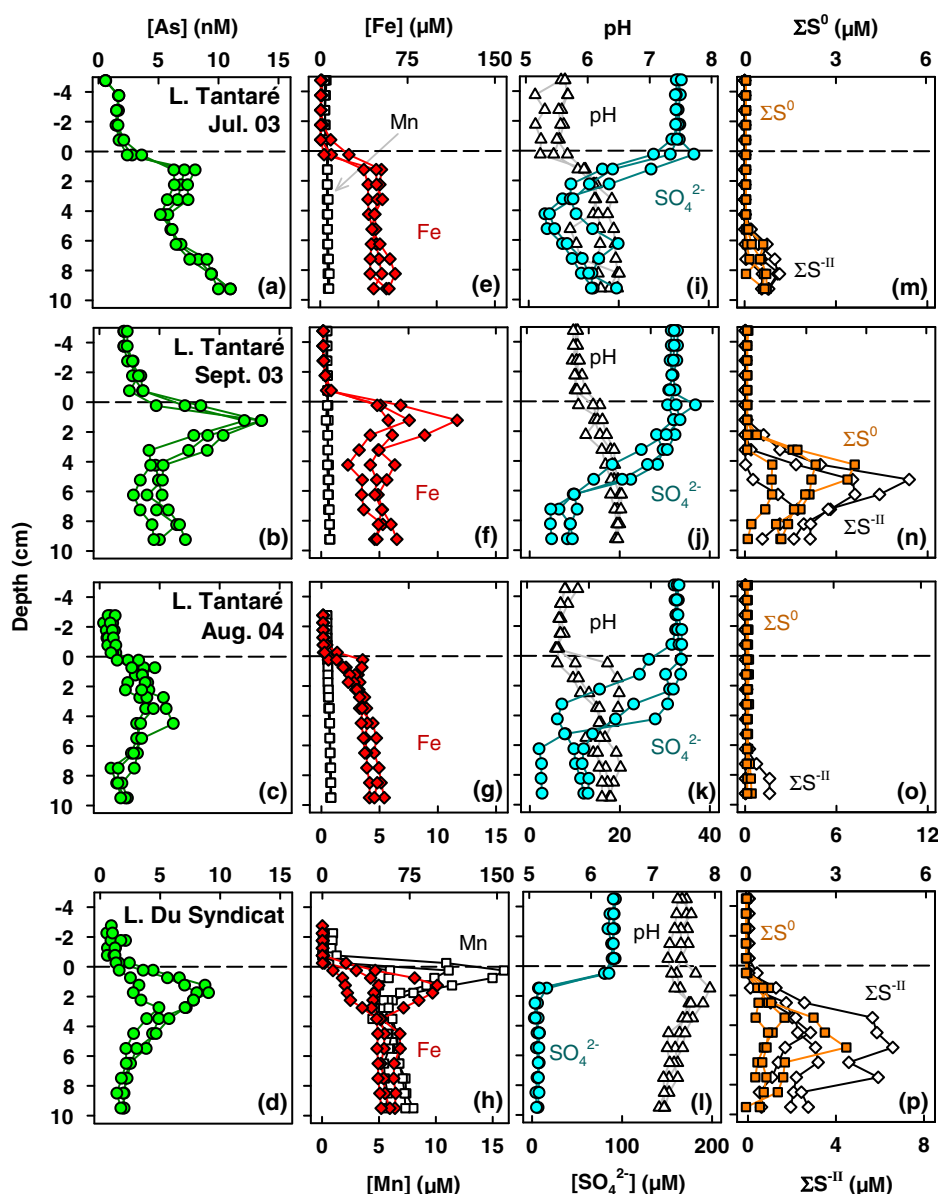


Fig. 3. Triplicate porewater profiles of As (a–d), Fe and Mn (e–h), pH and SO_4^{2-} (i–l), and ΣS^0 and $\Sigma\text{S}^{-\text{II}}$ (m–p) in the oxygenated Lakes Tantaré and Du Syndicat. The horizontal dashed lines indicate the sediment–water interface.

from the intensity of the [As] gradients, removal of As appears to be more pronounced in Lake Holland than in Lake Bédard. Contrary to the oxic lakes, dissolved sulfide was detected at concentrations varying between 0.2 and 25 μM above the sediment–water interface of Lakes Bédard and Holland (Fig. 4g and h), consistent with anoxic bottom waters. While [Fe] reached up to 970 μM in Lake Bédard, it remained <10 μM in Lake Holland where no parallel between the [Fe] and [As] profiles exists. In Lake Bédard, $\Sigma\text{S}^{-\text{II}}$ was undetectable in porewaters below 4 cm depth, likely due to the precipitation of Fe sulfide. In contrast, the concentration of $\Sigma\text{S}^{-\text{II}}$ remained >25 μM in the Fe-depleted porewaters of Lake Holland. In both lakes, the [Mn] profiles were featureless.

4. DISCUSSION

4.1. As speciation predicted by thermodynamic modeling

Both thermodynamic Models 1 and 2 predict that all As is in the form of arsenate species in the oxygenated overlying water of Lakes Tantaré and Du Syndicat (Fig. 5a–h). Depending on pH, [Ca] and [Mg], various arsenate species can predominate. In the acidic Lake Tantaré, the species $\text{H}_2\text{As}^{\text{V}}\text{O}_4^-$ is much more important (>85%) than $\text{HAS}^{\text{V}}\text{O}_4^{2-}$ (Fig. 5a–c and e–g), whereas in the circumneutral Lake Du Syndicat, the species $\text{HAS}^{\text{V}}\text{O}_4^{2-}$ is dominant (>60%). Because [Ca] and [Mg] are elevated in this lake, the $\text{CaHAS}^{\text{V}}\text{O}_4^0$ (<15%; Fig. 6d and h) and $\text{MgHAS}^{\text{V}}\text{O}_4^0$

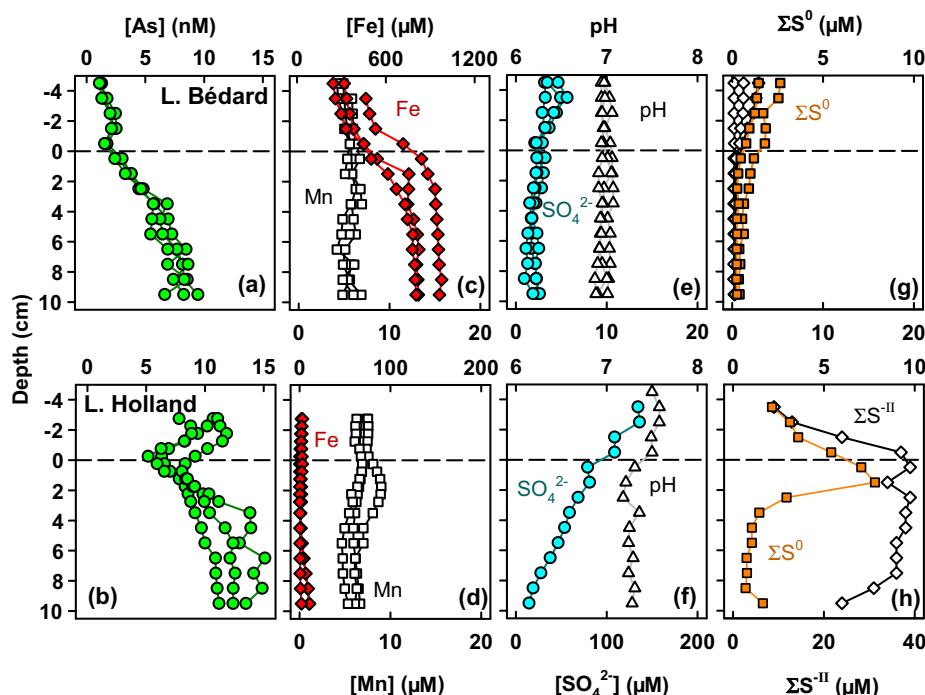


Fig. 4. Triplicate porewater profiles of As (a, b), Fe and Mn (c, d), pH and SO_4^{2-} (e, f) and ΣS^0 and $\Sigma\text{S}^{-\text{II}}$ (g, h) in the seasonally anoxic Lakes Bédard and Holland. The horizontal dashed lines indicate the sediment–water interface.

(<10%; data not shown) species are present in relatively high proportions.

In sulfidic waters, predictions of As speciation by the two models disagree on many aspects (Figs. 5a–h and 6a–d). According to Model 1, which considers only oxythioarsenites (i.e., no oxythioarsenates), the arsenite species $\text{H}_3\text{As}^{\text{III}}\text{O}_3^0$ dominates in the overlying water of Lake Bédard and in the sulfidic porewaters of all lakes, but Holland (Figs. 5a–d and 6a), while oxythioarsenite species remain marginal (<5%). It is only when $\Sigma\text{S}^{-\text{II}}$ reaches values above 25 μM that the concentrations of oxythioarsenite species can overcome those of arsenites. For example in Lake Holland, where $\Sigma\text{S}^{-\text{II}}$ reaches up to 40 μM (Fig. 4h), the $\text{HAs}^{\text{V}}\text{S}_3\text{O}_3^{2-}$ species prevails over $\text{H}_3\text{As}^{\text{III}}\text{O}_3^0$ (Fig. 6b).

Model 2, derived from Helz and Tossell (2008), predicts the co-existence of As^{V} and As^{III} species in sulfidic waters. According to this model, the distribution of As species is much more intricate than that predicted by Model 1, and it should depend in a complex manner on the values of several geochemical parameters of the sulfidic waters (ΣS^0 , $\Sigma\text{S}^{-\text{II}}$, pH and [As]). Accordingly, Fig. 7a shows that at a constant pH, and with [As] representative of those found in our lakes (5 nM), the proportion of As^{V} increases with the concentrations of $\text{S}_{(\text{aq})}^0$ and HS^- (which are related to ΣS^0 and $\Sigma\text{S}^{-\text{II}}$, respectively). Increasing $[\text{HS}^-]$ favors the formation of As^{V} thioanions, which are very stable complexes, whereas increasing $[\text{S}_{(\text{aq})}^0]$ for a given $[\text{HS}^-]$ drives the pE towards more positive values. Fig. 7b shows that at given $[\text{S}_{(\text{aq})}^0]$ and $\Sigma\text{S}^{-\text{II}}$ (10 nM and 10 μM , respectively), the proportion of As^{V} increases with pH. Raising the pH above 6 increases the proportion of $[\text{HS}^-]$ and allows As^{V} species to dominate, provided that $\Sigma\text{S}^{-\text{II}}$ is greater than [As].

Comparison of Figs. 3m–p and 5e–h shows that As^{V} oxythioanions (e.g., $\text{HAs}^{\text{V}}\text{S}_3\text{O}_3^{2-}$) become dominant over arsenite (e.g., $\text{H}_3\text{As}^{\text{III}}\text{O}_3^0$) only at depths where $\Sigma\text{S}^{-\text{II}}$ and ΣS^0 reach μM concentrations in Lake Tantaré and Du Syndicat. Similarly, in Lake Bédard, the prevalence of the As^{V} oxythioanions (mainly $\text{HAs}^{\text{V}}\text{S}_3\text{O}_3^{2-}$) over the arsenite species ($\text{H}_3\text{As}^{\text{III}}\text{O}_3^0$) occurs only in the overlying water and in the top 3 cm of porewaters (Fig. 6c), i.e., at depths where $\Sigma\text{S}^{-\text{II}}$ and ΣS^0 reach the μM level (Fig. 4g). When $\Sigma\text{S}^{-\text{II}}$ and ΣS^0 increase, as in Lake Holland (Fig. 4h), As^{V} oxythioanions (e.g., $\text{HAs}^{\text{V}}\text{S}_3\text{O}_3^{2-}$) and thioanions (e.g., $\text{As}^{\text{V}}\text{S}_4^{3-}$) are present in greater proportion than the As^{III} species (Fig. 6d).

4.2. Net reaction rates of porewater As production or consumption

Visual inspection of porewater As distribution (Figs. 3a–d and 4a and b) indicates depth intervals (hereafter called zones) where As is either remobilized or removed from porewaters. Inverse diagenetic modeling can be used to objectively define these zones and constrain the net rate of the reactions involved in As consumption or production. Porewater As profiles were modeled assuming the absence of significant advective flux and the quasi steady-state (i.e., $\partial[\text{As}]/\partial t \approx 0$) of the system. Although the steady-state assumption may not be strictly valid for an environment subject to variations in dissolved O_2 and temperature, it has been useful to explore the parameters that cause either the sequestration or the mobilization of trace elements (Gallon et al., 2004; Chappaz et al., 2008; Merritt and Amirbahman, 2008) and the quantification of As post-depositional mobility (Couture et al., 2008). For this

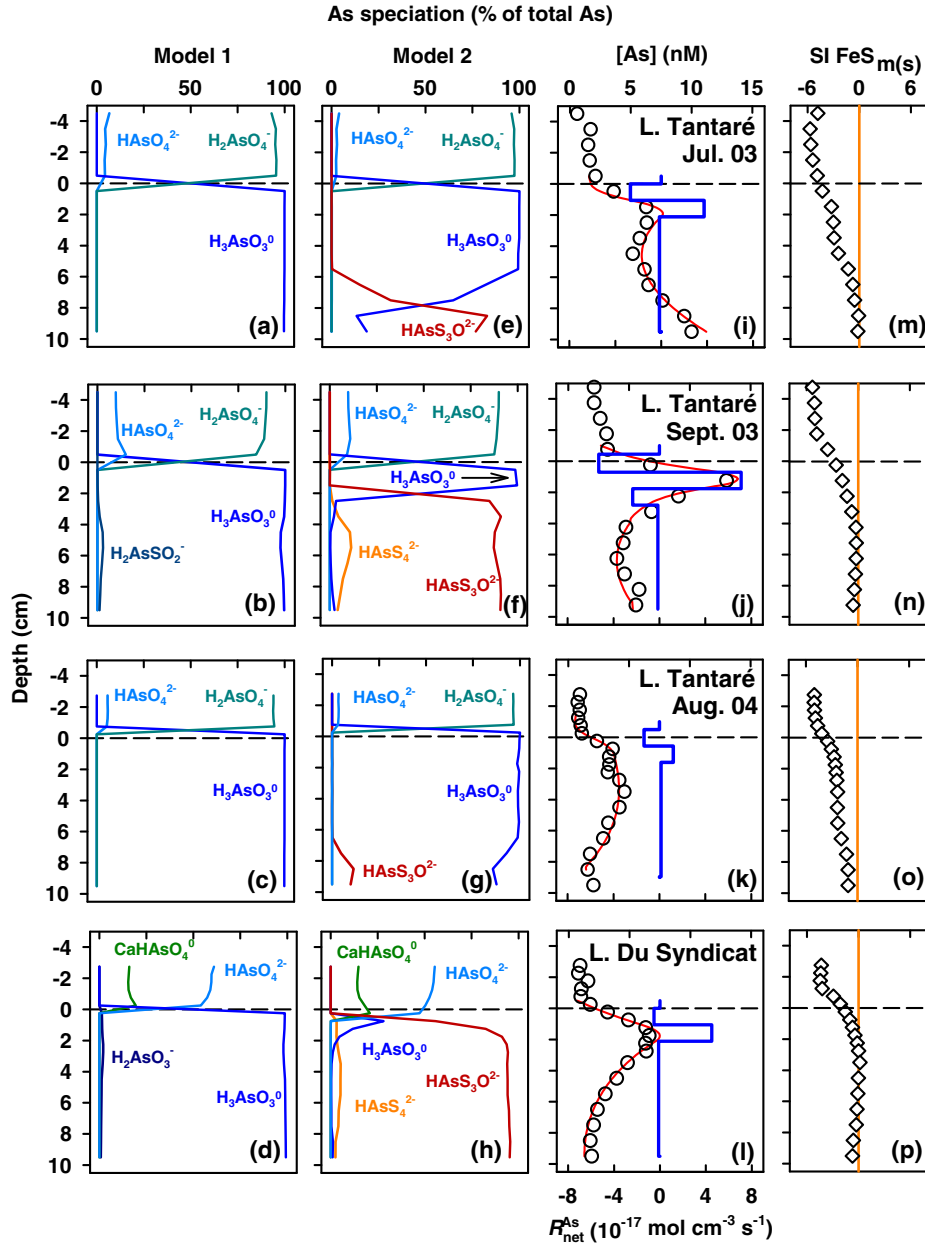


Fig. 5. Arsenic speciation in the oxygenated lakes as calculated using thermodynamic Model 1 (a–d) and Model 2 (e–h), as well as comparison of modeled and measured average ($n = 3$) porewater As concentrations (i–l) and saturation index of porewaters (m–p) with respect to $\text{FeS}_{\text{m(s)}}$. The horizontal dashed lines indicate the sediment–water interface. In panels i–l the thin solid line is the PROFILE model fit and the thick solid line is the net As consumption/production rate.

modeling exercise, the one-dimensional mass conservation equation provided by Boudreau (1997) at steady-state:

$$\left(\frac{\partial [\text{As}]}{\partial t} \right)_x = \frac{\partial}{\partial x} \left(\phi (D_s + D_B) \frac{\partial [\text{As}]}{\partial x} \right) + \phi \alpha ([\text{As}]_{\text{burrow}} - [\text{As}]) + R_{\text{net}}^{\text{As}} = 0 \quad (3)$$

was solved numerically for the net rate of As production or consumption per unit volume ($R_{\text{net}}^{\text{As}}$, mol cm^{-3} of whole sediment s^{-1}) using the computer code PROFILE (Berg et al., 1998). In Eq. (3), $[\text{As}]$ and $[\text{As}]_{\text{burrow}}$ (mol cm^{-3}) are the As concentrations in porewaters and overlying waters, respec-

tively, x is depth (positive downward from the sediment–water interface), t (s) is time, ϕ is sediment porosity, D_s ($\text{cm}^2 \text{s}^{-1}$) is the effective diffusion coefficient, D_B ($\text{cm}^2 \text{s}^{-1}$) is the biodiffusion coefficient, which represents the random physical mixing of sediment by benthic fauna and α (s^{-1}) is the bioirrigation rate coefficient. Values of $R_{\text{net}}^{\text{As}}$ inferred by diagenetic modeling may range from positive (As production to porewaters) to negative values (As consumption from porewaters) and vary as a function of sediment depth. Eq. (3) does not take into account advective flux due to sediment compaction during burial. To verify if the latter

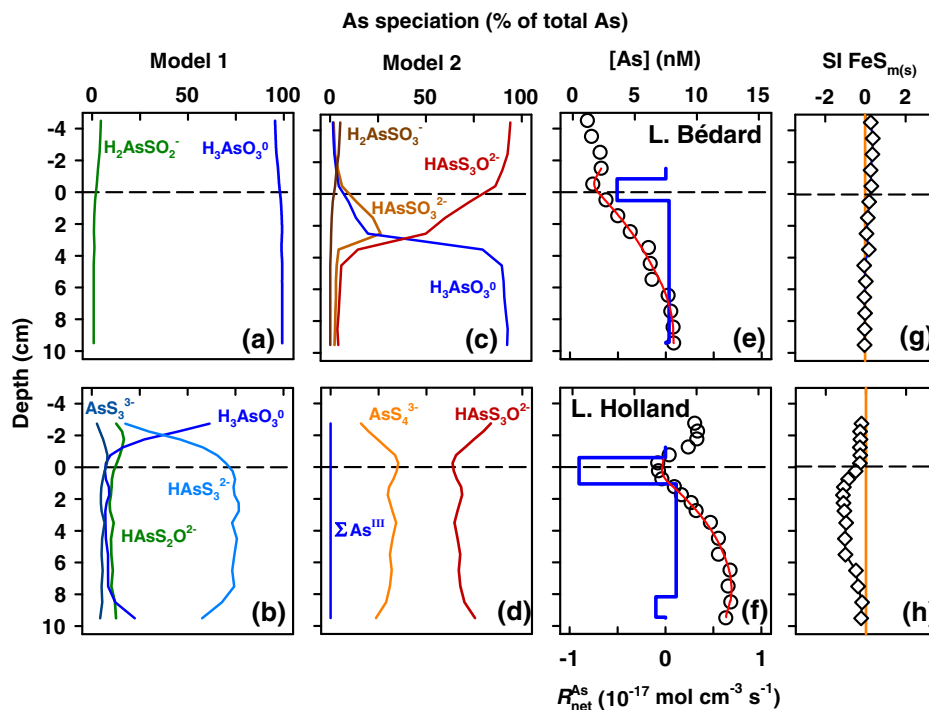


Fig. 6. Arsenic speciation in the seasonally anoxic lakes as calculated using thermodynamic Model 1 (a, b) and Model 2 (c, d), as well as comparison of modeled and measured average ($n = 3$) porewater As concentrations (e, f) and saturation index of porewaters (g, h) with respect to $\text{FeS}_{\text{m(s)}}$. The horizontal dashed lines indicate the sediment–water interface. In panels e and f the thin solid line is the PROFILE model fit and the thick solid line is the net As consumption/production rate.

process can be neglected, we calculated the Peclet number as follows: $Pe = lv_s/D_s$ (where l is the thickness of sediment column considered, i.e., 10 cm). This leads to values of Pe smaller than 0.02 in all lakes, indicating that advection resulting from sediment compaction during burial can be neglected compared to diffusion (Boudreau, 1997).

For Lake Tantaré, we used the D_B value ($2.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) determined by Gallon et al. (2004) considering a sparse benthic community of 1690 ± 180 animals m^{-2} at the sampling site, with the chironomid *Sergentia coracina* being the major taxon (Hare et al., 1994), and the biodiffusion coefficients for chironomids provided by Matisoff and Wang (2000). Since this benthic organism is generally not found below 10 cm, we assumed that the bioirrigation coefficient (α) decreased linearly from α^0 at the sediment–water interface to zero at 10 cm depth. The value of α^0 was set to $4.58 \times 10^{-7} \text{ s}^{-1}$ according to equations presented by Boudreau (1984) and animal densities at the sampling site (Alfaro-De la Torre and Tessier, 2002). We assumed negligible bioturbation and bioirrigation (i.e., $D_B = \alpha = 0$ in Eq. (3)) for the seasonally anoxic Lakes Bédard and Holland, as well as for the oxic Lake Du Syndicat for which no data on the population of benthic animal is available.

In Lakes Tantaré and Du Syndicat, whose hypolimnion was oxygenated at the time of sampling, PROFILE consistently defined two zones where reactions are relatively fast: one close to the sediment–water interface where porewater As is consumed and the other, just below, where porewater As is produced; at greater depths, As is slowly consumed,

except in August 2004 at Lake Tantaré where it is slowly produced (Fig. 5i–l; zones are numbered downward from the sediment–water interface in Table 3). In Lakes Bédard and Holland, whose hypolimnion was anoxic, PROFILE consistently determined zones of As consumption at the sediment–water interface (Fig. 6e and f) and zones of slow As production over large sediment intervals (0.5–10 cm and 1–8 cm depth for Lakes Bédard and Holland, respectively). In Lake Holland, an additional consumption zone is defined between 8 and 10 cm depth (Fig. 6f).

A sensitivity analysis has been conducted to determine the variability in $R_{\text{net}}^{\text{As}}$ when the density of *S. coracina* in Lake Tantaré, and the average porewater As concentrations in all lakes are varied by ± 1 SD. For Lake Tantaré, variations in either [As] or the density of benthic animals (which influences the bioirrigation and bioturbation coefficients) had a small effect on the value of $R_{\text{net}}^{\text{As}}$ ($< 6\%$), whereas simultaneous variations in both parameters modified the value of $R_{\text{net}}^{\text{As}}$ by a maximum of 15%. In the other lakes, the highest observed change in the value of $R_{\text{net}}^{\text{As}}$ due to variations in [As] was 15%. Calculations of the dimensionless Damköhler number DaD , to evaluate the importance of diffusion compared to that of the reaction rates, also provides a relative scale of the uncertainty on the values of $R_{\text{net}}^{\text{As}}$. DaD is equal to τ_D/τ_R , where τ_D is the characteristic time for diffusion ($\tau_D = l^2/D_s$, l being the thickness of a consumption/production zone given in Table 3) and τ_R the characteristic time for reaction ($\tau_R = [\text{As}]/R_{\text{net}}^{\text{As}}$); values of DaD larger than 1 imply that reaction dominates over diffusion. It follows that the uncertainty on the reaction

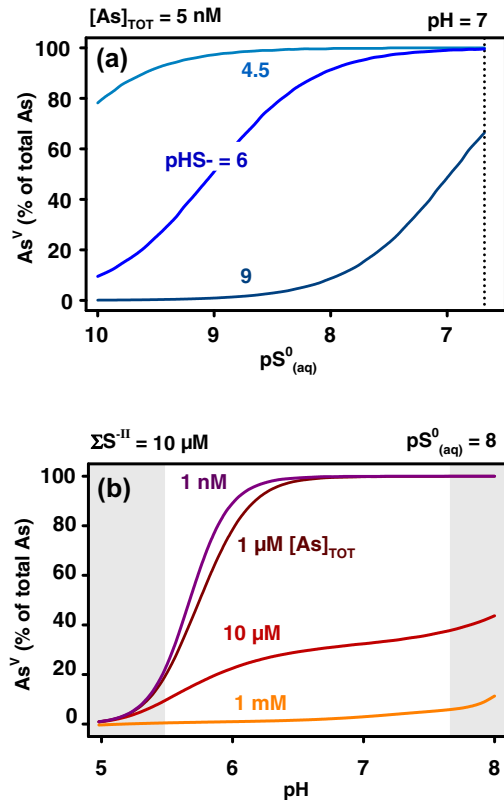


Fig. 7. Relative abundance of As^{V} predicted by the speciation code MINEQL+ using Model 2 when $[\text{S}_{\text{aq}}^0]$ varies from 10^{-10} M to $10^{-6.68}$ M at three different pHS^- values (a) and when pH varies from 5 to 8 at four different As concentrations (b). In panel a, the vertical dotted line indicates saturation with respect to $\text{S}(\alpha)_{\text{S}(\text{s})}$. Shaded areas correspond to pH values outside of the range found in the sulfidic porewaters of our lakes. Invariant parameters are indicated at the top of each panel.

Table 3

Values of $R_{\text{net}}^{\text{As}}$ as a function of depth inferred by inverse diagenetic modeling for each lake and sampling date along with rate constant for As adsorption ($k_{\text{ads}}^{\text{As}}$) onto Fe oxyhydroxides and observed K_{D} for As adsorption onto $\text{FeS}_{\text{m}(\text{s})}$.

Sampling site	Zone No.	Depth interval (cm)	$R_{\text{net}}^{\text{As}}$ (10^{-18} mol cm^{-3} s^{-1})	$k_{\text{ads}}^{\text{As}}$ (cm^3 mol $^{-1}$ s^{-1})	K_{D} (L g^{-1})
L. Tantaré	1	0–1.1	–27	$0.15 \pm 0.02^{\text{a}}$	24 ± 6
Jul. 2003	2	1.1–2.1	+37		
	3	2.1–9.5	–1.5		
L. Tantaré	1	–0.5–0.3	–53	$0.10 \pm 0.02^{\text{a}}$	32 ± 2
Sept. 2003	2	0.3–1.4	+71		
	3	1.3–2.4	–23		
	4	2.4–9.5	–1.5	$0.11 \pm 0.02^{\text{a}}$	25 ± 8
L. Tantaré	1	–0.5–0.6	–13		
Aug. 2004	2	0.6–1.6	+12		
	3	1.6–9.5	+1.0		10 ± 1
L. Du Syndicat	1	0–1.1	–5		
	2	1.1–2.1	+45		
	3	2.1–9.5	–1.5		5 ± 2
L. Bédard	1	–0.7–0.5	–5.1		
	2	0.5–9.5	+0.5		
L. Holland	1	–0.5–1.1	–9.0		10 ± 6
	2	1.1–8.3	+1.0		
	3	8.3–9.5	–1.0		

^a Uncertainty was calculated by error propagation based on uncertainties on the analytical concentrations of Fe oxyhydroxides ($\pm 2\%$) and $[\text{As}]$ ($\pm 2\%$), and on the $R_{\text{net}}^{\text{As}}$ values ($\pm 15\%$).

rates obtained by the code PROFILE decreases with increasing values DaD. In all cases but two, our values of DaD ranged between 2 and 25 (Table EA1), indicating that reactions dominated over diffusion. For zones #3 of Lakes Holland and Du Syndicat, DaD values are 0.5 and 1, respectively. Although reactions do not dominate over diffusion in these two zones, they nevertheless contribute significantly to shape the profiles of As in the porewaters since DaD is equal or only slightly lower than 1. Thus, extraction of reaction rates by modeling the porewater $[\text{As}]$ profiles is a reasonable approach.

The $[\text{As}]$ profiles obtained at Lake Tantaré show differences among sampling dates (see Fig. 3a–c), indicating seasonal changes in lake conditions. To evaluate if the reactions are fast enough so that the steady-state treatment can lead to reasonable estimates of $R_{\text{net}}^{\text{As}}$, we compared the characteristic time of As reactions ($\tau_{\text{R}} = [\text{As}]/R_{\text{net}}^{\text{As}}$) with that of a seasonal change in lakes (τ_{S}) occurring over a 75-days period ($\tau_{\text{S}} \sim 6.5 \times 10^6$ s). Table EA1 in the Electronic Annex shows that the $\tau_{\text{S}}/\tau_{\text{R}}$ ratio ranged between 2 and 180 with only one exception (zone #2 in Lake Bédard where $\tau_{\text{S}}/\tau_{\text{R}} = 0.9$). We can therefore conclude that characteristic time of reactions is smaller than the time-scale of a seasonal change and that our assumption of quasi steady-state is reasonable.

In the following two sections, we use our porewater and sediment concentration profiles in combination with the As concentration in the Fe-rich diagenetic material collected on Teflon sheets to constrain reactions involving As.

4.3. Reactions controlling As mobility under oxic conditions

As a first step in investigating the mechanisms responsible for As removal in Zone 1 of Lakes Tantaré and Du Syndicat (Table 3), we calculated the saturation index

($SI = \log IAP/K_{sp}$, where IAP is the ion activity product and K_{sp} is the solubility product) of porewaters with respect to solid arsenates (reactions 1–10 in Table 4). This calculation indicates that porewaters were undersaturated ($SI \leq -10.3$) with respect to solid arsenates.

In the absence of As precipitation, its adsorption to freshly formed Fe oxyhydroxides is the most likely mechanism to explain its removal from porewaters. Similarities in the [As] and [Fe] profiles (Fig. 3a–h) and in the {As} and {Fe} enrichment layers (Fig. 2a, b, e, and f), as well as the presence of As in the Fe-rich diagenetic material collected on Teflon sheets in Lake Tantaré, all support this adsorption mechanism. Moreover, a large number of field (Belzile and Tessier, 1990; Martin and Pedersen, 2002; Root et al., 2007; Senn et al., 2007) and laboratory (Pierce and Moore, 1982; Fuller et al., 1993; Raven et al., 1998; Dixit and Hering, 2003; Banerjee et al., 2008) measurements have demonstrated the importance of As adsorption onto Fe oxyhydroxides.

Surface complexation models comprising consistent sets of intrinsic adsorption constants have been developed to study As adsorption onto Fe oxyhydroxides (Dzombak and Morel, 1990; Dixit and Hering, 2003). We used the model provided by Dixit and Hering (2003) (reactions 19–23 in Table 4) to test if it could predict the {As}:{Fe} molar ratio measured in the Fe-rich diagenetic material collected on Teflon sheets in Lake Tantaré. In this calculation, performed with the code MINEQL+, we used our geochemical measurements in the overlying waters of Lake Tantaré as

input parameters and the intrinsic constants for adsorption of $As^V O_4^{3-}$ and H^+ onto ferrihydrite (Table 4) as well as the specific surface area of $600 \text{ m}^2 \text{ g}^{-1}$ for ferrihydrite and the concentration of adsorption sites of $0.205 \text{ mol per mol}$ of ferrihydrite used by Dixit and Hering (2003) to extract their adsorption constants.

The {As}:{Fe} molar ratio ($8.1 \pm 5.9 \times 10^{-4}$; $n = 9$) predicted by MINEQL+ is 2.5-fold higher than the ratio that we measured ($2.8 \pm 0.1 \times 10^{-4}$; $n = 7$). This slight over prediction of the {As}:{Fe} ratio, as well as the presence of [As] peaks at depths ($\sim 1 \text{ cm}$; Fig. 3a, b, and d) where Fe oxyhydroxides are abundant in the sediments (Fig. 2e), can be ascribed to slow kinetics of *in situ* adsorption of As onto natural Fe oxyhydroxides. This latter hypothesis is supported by recent work (Redman et al., 2002), which showed that the presence of dissolved natural organic matter (NOM) in As adsorption experiments greatly reduces the rate of As adsorption onto Fe oxyhydroxides. Because the Fe-rich diagenetic material collected from Lake Tantaré had a $\{C_{ORG}\}:\{Fe\}$ molar ratio of 2.6 ± 0.3 , it is thus conceivable that NOM associated with the Fe-rich diagenetic material slowed down the reaction of As with Fe oxyhydroxides in Lake Tantaré sediments.

Given that our results indicate that As adsorption onto Fe oxyhydroxides in the sediments is slow, the value R_{net}^{As} inferred by Eq. (3) for Lake Tantaré can provide information on the *in situ* kinetics of this reaction. Since R_{net}^{As} in the zone of As removal is the net result of As production and consumption, it can be written that:

Table 4

Selected surface complexation and precipitation reactions, and their corresponding equilibrium constants. The surface complexation constants are intrinsic constants.

#	Reactions	Log K	Ref.
<i>Precipitation reactions</i>			
1	$2AsO_4^{3-} + 6H^+ = As_2O_5(s) + 3H_2O$	61.95	a
2	$2AsO_4^{3-} + 3Fe^{2+} = Fe_3(AsO_4)_2(s)$	34.41	b
3	$2AsO_4^{3-} + 3Mn^{2+} = Mn_3(AsO_4)_2(s)$	31.39	b
4	$2AsO_4^{3-} + 3Mn^{2+} + 8H_2O = Mn_3(AsO_4)_2(s) \cdot 8H_2O$	29.02	b
5	$2AsO_4^{3-} + 3Mg^{2+} = Mg_3(AsO_4)_2(s)$	30.02	b
6	$2AsO_4^{3-} + 3Ca^{2+} + 4H_2O = Ca_3(AsO_4)_2(s) \cdot 4H_2O$	21.15	c
7	$3AsO_4^{3-} + 5Ca^{2+} + OH^- = Ca_5(OH)(AsO_4)_3(s)$	38.3	c
8	$AsO_4^{3-} + Ca^{2+} + H^+ = CaHAsO_4(s)$	16.34	c
9	$4AsO_4^{3-} + 5Ca^{2+} + 2H^+ = Ca_5(HAsO_4)_2(AsO_4)_2(s)$ (ferrarisite)	56.61	c
10	$4AsO_4^{3-} + 5Ca^{2+} + 2H^+ = Ca_5(HAsO_4)_2(AsO_4)_2(s)$ (guerinite)	55.81	c
11	$2AsO_3^{3-} + 6H^+ = As_2O_3(s)$ (arsenolite) + $3H_2O$	77.92	a
12	$2AsO_3^{3-} + 6H^+ = As_2O_3(s)$ (claudetite) + $3H_2O$	77.95	a
13	$2AsO_3^{3-} + 9H^+ + 3HS^- = As_2S_3(s)$ (orpiment) + $6H_2O$	122.8	a
14	$2AsO_3^{3-} + 9H^+ + 3HS^- = As_2S_3(s)$ (orpiment, amorphous) + $6H_2O$	121.4	a
15	$AsO_3^{3-} + 4H^+ + HS^- - 0.25O_2 = AsS(s)$ (realgar) + $2.5H_2O$	36.9	a
16	$Fe^{2+} - H^+ + HS^- = FeS_{m(s)}$ (mackinawite, disordered)	3.5	d
17	$3Fe^{2+} - 3H^+ + 3HS^- + S^0 = Fe_3S_4(s)$ (greigite)	13.2	e
18	$Fe^{2+} - 2H^+ + 2HS^- - 2e^- = FeS_2(s)$ (pyrite)	16.40	e
<i>Adsorption reactions</i>			
19	$\equiv FeOH(am.) + 3H = H^+ + AsO_4^{3-} \rightleftharpoons \equiv FeH_2AsO_4 + H_2O$	29.88	f
20	$\equiv FeOH(am.) + 2H^+ + AsO_4^{3-} \rightleftharpoons \equiv FeHAsO_4^- + H_2O$	24.43	f
21	$\equiv FeOH(am.) + H^+ + AsO_4^{3-} \rightleftharpoons \equiv FeAsO_4^{2-} + H_2O$	18.10	f
22	$\equiv FeOH(am.) + H^+ \rightleftharpoons \equiv FeOH_2^+$	7.29	g
23	$\equiv FeOH(am.) \rightleftharpoons \equiv FeO^- + H^+$	-8.93	g

References: a, Nordstrom and Archer (2003); b, Essington (1988); c, Bothe and Brown (1999); d, Rickard (2006); e, Davison (1991); f, Dixit and Hering (2003); g, Dzombak and Morel (1990).

$$R_{\text{net}}^{\text{As}} = N_{\text{av}} R_{\text{red}}^{\text{Fe}} - k_{\text{ads}}^{\text{As}} \left([\text{As}] \frac{\text{DBD} \{ \text{Fe-ox} \}_{\text{av}}}{\phi} \right) \quad (4)$$

where the two terms on the right-hand side represent As release from the reductive dissolution of Fe oxyhydroxides and adsorption of As onto Fe oxyhydroxides, respectively. In Eq. (4), $R_{\text{red}}^{\text{Fe}}$ (g cm^{-3} of whole sediment) is the rate of reductive dissolution of Fe oxyhydroxides, $k_{\text{ads}}^{\text{As}}$ (cm^3 of porewater $\text{mol}^{-1} \text{s}^{-1}$) is the apparent second-order rate constant for the adsorption of As onto Fe oxyhydroxides, $\{ \text{Fe-ox} \}$ (mol g^{-1}) is the concentration of authigenic Fe oxyhydroxides and N_{av} is the $\{ \text{As} \} : \{ \text{Fe} \}$ molar ratio in the Fe-rich diagenetic material. The value of $\{ \text{Fe-ox} \}$ was taken as the excess $\{ \text{Fe} \}$ over the constant background Fe concentration below 15.5 cm depth in the sediments (Fig. 2c). The subscript “av” indicates that we have considered the average value over the thickness of consumption zone 1, because R values are piece-wise constants. The net reaction rate of porewater Fe production or consumption ($R_{\text{red}}^{\text{Fe}}$) was estimated by fitting the $[\text{Fe}]$ profiles (Fig. 3e–g) using the inverse modeling approach described for As in Section 4.2, i.e., As was replaced by Fe in Eq. (3) (see Chap-paz et al., 2008 for details). Values of $R_{\text{red}}^{\text{Fe}}$, calculated for the depths of As removal in zone 1 of Lake Tantaré sediments (see Table 3) were always < 0 (data not shown). Therefore, we assumed that As release by the reductive dissolution of Fe oxyhydroxides contributed negligibly to $R_{\text{net}}^{\text{As}}$ in the zone where As was removed from porewaters, and we neglected the term $N_{\text{av}} R_{\text{red}}^{\text{Fe}}$ in Eq. (4).

The mean value of $k_{\text{ads}}^{\text{As}}$ obtained with Eq. (4) for all three sampling dates in Lake Tantaré is $0.12 \pm 0.03 \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$ (Table 3). To our knowledge, no other values of $k_{\text{ads}}^{\text{As}}$ for the adsorption of As onto Fe oxyhydroxides have been reported for sediments. However, several laboratory studies of As adsorption onto Fe oxyhydroxides, in which the concentrations of Fe oxyhydroxides were in large excess compared to those of As, provide curves of $[\text{As}]$ removal versus reaction time (Fuller et al., 1993; Raven et al., 1998; Redman et al., 2002; Banerjee et al., 2008). Assuming that As consumption in these experiments is first-order with respect to both As and Fe oxyhydroxides concentrations, we graphically estimated laboratory-derived $k_{\text{ads}}^{\text{As}}$ values. For simple systems where only As was incubated with Fe oxyhydroxides, values of $k_{\text{ads}}^{\text{As}}$ obtained ($35\text{--}375 \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$) are 2–3 orders of magnitude larger than our field-derived value of $0.12 \pm 0.03 \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$. On the other hand, we estimate from the work of Redman et al. (2002) that the addition of 10 mg C L^{-1} of NOM to hematite suspensions decreased $k_{\text{ads}}^{\text{As}}$ from $360 \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$ to $3.4 \text{ cm}^3 \text{ mol}^{-1} \text{s}^{-1}$, which is only 30-fold higher than our *in situ* measured value. The low $k_{\text{ads}}^{\text{As}}$ value derived from Redman et al. (2002) cannot be compared directly with our *in situ* value because the hematite (Fe_2O_3) they studied should have a different reactivity towards NOM than the ferrihydrite found in the Fe-rich diagenetic material from Lake Tantaré (Tipping, 1981). Moreover, the temperature in their experiments (22°C) was higher than in Lake Tantaré’s bottom water ($\sim 4^\circ\text{C}$), which would increase the value of the rate constant. The important point, however, is that the presence of NOM strongly reduces the rate of As adsorption onto Fe oxyhydroxides. According to

Redman et al. (2002), this slowing down of the As adsorption rate could be due: (i) to a reduction in available surface adsorption sites resulting from coagulation of the Fe oxyhydroxides by NOM or simply from occupation of these sites by NOM, and (ii) to its dependence on NOM desorption from the Fe oxyhydroxides. Therefore, we propose that diagenetic coupled transport-reaction models should not take for granted that adsorption reactions involving As in aquatic systems have fast kinetics, i.e., that they are at equilibrium (e.g., Postma et al., 2007). Instead, they should consider the possibility of slow kinetics of adsorption and use field-derived rate constants.

4.4. Reactions controlling As mobility under sulfidic conditions

Diagenetic modeling of the porewater As profiles reveals zones of As removal when $\Sigma \text{S}^{\text{II}}$ concentrations are $\geq 0.1 \mu\text{M}$ (Figs. 5 and 6). To test if the precipitation of pure As phases such as arsenolite or claudelite ($\text{As}_2\text{O}_3(\text{s})$), orpiment ($\text{As}_2\text{S}_3(\text{s})$), realgar ($\text{AsS}(\text{s})$) or amorphous As sulfide ($\text{As}_2\text{S}_3(\text{s})$) could explain As removal, as reported in other studies (McCreadie et al., 2000; O’Day et al., 2004), we calculated the SI of porewaters with respect to these solids (reactions 11–15 in Table 4). We found that the overlying waters and porewaters of all of our lakes were always undersaturated by several orders of magnitude with respect to all As oxide or sulfide phases ($\text{SI} \leq -6.2$).

Another As sequestration mechanism that has been examined in the literature is its adsorption onto $\text{FeS}(\text{s})$ (Farquhar et al., 2002; Bostick and Fendorf, 2003; Bostick et al., 2004; Wolthers et al., 2005; Wilkin and Ford, 2006). To our knowledge, the only study that provides usable equilibrium constants is that of Wolthers et al. (2005); they reported that for pH values ranging between 5.5 and 8.5, the adsorption of As onto disordered mackinawite ($\text{FeS}_{\text{m}(\text{s})}$) was best predicted by linear adsorption isotherms with K_{D} values of 2 and 9 L g^{-1} for As^{III} and As^{V} , respectively ($K_{\text{D}} = [\text{As}] / \{ \text{As-FeS} \}$, where $\{ \text{As-FeS} \}$ is the concentration of As adsorbed onto $\text{FeS}_{\text{m}(\text{s})}$). We verified the saturation state of our porewaters with respect to disordered mackinawite (reaction 16 in Table 4) using the K_{sp} value of $10^{-3.5}$ provided by Rickard (2006); results indicate that porewaters reach saturation ($\text{SI} = 0$) with respect to disordered mackinawite in each lake over certain depth intervals (Figs. 5m–p and 6g and h). It should be noted that at these depths, porewaters remain undersaturated with respect to greigite ($\text{Fe}_3\text{S}_4(\text{s})$; $\text{SI} \leq -3$) and supersaturated by several orders of magnitude with respect to pyrite ($\text{FeS}_2(\text{s})$; $\text{SI} \geq 11$). We thus assume that the equilibrium of porewaters was occurring with respect to mackinawite and not to the other two iron sulfides, as previously suggested by Davison (1991) for freshwaters. The equilibrium of porewaters with respect to poorly crystallized iron sulfides, such as amorphous $\text{FeS}(\text{s})$ or disordered mackinawite, is consistent with AVS being found at the same depths in the sediments (Fig. 2i–l). We estimated K_{D} values for our sediments, using the values of $\{ \text{As} \}$ in excess of the background concentration deeper in the cores (mol per g of sediments) divided by the AVS concentration (g FeS per g of sediment) as an estimation of

{As–Fe}; the average K_D values ($\pm$ SD) over the zones of As removal are given in Table 3.

To examine if adsorption of As onto $\text{FeS}_{\text{m(s)}}$ is a plausible mechanism for As removal from sulfidic porewaters, the profiles of As consumption/production were compared to those of As speciation using Models 1 and 2 and of saturation index with respect to $\text{FeS}_{\text{m(s)}}$ (Figs. 5e–p and 6c–h). If allowance is made for errors in the calculations of SI and As speciation and in the depth definition of the As removal zones, we observe that for all the lakes and sampling dates, the removal of As from sulfidic porewaters occurs over depth intervals where: (i) porewater is saturated with respect to disordered mackinawite and (ii) As^{V} oxythioanions dominate As speciation predicted by Model 2.

Indeed, As removal from the sulfidic porewaters of Lake Tantaré in July 2003 and September 2003 and from those of Lake Du Syndicat (Fig. 5i, j, and l) occurred over depth intervals where the $\text{HAS}^{\text{VS}}\text{S}_3\text{O}_2^-$ species dominated predicted As speciation (Fig. 5e, f and h) and where porewater was saturated with respect to $\text{FeS}_{\text{m(s)}}$ (Fig. 5m, n and p). Consistent with this interpretation, no As removal zones were found for Lake Tantaré between 0.5 and 9.5 cm in August 2004 (Fig. 5k) because porewaters remained undersaturated with respect to $\text{FeS}_{\text{m(s)}}$ (Fig. 5o) and As speciation was predicted to be dominated by $\text{As}^{\text{III}}(\text{OH})_3^0$ (Fig. 5g).

In Lake Bédard, As was removed from porewaters only over the depth interval where an As^{V} oxythioanion prevailed over arsenite species (–0.7 to 0.5 cm; Fig. 6e and Table 3), even if porewaters were saturated or slightly supersaturated with respect to $\text{FeS}_{\text{m(s)}}$ (Fig. 6g) over the whole sampling depth. In other words, we infer that between 0.5 and 9.5 cm, As removal did not occur because arsenite dominated As speciation. In Lake Holland, As was removed from the sulfidic porewaters in zone 1 located close to the sediment–water interface (–0.5 to 1.1 cm; Fig. 6f and Table 3) and in zone 3 at 8.3–9.5 cm depth. Over these two zones, porewaters were saturated or close to saturation with respect to $\text{FeS}_{\text{m(s)}}$ (Fig. 6h) and the species $\text{HAS}^{\text{VS}}\text{S}_3\text{O}_2^-$ and $\text{As}^{\text{VS}}\text{S}_4^{3-}$ were predicted to be prevalent. Between these two zones, $\text{FeS}_{\text{m(s)}}$ dissolved as shown by porewaters undersaturation in Fig. 6h and As was released to porewaters as evidenced by a zone of slightly positive $R_{\text{net}}^{\text{As}}$ values.

It should be stressed that Model 1 does not offer such a consistent interpretation of all our datasets as does Model 2. For example, it would fail to explain why As removal occurs only close to the sediment–water interface in Lake Bédard, while porewaters are saturated with respect to $\text{FeS}_{\text{m(s)}}$ over the whole sampling interval. The above interpretation of the various profiles points to adsorption of As^{V} species to $\text{FeS}_{\text{m(s)}}$ as a plausible mechanism for As removal from sulfidic porewaters. The K_D values that we calculated at depths corresponding to As removal vary between $5 \pm 2 \text{ L g}^{-1}$ and $32 \pm 2 \text{ L g}^{-1}$ (Table 3); these values are of the same order of magnitude as the value of 9 L g^{-1} reported by Wolthers et al. (2005) for the adsorption of As^{V} onto disordered mackinawite and provide additional support to our proposed mechanism for As removal from porewaters. However, the inferred mechanism of As adsorption onto $\text{FeS}_{\text{m(s)}}$ needs to be validated by further measurements

in a variety of natural environments and by laboratory experiments with well characterized $\text{FeS}_{\text{(s)}}$ sorbent and As sorbate.

4.5. Anthropogenic imprint on the sedimentary record

For Lakes Tantaré, Bédard and Holland, where sediment mixing was negligible, the {As} depth profiles (Fig. 2a, c, and d) represent the sum of: (i) {As} at the time of deposition and (ii) As released from or added to the sediment due to diagenesis during burial (hereafter called {As}_{diag}). Even though As undergoes significant post-depositional redistribution during early diagenesis, {As}_{diag} can be estimated as (Couture et al., 2008):

$$\begin{aligned} \{\text{As}\}_{\text{diag}} &= - \int_{x=0}^{x=x_i} \frac{R_{\text{net}}^{\text{As}}}{\text{DBD} \times v_s} dx \\ &\approx - \sum_{x=0}^{x=x_i} \frac{R_{\text{net}}^{\text{As}}}{\text{DBD} \times v_s} \Delta x \end{aligned} \quad (5)$$

where x_i is depth of the sediment layer, the maximum depth being 10 cm. We therefore assumed that sizeable As remobilisation and redistribution only take place above 10 cm depth, given that most important primary early diagenetic reactions, including sulfate reduction, were already completed above that horizon. As concentration in the sediment particles at the time of deposition ({As}_{hist}) is then obtained by subtracting {As}_{diag} from measured {As}, and the flux of atmospheric As (J_{As}) from anthropogenic sources delivered to the lake surface can be estimated as:

$$J_{\text{As}} = (\{\text{As}\}_{\text{hist}} - \{\text{As}\}_{1850}) \times \omega \times \frac{{}^{210}\text{Pb} I_{\text{atm}}}{{}^{210}\text{Pb} I_{\text{sed}}} \quad (6)$$

where {As}₁₈₅₀ is the average pre-1850 {As}_{hist} at the sampling site, ${}^{210}\text{Pb} I_{\text{sed}}$ is the inventory of unsupported ${}^{210}\text{Pb}$ in the sediment cores (Table 1) and ${}^{210}\text{Pb} I_{\text{atm}}$ is the cumulative atmospheric input of ${}^{210}\text{Pb}$, which was assumed to be identical to the average inventory of ${}^{210}\text{Pb}_{\text{uns}}$ in soils on the Precambrian Shield in Eastern Ontario (0.44 Bq cm^{-2} ; Cornett et al. (1984). The ratio ${}^{210}\text{Pb} I_{\text{atm}}/{}^{210}\text{Pb} I_{\text{sed}}$ in Eq. (6) allows correcting for lake-specific processes such as sediment focusing and loss of As by lake outflow (Kada and Heit, 1992); such a correction implies that As and ${}^{210}\text{Pb}$ react similarly with particles. Values of J_{As} were not calculated for Lake Du Syndicat because sediment mixing occurred in this lake (see Electronic Annex).

Temporal trends of J_{As} were very similar in Lakes Tantaré and Bédard although the maximum value was 34% lower in Lake Bédard than in Lake Tantaré (Fig. 8). In both lakes, which are located only 40 km apart, J_{As} increased from ~1850, peaked in the 1950s and then decreased by almost 90% to the present time value. Based on a positive correlation between J_{As} and the depositional flux of polycyclic aromatic hydrocarbons (PAHs) in Lake Tantaré sediments, the maximum value in the 1950s was previously attributed to coal burning for house heating and industrial purposes, which peaked in mid-20th century in Eastern Canada (Couture et al., 2008). In Lake Holland, which is located only 8 km from Murdochville where a non-ferrous metal smelter was operated during several decades, much higher As deposi-

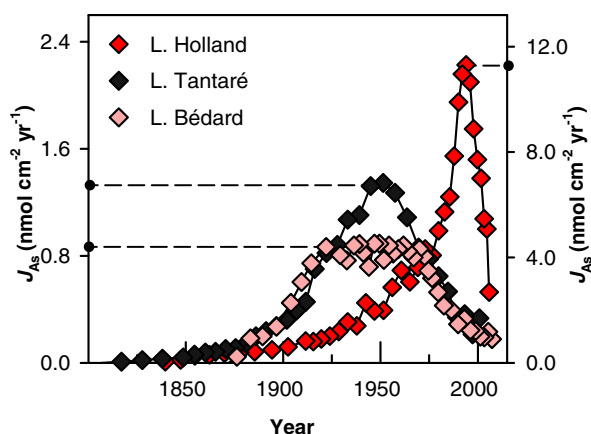


Fig. 8. Chronological records of atmospheric As fluxes (J_{As}) from anthropogenic sources to the surface of Lakes Tantaré, Bédard and Holland.

tional fluxes were recorded (Fig. 8). Production at the smelter began in 1950 and reached its maximum just before the plant was temporally shut down in the 1980s. When production restarted in 1989, metal emissions into the atmosphere were reduced as a result of new technology implementation. Consistently, the depositional flux of As in Lake Holland increased significantly after the mid-20th century, reached a maximum during the 1980s and diminished markedly after that, indicating that the smelter was the main source of the As contamination.

5. CONCLUSIONS

Adsorption of As onto diagenetic Fe oxyhydroxides controls As mobility at the vicinity of the sediment–water interface of the two lakes with an oxygenated hypolimnion. Recycling of As due to its release to the porewaters by the reductive dissolution of Fe oxyhydroxides upon sediment burial, followed by its upward migration and its adsorption onto the freshly formed Fe oxyhydroxides is responsible for the As enrichment observed in the surface sediments of these lakes. Peaks in [As] porewater profiles and inverse diagenetic modeling suggest that As adsorption onto the authigenic Fe oxyhydroxides is relatively slow, in contrast with laboratory adsorption experiments carried out with pure As solutions. We infer, based on the report that NOM greatly decreases the rate of As adsorption onto hematite (Redman et al., 2002), that the presence of natural organic matter in our lake sediments is responsible for the slow adsorption of As onto authigenic Fe oxyhydroxides. In line with the work of Redman et al. (2002), further experiments should be performed to evaluate the importance of natural organic matter in slowing down As adsorption onto Fe oxyhydroxides representative of the authigenic forms present in lake sediments (e.g., ferrihydrite, lepidocrocite). We suggest that kinetic treatment of As adsorption onto Fe oxyhydroxides be considered in the development of coupled reaction-transport models to describe As behavior in sediments.

In contrast to the other previously published models, the thermodynamic model proposed by Helz and Tossell (2008), identified as Model 2 in this study, allows for the

formation of As^V thioanions in sulfidic waters. Our field-derived observations are that As removal in sulfidic waters occurred only when As^V oxythioanions were (according to Model 2) an important fraction of total dissolved As and when saturation with respect to $FeS_{m(s)}$ was reached. Based on these findings, we infer that adsorption of As^V onto poorly crystalline Fe sulfide stands as a plausible mechanism for As removal from the sulfidic waters of all the lakes studied. This inference has potential implications for As transport in anoxic waters and should be tested in a wider variety of natural environments. It should also be supported by measurements of dissolved As speciation and by characterization of the nature of the sorbent and of the redox state of solid As in sulfidic environments.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2009.11.028.

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