Non-steady state diagenesis of organic and inorganic sulfur in lake sediments

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RAOUL-MARIE COUTURE^{1,2,*}, RACHELE FISCHER², PHILIPPE VAN CAPPELLEN² AND CHARLES GOBEIL³

¹ Norwegian Institute for Water Research, Gaustadalléen 21, Oslo, 0349, Norway

(*correspondence: rmc@niva.no)

² Ecohydrology Research Group, Water Institute and Department of Earth and Environmental Sciences, University of Waterloo, Waterloo, ON N2L 3G1, Canada

³ Université du Québec, INRS-ETE, 490 de la Couronne, Québec, G1K9A9, Canada

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ABSTRACT

Sulfur controls the fate of many geochemical elements in lake sediments, including iron, phosphorus and environmentally important trace elements. We measured the speciation of pore-water and sediment-bound sulfur (aqueous sulphate and sulfides, elemental sulfur, iron monosulfide, pyrite, organic sulfur) and supporting geochemical variables (carbon, oxygen, iron) in the sediments of a perennially oxygenated and a seasonally anoxic basin of an oligotrophic lake in Québec, using a combination of pore-water analyses, sequential extractions and X-ray absorption near edge structure. A non-steady state early diagenetic model was developed and calibrated against this extensive dataset to help unravel the pathways and quantify the rates of S transformations. Results suggest that the main source of S to the sediments is the settling of organic ester-sulfate (R-O-SO₃-H). Hydrolysis of these compounds provides an additional source of sulfate for anaerobic microbial oxidation of sedimentary organic matter, releasing sulfide to the pore-water. Reduced solid-bound S species accumulate as thiols (R-SH) and iron sulfides in the perennially oxygenated and seasonally anoxic basin, respectively. The model-estimated rate constant for R-SH formation is lower than previously estimated for this particular lacustrine site, but similar to that proposed for marine shelf sediments. The solid sediment S profiles, however, carry the imprint of the time-dependent sulfate input to the lake. Iron sulfide enrichments formed during past decades of elevated atmospheric SO₄ deposition are presently dissolving. In the sediments of the perennially oxygenated basin this reaction hampers the build-up of Fe(III) (oxy)hydroxide near the sediment-water interface.

1. INTRODUCTION

Sulfur (S) biogeochemistry is complex and of widespread interest due to its impact on many fundamental environmental processes, ranging from terrestrial primary productivity (Scherer, 2009) and sediment microbial metabolism (Canfield et al., 2006), to organic matter (OM) preservation at long time-scales (Arndt et al., 2013; Werne et al., 2004). In lakes, the cycling of S in sediments is spatially and temporally dynamic, and tightly coupled to other biogeochemical species and processes (Holmer and Storkholm, 2001), as it partakes in an intricate network of geochemical reactions involving 8 valence states, ranging from +6 (e.g., sulfate, SO_4^{2-}), 0 (e.g., elemental sulfur, S^0), to -2 (e.g., sulfide, $\text{S}^{-\text{II}}$, and reduced organic sulfur) (Sievert et al., 2007).

The majority of S fluxes to lakes come from soils (Likens et al., 2002) and wetlands (Mandernack et al., 2000) within the catchment, generally as allochthonous organic matter containing oxygen-bound S (e.g., R-O-SO₃-H groups such as ester-SO₄ and other organo-sulfates) or carbon-bound S (e.g., R-SH groups such as amino-acids and other thiols). The latter two groups may constitute up to 98% of soil S pool (Vestergren et al., 2012). Aqueous fluxes of S to lakes originate from mineralisation of such organics (Zhao et al., 2006), rocks weathering or direct atmospheric SO_4^{2-} deposition (Brimblecombe et al., 2003). Upon entering the water column, organic S (S_{org}) can be utilized by micro-organisms via enzymes that cleave the R-O-SO₃-H (e.g., aryl sulfatase) and R-SH (e.g., cysteine liase) bonds, thus replenishing SO_4^{2-} and HS^- , respectively (Bunemann, 2008). Sources of S to the sediment surface comprises catchment-derived S, water-column SO_4^{2-} as well as S_{org} settling with seston (King and Klug, 1982; Likens et al., 2002). In the sediments, once dioxygen is depleted, SO_4^{2-} is mainly reduced to sulfide via dissimilatory reduction, from which the sulfate-reducing bacteria gain energy for growth and maintenance (Canfield et al., 2005).

Sulfide reacts with Fe to form amorphous monosulfide (mackinawite, $\text{FeS}_{(\text{m})\text{s}}$) to crystalline pyrite ($\text{FeS}_{2(\text{s})}$). The transformation of $\text{FeS}_{(\text{m})\text{s}}$ to $\text{FeS}_{2(\text{s})}$ is influenced by various factors, including the ratio of reactive Fe to available $\text{S}^{-\text{II}}$ (Burton et al., 2011; Kraal et al., 2013), the inhibition by labile organic carbon (C_{org} ; (Morgan et al., 2012; Morse and Wang, 1997), the ability of $\text{S}^0_{(\text{aq})}$ to promote pyritization via the polysulfide pathway (Sundby et al., 2004) and the effect of pH on $\text{FeS}_{(\text{m})\text{s}}$ transformation kinetics (Morse and Luther, 1999). Overall, the interactions between S and Fe in anoxic waters, water-logged soils and sediments have been extensively studied (e.g., Burton et al., 2011; Carignan and Tessier, 1988; Hansel et al., 2015; Holmer and Storkholm, 2001; Johnston et al., 2014; Morgan et al., 2012; Peiffer and Gade, 2007; Poulton et al., 2004; Rickard and Luther, 2007; Rickard and Morse, 2005; ThomasArrigo et al., 2016).

Sulfide can also be sequestered as S_{org} (Francois, 1987), for instance as R-SH during OM sulfurization and assimilatory SO_4^{2-} reduction. Sulfide incorporation in OM has frequently been reported in marine sediments (Werne et al., 2008), but less so in lakes despite evidence of high

thiols concentrations in freshwater sediments (Bostick et al., 2005; Sleighter et al., 2014; Urban et al., 1999). Sulfides can further be oxidized to form S^0 species, abundant both in solid (Burton et al., 2006b) and aqueous (Wang and Tessier, 2009) phases. S^0 reacts with Fe (Rickard and Luther, 2007) and metal(loid)s (Helz, 2014; Helz and Tossell, 2008; Helz et al., 2002; Wang and Tessier, 2009; Weber et al., 2009), and serves as a precursor for the formation of S_{org} compounds, including volatile species (Gun et al., 2000).

Here, we rely on two established approaches to gain a quantitative understanding of the biogeochemical cycling of S in sediment: (1) detailed solid-phase speciation measurements (e.g., Bostick et al., 2005; Burton et al., 2011; Johnston et al., 2014; Kraal et al., 2013; Morgan et al., 2012; Urban et al., 1999; Zeng et al., 2013), and (2) reactive-transport diagenetic modelling (e.g., Katsev et al., 2006; Paraska et al., 2014). Table 1 lists 14 studies that have included the cycling of S in diagenetic models for freshwater sediments, nine of which present measured depth profiles of S species against which the model predictions are evaluated. In five cases SO_4^{2-} is the only species considered while in the four others data on aqueous reduced S species (i.e. S^{2-}) and on $FeS_{m(s)}$ and $FeS_{2(s)}$ are also considered. None of the models have reproduced the features of the depth-profiles of S_{TOT} in the solid-phase, or been tested against measurements of other dominant solid-phase species in lake sediments, such as S_{org} which has been shown to dominate S speciation in lake sediments (Loshier and Kelts, 1989; Urban et al., 1999), or against measurements of S^0 , which is ubiquitous both in sediment and in pore-water (Wang and Tessier, 2009).

In recognizing the critical importance of S in controlling the fate of nutrients and of major and trace elements, our goal is to improve our quantitative understanding of the speciation and fate of S in freshwater sediments. Indeed, a more comprehensive integration of the S cycle in diagenetic models, is a stepping stone for the more accurate prediction of the biogeochemical cycles of other elements, such as C, O, Fe, and P (Meysman and Middelburg, 2005). We combine an extensive dataset on aqueous and solid-phase S speciation, gathered using aqueous analysis, sequential extraction and X-ray absorption near-edge structure (XANES) spectroscopy, with an updated reactive-transport model for S, C, O and Fe diagenesis. We estimate the rates of organic and inorganic S transformations in the sediment of two oligotrophic lacustrine basins experiencing different oxygenation conditions throughout the year, enabling us to quantify the pathways of S sequestration under both oxic and anoxic conditions.

2. METHODS

2.1 Sampling

Samples of settling particles in the water column, sediments, and sediment pore-water were collected in Lake Tantaré (47° 04' 15" N, 71° 33' 42" W), a Canadian Shield headwater oligotrophic lake located in an ecological reserve 38 km Northwest of Québec City, Central Canada. Atmospheric deposition is the only input of anthropogenic S to this 1.16 km² lake whose

drainage basin has never been inhabited. This study was carried out in two adjacent basins of Lake Tantaré where depths reach 15 m (Basin A) and 21 m (Basin B). The shallow basin is perennially oxygenated, whereas the deep basin is occasionally anoxic. Sediment accumulation rates (ω ; $\text{mg cm}^{-2} \text{yr}^{-1}$) and ages of the sediment layers in Basin A and B have been previously derived from unsupported ^{210}Pb data, obtained by low-background gamma spectrometry on freeze-dried sediment (Couture et al., 2008), and validated using ^{137}Cs stratigraphy. Sediment porosity (ϕ), determined from the dry sediment weight and water content after freeze-drying, as well as dry bulk density (DBD; g cm^{-3} of whole sediment), are provided in Couture et al. (2008).

Pore-water sampling occurred in August 2005 in Basin A and in September 2006 and July 2007 in Basin B. Near bottom O_2 concentrations, measured using a YSI Model 58 dissolved O_2 meter, were $>118 \mu\text{M}$ in August 2005 in Basin A and $<0.3 \mu\text{M}$ and $<125 \mu\text{M}$ in September 2006 and July 2007, respectively, in Basin B. Pore-water samples were obtained by *in situ* dialysis using acrylic peepers designed to collect 8 mL of samples from 5 cm above the sediment-water interface (SWI) to 10 cm below with a vertical resolution of 1 cm. Three peepers were deployed by divers at the deepest point of each basin and left to equilibrate for 21 days, yielding enough sample volume for triplicate measurements of pH, Fe, SO_4^{2-} , total sulfide ($\Sigma\text{S}^{-\text{II}}_{(\text{aq})}$) and total zero-valent sulfur ($\Sigma\text{S}^0_{(\text{aq})}$). Peeper preparation and sampling procedures, including complete O_2 removal (Carignan et al., 1994), are described elsewhere (Couture et al., 2008). Within two minutes of peeper recovery, sample aliquots for the measurements of $\Sigma\text{S}^{-\text{II}}_{(\text{aq})}$ and $\Sigma\text{S}^0_{(\text{aq})}$ were taken with nitrogen-purged polypropylene syringes equipped with a polyethylene plunger. Samples for analysis of $\Sigma\text{S}^{-\text{II}}_{(\text{aq})}$ were delivered to 4 mL Teflon-lined septa amber vials containing 40 μL of 2.7 mM N,N'-dimethyl-p-phenylenediamine- SO_4 and 5.5 mM FeCl_3 (Alfa-Aesar), while samples for $\Sigma\text{S}^0_{(\text{aq})}$ were delivered to similar vials containing 2 mL of double-distilled ethanol, 40 μL of tetrahydrofuran, 0.4 mL of 1M NaNO_3 , and 10 μL of 1 M HNO_3 . Samples for SO_4^{2-} determinations were delivered to polypropylene tubes and kept at 4°C and analyzed within two days. Samples (3 mL) for Fe were obtained with an acid-washed pipette tip and injected into prewashed and pre-acidified (45 μL of 1.5 M HNO_3 , final pH 2.5) 4 mL vials. Samples (1 mL) were also collected for on-site pH measurements with a combination microelectrode (Microelectrode Inc., Model MI-710).

Three sediment cores were collected by divers in October 2011 at each of the pore-water sampling sites using 9.5-cm internal diameter butyrate tubes. One of the cores was used to determine on-site the O_2 concentration profile across the SWI at a sub-millimeter vertical resolution. The measurements were done within 30 minutes of core retrieval with a microprobe (Unisense OX-100) having a built-in reference electrode and a silver guard cathode (Revsbech, 1989). A two-point calibration line was made between the air-saturated water and the anoxic sediment. The electrode position was controlled in two dimensions by a micro-manipulator, and sensor currents were converted to voltages by a picoampere-millivolt converter (Unisense PA2000). The other two cores were extruded at 0.5-cm intervals from the sediment surface to 10 cm or 15 cm depth and then at 1-cm intervals to 30 cm depth. One of them was analyzed for C_{org} ,

Fe and S, and the other for acid volatile sulfides (AVS), chromium reducible sulfides (CRS) and elemental sulfur (ES) through sequential extraction techniques, and for S speciation by X-ray absorption near-edge spectroscopy (XANES) as described below. To minimize oxidation, sediment samples dedicated to determination of the S speciation were individually sealed in plastic bags and buried into a larger bag filled with anoxic sediment and kept frozen until analysis.

Fixed conical sediment traps (Alfaro-De la Torre and Tessier, 2002) with an open surface area of 45 cm² were deployed at about 2 m above the SWI in the hypolimnion of Basins A and B on May 31st and recovered on June 21st, 2012. Contents of the traps were filtered through 1 µm Nuclepore membrane, freeze-dried and weighted to estimate the vertical particle fluxes in the water column (mg cm⁻² yr⁻¹).

2.2 Analyses

2.2.1 Pore-water. The aqueous S species SO₄²⁻, ΣS^{-II}_(aq) and ΣS⁰_(aq) were measured by ion chromatography (Subosa et al., 1989), UV/Vis spectrometry following calibration using solutions standardized by iodometric titration (Cline, 1969), and square-wave cathodic stripping voltammetry in hanging Hg drop mode (Wang and Tessier, 2009; Wang et al., 1998), respectively. Total pore-water Fe, was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES; VISTA AX CCD) using external calibration. Hereafter, we assume that total dissolved Fe is Fe^{II}

2.2.2 Solid-phase. Bulk solid-phase C_{org} and total S (S_{TOT}) were determined using a CNS Carbo Erba analyzer. Total Fe (Fe_{TOT}) was analyzed by ICP-OES after complete digestion of ground, freeze-dried sediment aliquot using ultra-pure HNO₃, HClO₄ and HF (McLaren et al., 1995). In addition, three operationally defined pools of inorganic solid-phase S were determined through a sequential extraction (SE) scheme proposed by Hsieh and Shieh (1997). This protocol is optimized for room temperature and is safer than protocols involving heated acidic oxidizing solutions (Burton et al., 2008; Couture et al., 2013b; Hsieh et al., 2002). The SE protocol included the following steps: (1) the extraction of acid volatile sulfide (AVS) with a solution of 6 N HCl containing 0.1 M ascorbic acid to prevent sulfide re-oxidation, (2) the extraction of chromium reducible sulfide (CRS) with a solution of Cr(II) prepared by dissolving CrCl₃·6H₂O in HCl (0.5 N) followed by the reduction of Cr(III) to Cr(II) in a column of Zn amalgam, and (3) the extraction of operationally defined elemental S (ES) with 10 mL of dimethylformamide in the presence of Cr(II) and HCl. The evolving H₂S was trapped during each extraction in a NaOH solution and determined colorimetrically by the methylene blue method (Cline, 1969). Note that we used Teflon material for the extractions and ultra-pure N₂ as a carrier gas for sulfide. The S species of the operational AVS pool are believed to include ΣS^{-II}_(aq), aqueous Fe-S clusters, and amorphous metal sulfides (Morse and Rickard, 2004), while those of the CRS and ES pools likely comprise mainly pyrite (FeS_{2(s)}) and rhombohedral S (S(α)_{8(s)}), respectively (Burton et al., 2011). Residual sediments remaining after the extractions contain acid-insoluble S^{-II}, such as

metalloid sulfides (Wilkin and Ford, 2006), and S_{org} . Because acid-insoluble S^{II} associated with metalloids should be of minor importance in the sediments studied, we assumed that S_{org} is given by the difference between S_{TOT} and the sum of AVS, CRS and ES.

We used XANES to mitigate the drawbacks of partial extraction techniques and improve our information on S speciation (Morgan et al., 2012; see Discussion) in Lake Tantaré sediments. XANES allows for an estimation of the redox status and the coordination chemistry of S in sediments (Bostick et al., 2005; Prietzel et al., 2011; Xia et al., 1998; Zeng et al., 2013). XANES spectra were recorded in the energy range of 2440-2640 eV at the wiggler beamline 4-3 of the Stanford Synchrotron Radiation Laboratory lightsource (SSRL, Stanford, USA). Anoxic sediment samples were thawed and air-dried under N_2 , grounded using an agate mortar and pestle, and mounted on a sample holder protected by 5 μm S-free polypropylene windows (SPEX XRF PP film #3520). Analyses were carried out with the sample compartment and detector under slight helium (He) over-pressure. The X-ray energy resolution was achieved using a (111)-Si crystal monochromator calibrated relative to the white line of a $Na_2S_2O_3$ standard at 2479.3 eV. Spectra were collected in transmission mode using an ionization chamber or in fluorescence mode using a 4-element solid-state Si detector. Higher-order harmonics were reduced by detuning the second monochromator to 20% of its maximum intensity. Background removal, normalization and merging of the spectra were carried out with the ATHENA software package. The raw spectra data were imported into ATHENA and converted to $\mu(E)$. $E(0)$ was set to the absorption energy of the highest derivative. The pre-edge and post-edge ranges were specified generally over the energies of 2440-2465 eV and 2485-2500 eV, respectively.

We estimated the proportion of each S species within all samples using both Linear Combination Fitting (LCF) and Gaussian Curve Fitting (GCF). LCF reconstructs the sample's spectra by linear addition of the spectra of reference compounds (Prietzel et al., 2011), while the GCF calculates the contribution of individual Gaussian curves, ascribed to discrete oxidation states (Lehmann et al., 2008; Solomon et al., 2011), to the overall spectra (Manceau and Nagy, 2012; Xia et al., 1998). LCF and GCF are semi-quantitative and only estimate the bulk proportion of a given species in a sample. Moreover, oxidized S species have larger magnitude XANES signals even when they are only minor spectral components. As a consequence of these differences in spectral magnitude, fitting procedures are less sensitive to changes in the proportion of reduced sulfides, particularly $FeS_{m(s)}$ (Bostick et al., 2005; Prietzel et al., 2011).

LCF was performed in ATHENA over the energy range 2465-2490 eV using edge-normalized spectra of reference compounds. The references analysed were chosen to cover a range of functional groups: (i) sulfides (Na_2S , $FeS_{m(s)}$, $FeS_{2(s)}$), (ii) thiols (L-cysteine), (iii) thioethers (methionine), (iv) alkyl disulfides (L-cystine), (v) rhombohedral S, (vi) sulfoxides (L-methionine sulfoxide), (vii) sulfonates (L-cysteic acid), (viii) sulfones (dimethyl sulfone), (ix) thioesters (dodecyl- SO_4), and (x) sulfates (chondroitin sulfate, Na_2SO_4). Na_2S and $FeS_{m(s)}$ were synthesized in the laboratory (Couture et al., 2013a), $FeS_{2(s)}$ was provided by Strem Chemicals, rhombohedral S and Na_2SO_4 by Alpha-Aesar and all other compounds by Sigma-Aldrich. GCF

was performed by least-square fitting according to Xia et al. (1998). Parameters of the Gaussian curves, each assumed to represent a unique oxidation state, were the amplitude, the centroid (or $E(0)$, in eV), and the width of the curve. Two arctangent step functions representing the X-ray absorption step-heights were parametrized with step height, point of inflection and gradient of the step (Manceau and Nagy, 2012). The position and shape of the Gaussian curves were allowed to vary so that their sum closely matched the data. Species were deemed identical if the centroids values were within ± 0.32 eV (loose constraint for species with valence $< +4$) or of ± 0.07 eV (tight constraint for species with valence $> +4$) (Xia et al., 1998). The number of curves was constrained such that a set of 5 curves was able to fit the entire dataset. We associated a unique oxidation state with each Gaussian curve using the relationship between oxidation state of S in reference compounds and the position of their white line ($r^2 = 0.995$) in the XANES spectra. We then corrected the integrated area of each Gaussian curve using the linear relationship between the white line intensity and the oxidation state of the species ($r^2 = 0.96$). Finally, all areas were normalized to the area of the curve representing S^0 . It follows that both the oxidation state and the relative abundance of the S species can be identified from the position of the Gaussian curve on the energy axis and surface area under the curve.

2.3 Diagenetic modelling

The dataset obtained for this study provides snapshots of the distributions of S species and ancillary geochemical variables in the sediments and their pore-water. The modeling therefore aims to capture the features of the measured depth-profiles of the various aqueous and solid-phase species but also to generate time-series of the distributions of organic and inorganic S species concentrations and of reaction rates and of species fluxes, without imposing steady-state bottom water concentrations of SO_4^{2-} and O_2 at the model's upper boundary. Such information is hardly accessible from field data only. Several packages for sediment diagenetic modelling are publicly available, including ReacTran developed in R (Soetaert and Meysman, 2012), LSSE-MEGA developed in Fortran (e.g., Katsev and Dittrich, 2013; Katsev et al., 2006), BNRS developed in Fortran and Maple (Canavan et al., 2006; Dale et al., 2009; Regnier et al., 2002) and Matsedlab developed in Matlab (Couture et al., 2010c). Here we build on Matsedlab (Couture et al., 2010c), taking into account the reactions listed in Table 2. The code was configured to be automatically calibrated using the model-independent parameter estimation software PEST (Doherty, 2015). Simulations were run for 300 yr ending in 2012, after a 250 yr spin up period. Results are presented as a snapshot of the model state chosen to correspond to the actual sampling dates in each basin.

Model development followed the general approach outlined by Van Cappellen and Wang (1996). Partial differential equations were used to define a coupled transport-reaction system in which all reactions are described by kinetic expressions; 13 reaction pathways and 15 chemical species were considered (Table 2 and Fig. 1). The reaction network includes primary redox reactions describing the degradation of OM via oxic respiration (R1), dissimilatory Fe reduction

(R2), and sulfate reduction (R3) (Table 2). The model considers two pools of Fe (oxy)hydroxides, $\text{Fe}(\text{OH})_3$ and FeOOH , representing ferrihydrite and goethite, respectively, and parametrized differently (Table 2) with respect to their reactivity during dissimilatory Fe reduction (DIR) (Liu et al., 2015). Nitrate reduction was not considered, because of the very low concentrations of this nutrient in Lake Tantaré (Couture et al., 2010b). Manganese oxyhydroxides were similarly excluded as potential electron acceptors, because neither solid-phase nor pore-water Mn profiles showed evidence of significant Mn redox cycling in Lake Tantaré (Couture et al., 2010a). This could possibly indicate that authigenic Mn oxyhydroxides do not form due to the acidic conditions near the SWI (pH 5.3-6.0). The consumption of a given terminal electron acceptor (TEA) was coupled to the rate of OM oxidation through a Monod kinetic dependency on the TEA concentration, and an inhibition term limiting the rate of a respiratory pathway in the presence of stronger oxidants (Table 3). OM degradation, the driver of diagenesis (Berner, 1980), follows the so-called 3G model, which assumes labile (OM1), semi-labile (OM2) and recalcitrant (OM3) pools of OM (Arndt et al., 2013).

The secondary redox reactions considered (Tables 2 and 3) were the oxidation of pore-water Fe^{II} (R5), H_2S (R6), and $\text{FeS}_{\text{m(s)}}$ by O_2 (R7) and of HS^- by $\text{Fe}(\text{OH})_{3(\text{s})}$ (R8). Both R6 (Poulton et al., 2004) and R13 (Burton et al., 2011; Burton et al., 2006b) yield $\text{S}^0_{(\text{aq})}$. The rates of precipitation and dissolution of $\text{FeS}_{\text{m(s)}}$ (R9 and R_9, respectively) were explicitly dependent on the corresponding pore-water saturation state (Davison, 1991). The rate of $\text{FeS}_{2(\text{s})}$ precipitation was presumed to be proportional to the concentrations of pore-water H_2S (R10) or $\text{S}^0_{(\text{aq})}$ (R11) and of solid-phase $\text{FeS}_{\text{m(s)}}$ (Dale et al., 2009). The rate of diagenetic sulfidization of sedimentary OM (R13; Rudd et al. (1986)) was assumed to depend on the concentrations of OM and dissolved H_2S (Couture et al., 2010b; Dale et al., 2009). Solid $\text{S}(\alpha)_{8(\text{s})}$ was expected to be in equilibrium with $\text{S}^0_{(\text{aq})}$ (R12 and R_12).

The release of SO_4^{2-} via enzymatic cleavage of the R-O-SO₃-H bond (R15) (Fitzgerald et al., 1982) by sulfatase was modelled using a Monod kinetic formulation. Sulfatase enzymes are synthesized by a variety of organisms to cleave ester-SO₄ bonds and replenish SO_4^{2-} to the aqueous phase (Kertesz, 2000). In soils, their production is regulated by SO_4^{2-} starvation, while accumulation of SO_4^{2-} in the aqueous phase can inhibit their activity (Solomon et al., 2011). However, because the SO_4^{2-} concentration at which inhibition takes place (i.e. KinSO_4) is not well characterized in lacustrine sediments, we constrained the value of this parameter using the model. This yielded KinSO_4 values of 95 and 6 μM for Basin A and B, respectively (Table 4). Such an order-of-magnitude difference between basins might reflect that the sediment structure protects ester groups from sulfatase attack to a greater extent in Basin B than in Basin A (Kertesz, 2000). Finally, in this modeling approach, sulfatase enzymatic activity is independent of substrate concentration assuming that the sediment is an infinite acting reservoir of substrate (Scherer, 2009).

Molecular diffusion, bioirrigation, bioturbation and sediment accumulation were included in the one-dimensional mass conservation equations following Boudreau (1997). Based on previous

work (Couture et al., 2010a), advection of pore-water due to sediment burial was neglected. Diffusion coefficients were taken from the literature (Table 4). In Basin A, coefficients of bioirrigation (α) and bioturbation (D_B) were constrained independently by Gallon et al. (2004) using data from biological field surveys (Hare et al., 1994) and the biodiffusion coefficient of chironomids (Matisoff and Wang, 2000). We assumed that α decreased exponentially from a fixed boundary value at the SWI to zero at 10 cm depth, since no benthic animals were found below this depth in the sediments. The low value of D_B ($2.2 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) reflects the sparse benthic community ($1690 \pm 180 \text{ animals m}^{-2}$; mostly chironomids) at the sampling site. Both α and D_B were assumed to be zero in Basin B during seasonal anoxia, while their values were adjusted by the model during the oxygenated period.

3. RESULTS

3.1 Pore-water solutes

Bottom water $[\text{O}_2]$ was $153 \pm 20 \text{ } \mu\text{M}$ in Basin A in August 2005 and $23 \pm 5 \text{ } \mu\text{M}$ in Basin B in July 2007 (Fig. 2a,b). At these sampling dates, O_2 penetrated to $\sim 260 \text{ } \mu\text{m}$ depth in Basin A, and to $\sim 120 \text{ } \mu\text{m}$ depth in Basin B (Fig. 2a,b). In Basin A, dissolved Fe concentrations ranged between $29 \pm 18 \text{ } \mu\text{M}$ and $52 \pm 23 \text{ } \mu\text{M}$, with maximum values around 2 cm depth. In Basin B, Fe concentrations were about one order of magnitude higher than in Basin A, and continuously increased with depth, reaching $306 \pm 60 \text{ } \mu\text{M}$ during the oxygenated period (July 2007) and $684 \pm 100 \text{ } \mu\text{M}$ in the anoxic period (September 2007; Fig. 2 c,d).

Sulfate concentrations in Basin A were highest at the SWI and decreased with depth, from 32.0 ± 0.5 to $11 \pm 3 \text{ } \mu\text{M}$; concentrations of $\Sigma\text{S}^{\text{II}}_{(\text{aq})}$ and $\Sigma\text{S}^0_{(\text{aq})}$ displayed subsurface maximum values of $6 \pm 5 \text{ } \mu\text{M}$ for $\Sigma\text{S}^{\text{II}}_{(\text{aq})}$ and $0.8 \pm 0.6 \text{ } \mu\text{M}$ for $\Sigma\text{S}^0_{(\text{aq})}$ at 5 cm depth (Fig 2. e, g, i). In Basin B, SO_4^{2-} concentrations were significantly lower and did not vary much with depth, except for a small decrease downward in the first two cm during the oxygenated period in July 2007 (Fig. 2f). The profiles of $\Sigma\text{S}^{\text{II}}_{(\text{aq})}$ and $\Sigma\text{S}^0_{(\text{aq})}$ in Basin B, however, showed differences between the two sampling dates: $\Sigma\text{S}^{\text{II}}_{(\text{aq})}$ concentrations were higher under anoxic conditions (Fig. 2h), whereas $\Sigma\text{S}^0_{(\text{aq})}$ concentrations were higher under oxygenated conditions (Fig. 2j). Overall, in both basins the concentrations of dissolved Fe were higher than those of $\Sigma\text{S}^{\text{II}}_{(\text{aq})} + \Sigma\text{S}^0_{(\text{aq})}$ by about 10-fold in Basin A and about 150- and 600-fold under oxygenated and anoxic hypolimnetic waters, respectively, in Basin B (Fig. 2).

3.2 Solid-phase organic carbon, iron and sulfur

The profiles of total C_{org} in the sediments exhibit relatively constant values as a function of depth in Basins A and B (Fig. 3a,b), with values of ~ 15 and $\sim 20 \text{ mmol g}^{-1}$, respectively. In Basin A, solid-phase Fe dropped exponentially from $\sim 1800 \text{ } \mu\text{mol g}^{-1}$ to $\sim 200 \text{ } \mu\text{mol g}^{-1}$ between the SWI and 15.5 cm depth. In contrast there was no pronounced Fe enrichment near the sediment surface in Basin B; concentrations remain relatively constant with depth ($\sim 525 \text{ } \mu\text{mol g}^{-1}$).

¹). Total S profiles displayed subsurface maxima in both basins, peaking at $\sim 150 \mu\text{mol g}^{-1}$ in Basin A and $\sim 350 \mu\text{mol g}^{-1}$ in Basin B, with similar background levels ($\sim 100 \mu\text{mol g}^{-1}$) at depth in the cores from both basins (Fig. 3e,f).

3.3 Speciation of solid-phase S

The concentrations of AVS, CRS and ES were lower in Basin A than in Basin B, but the profiles of the three species show maximum values at similar depths, several cm below the SWI in both basins (Fig. 4). The CRS inventories were about 4-fold higher than those of AVS and 2-fold higher than those of ES in both basins (Fig. 5a), and their maximum concentrations occurred deeper than those of AVS and ES (Fig. 4). Overall, the concentrations of the three species together accounted for less than 5% of S_{TOT} in the perennially oxygenated Basin A, but for 15-60% of S_{TOT} between 4 and 15 cm depth in the seasonally anoxic Basin B.

The treatment of the XANES results by the LCF approach identified chondroitin-SO₄, a plant-derived ester-SO₄ containing a R-O-SO₃-H group, as the dominant S species at the SWI in Basin A as well as in water column settling particles collected using sediment traps (Fig. 6a). GCF data treatment yields an oxidation state varying between +0.4 and +6 for the oxidized S_{org} species in the surface sediments (Fig. 6b). Moreover, the proportion of oxidized S_{org} species decreases with depth in the sediments, while that of thiol (R-SH) progressively increases (Fig. 6a). Ester-SO₄ is also present in Basin B sediments, although to a lesser extent than in Basin A. Based on the LCF approach (Fig. 6a), XANES results reveal that down to 8 cm depth in Basin B, FeS_{2(s)} and S(α)_{8(s)} represent about 30 and 25% of S_{TOT} , respectively. This finding is consistent with the GCF results, which reveal the occurrence of reduced S compounds with oxidation states varying between -0.35 and -0.15 at these depths (Fig. 6 b). Deeper in Basin B sediments, both types of data treatments suggest that R-SH becomes the dominant S species (Fig. 6), consistent with small leachable amounts of reduced S at these depths.

Ascribing S_{org} species with oxidation states > 0 and < 0 to R-O-SO₃-H and R-SH (Prietz et al., 2011), respectively, then the product of the proportions of each S_{org} species obtained through XANES times the S_{TOT} concentration can be used to reconstruct the vertical profiles in the sediments of both R-O-SO₃-H and R-SH (Prietz et al., 2011). As illustrated in Fig. 4g, in Basin A sediments the corresponding concentrations of R-O-SO₃-H decreased from $95 \mu\text{mol g}^{-1}$ to $60 \mu\text{mol g}^{-1}$ between the SWI and 20 cm depth, whereas those of R-SH increased with depth from values $< 10 \mu\text{mol g}^{-1}$ in surface sediments (0–0.5 cm depth) to $42 \mu\text{mol g}^{-1}$ down core. In the seasonally anoxic Basin B, both R-O-SO₃-H and R-SH concentrations remained comparatively low (Fig. 4h). XANES and SE yield average S_{org} values of 115 and $101 \mu\text{mol g}^{-1}$ for Basin A, respectively, and of 69 and $57 \mu\text{mol g}^{-1}$ for Basin B, respectively and significantly correlate together ($p < 0.01$; Fig. 5b). Such consistency between XANES and SE results for S_{org} was also found by Burton et al. 2011).

4. DISCUSSION

4.1 Model simulations

Measured bottom water concentrations of solutes were imposed as upper boundary values at the SWI for all solutes, except for SO_4^{2-} which was time-dependent due to variations in atmospheric deposition since 1940 in lakes from eastern North America. Based on the timing and magnitude of SO_4^{2-} deposition in lakes located about 375 km south of our sampling site in the Adirondack Region (Matisoff and Holdren, 1995), we assumed that SO_4^{2-} concentration in Lake Tantaré increased from 10 μM to 60 μM between 1940 and 1985 and then declined to the present-day value of 40 μM . For Basin A, the bottom water O_2 concentration was fixed at the measured value just above the SWI in August 2005. For Basin B, the measured bottom water O_2 concentration in July 2007 was used to represent oxygenated conditions, while a value of zero was imposed for Basin B. Fluxes of reactive solid-phase species were imposed as upper boundary values at the SWI. The deposition flux of reactive Fe oxyhydroxides in Basin A (6.7 $\mu\text{mol cm}^{-2} \text{ yr}^{-1}$) was estimated by Alfaro-De la Torre et al. (2000) using measurements of reducible Fe extracted from Basin A sediment trap material with $\text{NH}_2\text{OH.HCl}$ in a medium of CH_3COOH . Solid-phase S deposition at the SWI was evaluated by multiplying the S_{TOT} concentrations of the sediment trap samples by the measured sediment settling fluxes, i.e., 44 and 99 $\text{mg cm}^{-2} \text{ yr}^{-1}$ in Basin A and B, respectively. XANES identifies R-O-SO₃-H as the prevailing S species in the settling material (Figure 6). Imposed linear sedimentation rates (v) on the model were derived from previously published mass accumulation rates (Couture et al., 2008), i.e., 0.095 and 0.131 cm yr^{-1} for the pre- and post-1962 periods in Basin A, respectively, and of 0.150 cm yr^{-1} in Basin B. Lastly, the flux of OM (Table 4) to the SWI were adjusted by the calibration algorithm so that the model correctly reproduced the measured concentration profiles, firstly those of O_2 which are very sensitive to the fluxes of OM1, then those of the other pore water species which responds to both OM1 and OM2. OM2 was set to 50% of OM1 (Canavan et al., 2006), and OM3 was imposed based on measured sedimentation mass accumulation rates (Couture et al., 2008) and C_{org} content (Figure 3a & b).

In general, the model is able to reproduce the magnitude and trends of observed O_2 and SO_4^{2-} concentrations, as well as the magnitude of dissolved Fe, $\Sigma\text{S}^{\text{II}}_{(\text{aq})}$ and $\Sigma\text{S}^0_{(\text{aq})}$ concentrations (Figure 2). The auto-calibration algorithm aims for the best set of parameters that provides a satisfactory fit against the whole dataset, rather than trying to fit specific features of a single depth profile. As a result, some discrepancies are seen between measured and modelled concentrations. In Basin A, the model overestimates the pore-water Fe concentrations at 4-7 cm depth, and it does not fully capture the sharpness of the subsurface peak of $\Sigma\text{S}^{\text{II}}$. In Basin B, although the O_2 gradient just below the SWI is well reproduced, the model underestimates O_2 concentrations between 0.5 and 2 mm depth. Nevertheless, the model well captures the differences induced by the transition from an oxic to an anoxic hypolimnion in Basin B.

The depth profiles of total solid-phase Fe are similarly well captured by the model, especially in Basin A where it reflects the intense redox cycling of Fe below the SWI (Fig. 3 c,d). The model simulates the decrease of Fe_{TOT} through the decrease of $\text{Fe}(\text{OH})_3$ and then of FeOOH . In agreement with the measured depth profiles of AVS and CRS, the simulations yield subsurface peaks of $\text{FeS}_{\text{m(s)}}$ and $\text{FeS}_{2\text{(s)}}$ in both basins. The model also captures the order of magnitude differences in S species concentrations between the two basins (Fig. 4). However, the concentrations of $\text{S}(\alpha)_{8\text{(s)}}$ are over predicted in Basin A and under predicted in Basin B, possibly reflecting the high scattering of the data. The partitioning of the S_{org} species (Fig. 4g,h) appears to be correctly simulated in both basins, while the sum of all modelled S species (Fig. 3e,f), capture the 2-fold differences in S_{TOT} accumulation in Basin A and B sediments.

Following calibration of the model, we extracted time-series fluxes of dissolved species across the SWI, as well as calculated rates (e.g., R4, R9, R_9 and R13 shown on Fig. 7) as a function of time and depth at each site. This information, otherwise not obtainable solely from the measured data, helps to assess how the benthic fluxes across the SWI responded to changes in the water column SO_4^{2-} concentration. Sediment O_2 demand increased by $1 \text{ mmol cm}^{-2} \text{ yr}^{-1}$ between 1900 and the mid-1980s, i.e. the time period of maximum water column SO_4^{2-} levels (Table 5). Over the same time interval, the fluxes of SO_4^{2-} from the water column to the sediment increased by two orders of magnitude in Basin A, and by a factor about three in Basin B. Sediments remained a stable source of Fe^{II} to the hypolimnion of Basin A, but they switched from being a source to a sink of Fe^{II} in Basin B, concurrent with the increase in SO_4^{2-} fluxes into the sediment. Moreover, as SO_4^{2-} concentrations rose, the fluxes of $\text{S}^{\text{II}}_{\text{(aq)}}$ from the sediment to the water column increased in both sites, while those of $\text{S}^0_{\text{(aq)}}$ increased in Basin A.

As expected, the computed time-dependent reaction rates (Fig. 7) illustrate that SO_4^{2-} reduction (R4) was highest in the sediments of both basins during the period of water column SO_4^{2-} maximum (Fig. 7a,e), with twofold higher rates in Basin B than in Basin A. In Basin B, $\text{FeS}_{\text{m(s)}}$ precipitation rates also peaked during the SO_4^{2-} maximum, concurrent with a sharp decrease in the rate of $\text{FeS}_{\text{m(s)}}$ dissolution (Fig. 7g). The rate of $\text{FeS}_{\text{m(s)}}$ precipitation was much lower in Basin A than in Basin B (Fig. 7 a,b) and dissolution of this mineral only occurred in a narrow sediment layer close to the SWI in Basin A (Fig. 7c). Finally, in contrast to Basin B where reduced S mainly accumulated in sediments as $\text{FeS}_{\text{m(s)}}$, significant accumulation of R-SH occurred in Basin A (R13) throughout the period of high water column SO_4^{2-} concentrations (Fig. 7). Below, we discuss the conditions under which R-SH can form preferentially over Fe sulfide.

4.2 Fe and S coupling

In surface sediments of Basin A, the presence of reactive Fe phases such as ferrihydrite and lepidocrocite has been previously inferred from macroscopic and microscopic observations on diagenetic material deposited on inert collectors inserted vertically into the sediments (Fortin et al., 1993). These phases undergo reductive dissolution upon burial, resulting in a sharp

decrease in Fe_{TOT} concentration with depth (Fig. 3c). The model captures this feature of the Fe diagenetic cycle suggesting that DIR (R2 and R3) is the main Fe reduction pathway, rather than abiotic reduction by S^{II} (R8). This is consistent with previously measured Fe isotope fractionation factor between aqueous Fe^{II} and Fe^{III} oxyhydroxides ($-2.6 \pm 0.5 \text{ ‰}$) which also points to DIR as the mechanism releasing Fe^{II} to the pore-water (Liu et al., 2015). In Basin B, seasonal anoxia prevents a similar build-up of solid-phase Fe at the SWI.

In the pore-water of Basin A, the disappearance of SO_4^{2-} coincides with an increase of $\Sigma\text{S}^{\text{II}}$ (Fig. 2e), features reproduced by the model as a result of SO_4^{2-} reduction (R4). Pore-water Fe is consumed at the depth of the $\Sigma\text{S}^{\text{II}}$ peak in this basin, while in Basin B the large excess of pore water Fe likely titrates all $\Sigma\text{S}^{\text{II}}$ to form $\text{FeS}_{\text{m(s)}}$ (Fig. 2). AVS maxima were measured above those of ES and CRS at both sites, suggesting that $\text{FeS}_{\text{m(s)}}$ is a precursor to $\text{S}(\alpha)_{8(\text{s})}$ and $\text{FeS}_{2(\text{s})}$, a hypothesis supported by the model (Fig. 4). According to the model, $\text{FeS}_{\text{m(s)}}$ dissolves providing a source of S^{II} (R_9) when reactant concentrations fall below the solubility product for $\text{FeS}_{\text{m(s)}}$, or when it is oxidized by O_2 to form $\text{S}^0_{(\text{aq})}$ (R7). In organic rich sediments where Fe^{III} (oxy)hydroxides are present, such as in Basin A, reaction R8 (Table 2 and Fig. 1) may also be responsible for the production of $\text{S}^0_{(\text{aq})}$, leading to the formation of $\text{FeS}_{2(\text{s})}$ (Filley et al., 2002; ThomasArrigo et al., 2016). Our results on the accumulation of $\text{FeS}_{2(\text{s})}$ over other inorganic S species thus appear consistent with previous reports from oligotrophic freshwater lakes showing that $\text{FeS}_{2(\text{s})}$ is a stable sink of inorganic sulfide pool at depth in the sediments (Holmer and Storkholm, 2001; Zeng et al., 2013). Such observations were also made in marine sediments, where metastable $\text{FeS}_{\text{m(s)}}$ transforms into $\text{FeS}_{2(\text{s})}$ (Butler and Rickard, 2000), and in re-flooded wetland soils (e.g., Johnston et al., 2014), where inorganic S speciation is dominated by $\text{S}(\alpha)_{8(\text{s})}$ and contemporary $\text{FeS}_{2(\text{s})}$, with only minor amounts of $\text{FeS}_{\text{m(s)}}$.

Our results nonetheless show that $\text{FeS}_{\text{m(s)}}$ persists down to 3-5 cm depth in the sediments (Fig- 4a,b), where its concentration is about half that of $\text{FeS}_{2(\text{s})}$. The persistence of $\text{FeS}_{\text{m(s)}}$ has been observed in estuarine sediments (Gagnon et al., 1995; Kraal et al., 2013; Morgan et al., 2012; Sundby et al., 2004), and several mechanisms potentially slowing down or inhibiting the conversion of $\text{FeS}_{\text{m(s)}}$ to $\text{FeS}_{2(\text{s})}$ in sediments were posited under steady state conditions (Morgan et al. (2012). However, these mechanisms do not necessarily apply to a lake where anthropogenic S deposition has led to time-varying SO_4^{2-} concentrations in the water column. In lakes from north-eastern North America and most of Scandinavia, SO_4^{2-} inputs to lakes have been constantly changing over the past decades due to the rise and fall of acid precipitations (Garmo et al., 2014; Kopáček et al., 2015; Lynch et al., 2000; Wright et al., 2005). Thus, although lakes SO_4^{2-} concentrations are generally low, between ~ 10 and $500 \text{ } \mu\text{M}$ (Holmer and Storkholm, 2001), peak SO_4^{2-} deposition in the past have increased SO_4^{2-} concentrations several-fold. Non-steady state SO_4^{2-} inputs, due to acid deposition, contrast with the above-mentioned studies that mostly analyze Fe and S cycling in systems that are not limited by the availability of SO_4^{2-} , such as marine and estuarine environments where concentrations are in the millimolar range.

Predictive modelling allows us to explore the geochemical consequences of historical SO_4^{2-} deposition peaking at 6 times the baseline value (Couture et al., 2010b; Matisoff and Holdren, 1995). First, following increased SO_4^{2-} deposition, rates of SO_4^{2-} reduction increased (Fig. 7) generating higher fluxes of oxidized S to the sediment, along with a slight increase in reduced S fluxes in the opposite direction (Table 5). This resulted in an overall net accumulation of S in the sediments. Higher SO_4^{2-} consumption in Basin B is consistent with the lower availability of Fe^{III} and O_2 as terminal electron acceptors. The inversion of Fe^{II} fluxes in Basin B, initiated by Fe^{II} sulfides precipitation (R9), is notable (Table 5). The model further suggests that high SO_4^{2-} concentrations favoured $\text{FeS}_{\text{m(s)}}$ precipitation, but that present-day SO_4^{2-} inputs cannot sustain $\text{FeS}_{\text{m(s)}}$ formation and pyritization at the level that once allowed the formation of the subsurface peaks observed in the sediments during the 70s and 80s. These historical peaks are being buried as $\text{FeS}_{2\text{(s)}}$ and $\text{S}(\alpha)_{8\text{(s)}}$, while $\text{FeS}_{\text{m(s)}}$, which is now undersaturated, is progressively dissolving (Fig. 7).

4.3 Organosulfur transformation

The OM deposited in oligotrophic lake sediments originates mainly from the surrounding catchment and from autochthonous production (Likens et al., 2002). In both pools R-O- $\text{SO}_3\text{-H}$ appears to be the dominant species (King and Klug, 1982; Prietzel et al., 2011; Urban et al., 1999). Consistent with these findings, our results show the highest levels of R-O- $\text{SO}_3\text{-H}$ at the SWI (Fig. 4). The model suggests that the decrease in R-O- $\text{SO}_3\text{-H}$ observed with depth in Basin A is due to its hydrolysis (R15). XANES results indicate that, upon burial, this S pool evolves into reduced S_{org} , likely disulfide, mono-sulfide and thiol compounds (Zeng et al., 2013). Our results, however, reveal contrasts in the R-SH abundance between Basin A and B sediments (Fig. 4g,h).

To our knowledge, only Urban et al. (1999) have compared the formation of R-SH in lake sediments under oxic and anoxic conditions. Based on comparison of cores from the littoral and the profundal zones of oligotrophic and eutrophic lakes, these authors found that R-SH compounds are susceptible to oxidative losses and that the formation of these compounds is thus not favored when the water column is fully oxygenated. This is in contrast to our results showing that the formation of R-SH compounds takes place in the sediments of Basin A, despite the perennially oxygenated hypolimnion the presence of elevated sediment concentrations of Fe (oxy)hydroxides that apparently does not impede OM sulfidization. Both geochemical and modelling evidences point to S_{org} as the dominant sediment S form when OM does not compete with Fe for S (Morgan et al., 2012). OM sulfidization has been reported to occur in the presence of reactive Fe (oxy)hydroxides (Filley et al., 2002; Urban et al., 1999), and observed here. It is likely that the low dissolved Fe concentration allows R-SH formation to be kinetically favoured over the formation of Fe sulfides. As was reviewed by Werne et al. (2004), hypoxic episodes promote an excess of Fe in the pore-water which, in turn, causes the titration of the available $\text{S}^{-\text{II}}$ and S^0 as Fe sulfides.

Formation of R-SH leaves a durable imprint on the sedimentary record. Based on $C_{org}:S_{org}$ ratios measured in sediment cores from 50 lakes, Urban et al. (1999) found that low ratios (< 80) were diagnostic of eutrophic lakes, or of eutrophied periods throughout a lake's history, while higher ratios (< 750) were diagnostic of oligotrophic lakes. With an average $C_{org}:S_{org}$ of 198 and 167, respectively, Basins A and B fall within the expected range for oligotrophic lakes (Fig. 3g&h). We observe historical minima in the $C_{org}:S_{org}$ ratios at depths dated as *ca.* 1985, corresponding to the historical maximum in acid-S deposition rather than periods of eutrophication, as suggested in Urban et al. (1999). The dip in the $C_{org}:S_{org}$ ratio suggests S_{org} accumulation, while its timing suggests that it reached a maximum when SO_4^{2-} supplies were highest (Fig. 3). Moreover, the persistence of this feature in the sedimentary profiles implies that the preferential loss of S during OM degradation did not offset the diagenetic incorporation of S in OM.

The time scales of diagenetic OM sulfidization range from months (Bostick et al., 2005) to thousands of years (Werne et al., 2004; Werne et al., 2008), although evidence points to it being faster in lacustrine (Bostick et al., 2005; Urban et al., 1999) than in marine environments (Werne et al., 2004). Diagenetic models can be used to derive rates and rate constants from concentration data, but models are often limited by the lack of relevant data, such as R-SH measurements. When R-SH is included in diagenetic models without the corresponding measurements being available, other species are used as constraints, namely ΣS^{-II} and $FeS_{m(s)}$ (Couture et al., 2010b), ΣS^{-II} , $FeS_{m(s)}$ or $FeS_{2(s)}$ (Torres et al. 2015) or ΣS^{-II} , S_{TOT} , $FeS_{2(s)}$ and S isotopes (Dale et al., 2009). Such cases are not ideal because models may “leak” S by letting species present in the reaction network accumulate outside the model (Meysman and Middelburg, 2005).

A previous study on Lake Tantaré evaluated the rate constant for OM sulfidization (k_{OMS} , Table 5) at $4 \times 10^{-2} \text{ cm}^3 \mu\text{mol}^{-1} \text{ yr}^{-1}$ (Couture et al., 2010b), without direct R-SH measurements as constraints. Here, using the additional S species listed in Table 1 as model constraints we obtain a k_{OMS} value of $1 \times 10^{-4} \text{ cm}^3 \mu\text{mol}^{-1} \text{ yr}^{-1}$ (Table 4). This value is two orders of magnitude lower than the previous estimate for the site, but comparable to the value of $2 \times 10^{-4} \text{ cm}^3 \mu\text{mol}^{-1} \text{ yr}^{-1}$ calculated by Dale et al. (2009) for Namibian Shelf sediments. During peak SO_4^{2-} inputs, rates of OM sulfidization in Lake Tantaré reached ~ 2 and $\sim 0.5 \mu\text{mol g}^{-1} \text{ yr}^{-1}$ in Basin A and B, respectively (Fig. 7). Most of the enrichment in R-SH in Basin A occurred in the first 5 cm below the SWI (Fig. SE), resulting in maximum modelled rates being predicted in that depth interval (Fig. 7 d). The time required to reach the measured R-SH value of $45 \mu\text{mol g}^{-1}$ is ~ 22.5 yr, that is, half of the time needed for a sediment layer to be buried below the 5 cm horizon at a sedimentation velocity of 0.095 cm yr^{-1} . The time scale of 22.5 yr is consistent with previous estimates for OM sulfidization in lake sediments (< 60 yr, Urban et al. (1999)).

4. CONCLUSION

The main source of solid-phase S to the sediments of oligotrophic lake Tantaré is organically-bound S, principally under the form of R-O-SO₃-H compounds. In both basins, S_{org} is the dominant S sediment pool. In the perennially oxygenated Basin A, the solid-phase S distributions imply that reduced S preferentially accumulates through the formation of R-SH. The model simulations yield a second order rate constant for OM sulfidization of $1 \times 10^{-4} \text{ cm}^3 \mu\text{mol}^{-1} \text{ yr}^{-1}$, and a corresponding reaction time scale of 22.5 years. Due to abundance of dissolved Fe, reduced S preferentially accumulates as Fe sulfides in the sediments of the seasonally anoxic Basin B.

The model results show that the subsurface peaks of AVS measured in the sediments of both basins, and likely of other lakes that have experienced high level of SO₄²⁻ deposition in the past, are a transient feature. With atmospheric S deposition in decline (Vet et al., 2014), AVS formed in the sediments as a result of S diagenesis are unstable and continuously dissolve, causing both Fe (oxy)hydroxides reduction and FeS_{2(s)} formation. As time goes on, it is expected that the labile AVS sulfide pool will become depleted allowing further Fe (oxy)hydroxides build-up near the SWI of the perennially oxygenated basin, and favoring the formation of R-SH in the sediments. Such a scenario might have profound consequences for the biogeochemical cycles of elements in lacustrine environments, particularly for phosphorus whose retention in lake sediments is linked to the stability of an Fe (oxy)hydroxides enriched surface sediment layer (Lehtoranta et al., 2009).

The revised model for S diagenesis includes more measured chemical species and more stringent constraints for the simulation of the depth profiles of aqueous and solid-phase S species than previously published models. The proposed reaction network may be used to explore relevant non-steady state disturbances in the cycling of S, such as (i) recovery from acid deposition that peaked in the mid-1980s (Garmo et al., 2014; Lynch et al., 2000; Wright et al., 2005), (ii) the effects of tidal inundation of acid-sulfate soils in coastal regions (Burton et al., 2006a, b; Claff et al., 2011; Johnston et al., 2015; Schoepfer et al., 2014), (iii) acid drainage from mine tailings (Blowes et al., 2003; Johnson and Hallberg, 2005; Lindsay et al., 2009; Nordstrom, 2000), and (iv) S amendments carried out as management actions to correct for agricultural soil S deficiency (Scherer, 2009) or to control downstream eutrophication by attempting to sequester phosphorus using gypsum (Ekholm et al., 2012).

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REFERENCES

- Alfaro-De la Torre, M.C., Beaulieu, P.Y., Tessier, A., 2000. In Situ Measurement of Trace Metals in Lakewater Using the Dialysis and Dgt Techniques. *Anal. Chim. Acta* 418, 53-68.
- Alfaro-De la Torre, M.C., Tessier, A., 2002. Cadmium deposition and mobility in the sediments of an acidic oligotrophic lake. *Geochim. Cosmochim. Acta* 66, 3549-3562.
- Arndt, S., Jørgensen, B.B., LaRowe, D.E., Middelburg, J.J., Pancost, R.D., Regnier, P., 2013. Quantifying the degradation of organic matter in marine sediments: A review and synthesis. *Earth-Sci. Rev.* 123, 53-86.
- Berner, R.A., 1980. Early diagenesis: a theoretical approach. Princeton University Press, New York.
- Bessinger, B.A., Vlassopoulos, D., Serrano, S., O'Day, P.A., 2012. Reactive Transport Modeling of Subaqueous Sediment Caps and Implications for the Long-Term Fate of Arsenic, Mercury, and Methylmercury. *Aquat. Geochem.* 18, 297-326.
- Blowes, D.W., Ptacek, C.J., Jambor, J.L., Weisener, C.G., Heinrich, D.H., Karl, K.T., 2003. The Geochemistry of Acid Mine Drainage, *Treatise on Geochemistry*. Pergamon, Oxford, pp. 149-204.
- Bostick, B.C., Theissen, K.M., Dunbar, R.B., Vairavamurthy, M.A., 2005. Record of redox status in laminated sediments from Lake Titicaca: A sulfur K-edge X-ray absorption near edge structure (XANES) study. *Chem. Geol.* 219, 163-174.
- Boudreau, B.P., 1997. Diagenetic models and their implementation, 1st ed. Springer, Berlin.
- Brimblecombe, P., Heinrich, D.H., Karl, K.T., 2003. The Global Sulfur Cycle, *Treatise on Geochemistry*. Pergamon, Oxford, pp. 645-682.
- Bunemann, E.K., 2008. Enzyme additions as a tool to assess the potential bioavailability of organically bound nutrients. *Soil Biol. Biochem.* 40, 2116-2129.
- Burton, E.D., Bush, R.T., Johnston, S.G., Sullivan, L.A., Keene, A.F., 2011. Sulfur biogeochemical cycling and novel Fe–S mineralization pathways in a tidally re-flooded wetland. *Geochim. Cosmochim. Acta* 75, 3434-3451.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006a. Acid-Volatile Sulfide Oxidation in Coastal Flood Plain Drains: Iron–Sulfur Cycling and Effects on Water Quality. *Environmental Science & Technology* 40, 1217-1222.
- Burton, E.D., Bush, R.T., Sullivan, L.A., 2006b. Elemental sulfur in drain sediments associated with acid sulfate soils. *Appl. Geochem.* 21, 1240-1247.
- Burton, E.D., Sullivan, L.A., Bush, R.T., Johnston, S.G., Keene, A.F., 2008. A simple and inexpensive chromium-reducible sulfur method for acid-sulfate soils. *Appl. Geochem.* 23, 2759-2766.
- Butler, I.B., Rickard, D., 2000. Framboidal pyrite formation via the oxidation of iron (II) monosulfide by hydrogen sulphide. *Geochimica Et Cosmochimica Acta* 64, 2665-2672.
- Canavan, R.W., 2006. Biogeochemical Cycling of Nutrients and Trace Metals in the Sediment of Haringvliet Lake: Response to Salinization, *Geowetenschappen*. Utrecht University, p. 159.
- Canavan, R.W., Slomp, C.P., Jourabchi, P., Van Cappellen, P., Laverman, A.M., Van Den Berg, G.A., 2006. Organic matter mineralization in sediment of a coastal freshwater lake and response to salinization. *Geochim. Cosmochim. Acta* 70, 2836-2855.
- Canavan, R.W., Van Cappellen, P., Zwolsman, J.J.G., van den Berg, G.A., Slomp, C.P., 2007. Geochemistry of trace metals in a fresh water sediment: Field results and diagenetic modeling. *Sci. Total Environ.* 381, 263-279.

- Canfield, D., Kristensen, E., Thamdrup, B., 2005. *Aquatic Geomicrobiology*. Elsevier Academic Press, San Diego, USA.
- Canfield, D.E., Rosing, M.T., Bjerrum, C., 2006. Early anaerobic metabolisms. *Philosophical Transactions of the Royal Society B-Biological Sciences* 361, 1819-1834.
- Carignan, R., St-Pierre, S., Gachter, R., 1994. Use of diffusion samplers in oligotrophic lake-sediment: effects of free oxygen in sampler material. *Limnol. Oceanogr.* 39, 468-474.
- Carignan, R., Tessier, A., 1988. The co-diagenesis of sulfur and iron in acid lake sediments of southwestern Quebec. *Geochim. Cosmochim. Acta* 52, 1179-1188.
- Choi, J.H., Park, S.S., Jaffé, P.R., 2006. Simulating the dynamics of sulfur species and zinc in wetland sediments. *Ecol. Model.* 199, 315-323.
- Claff, S.R., Sullivan, L.A., Burton, E.D., Bush, R.T., Johnston, S.G., 2011. Partitioning of metals in a degraded acid sulfate soil landscape: Influence of tidal re-inundation. *Chemosphere* 85, 1220-1226.
- Cline, J.D., 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnol. Oceanogr.* 14, 454-458.
- 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., Rose, J.C., Kumar, N., Mitchell, K., Wallschläger, D., Van Cappellen, P., 2013a. Sorption of arsenite, arsenate and thioarsenates to iron oxides and iron sulfides: a kinetic and spectroscopic investigation. *Environ. Sci. Technol.* 47, 5652-5659.
- 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.
- Couture, R.-M., Wallschläger, D., Rose, J., Van Cappellen, P., 2013b. Arsenic binding to organic and inorganic sulfur species during microbial sulfate reduction: a sediment flow-through reactor experiment. *Environ. Chem.* 10, 285-294.
- Couture, R.M., Shafei, B., Van Cappellen, P., Tessier, A., Gobeil, C., 2010c. Non-Steady State Modeling of Arsenic Diagenesis in Lake Sediments. *Environ. Sci. Technol.* 44, 197-203.
- Dale, A.W., Brüchert, V., Alperin, M., Regnier, P., 2009. An integrated sulfur isotope model for Namibian shelf sediments. *Geochim. Cosmochim. Acta* 73, 1924-1944.
- Davison, W., 1991. The solubility of iron sulphides in synthetic and natural waters at ambient temperature. *Aquat. Sci.* 53, 1015-1621.
- Davison, W., Phillips, N., Tabner, B.J., 1999. Soluble iron sulfide species in natural waters: Reappraisal of their stoichiometry and stability constants. *Aquat Sci* 61, 23-43.
- Dittrich, M., Wehrli, B., Reichert, P., 2009. Lake sediments during the transient eutrophication period: Reactive-transport model and identifiability study. *Ecol. Model.* 220, 2751-2769.
- Doherty, J., 2015. *Calibration and Uncertainty Analysis for Complex Environmental Models*. Watermark Numerical Computing, Brisbane, Australia.
- Ekholm, P., Valkama, P., Jaakkola, E., Kiirikki, M., Lahti, K., Pietola, L., 2012. Gypsum amendment of soils reduces phosphorus losses in an agricultural catchment. *Agricultural and Food Science* 21, 279-291.
- Filley, T.R., Freeman, K.H., Wilkin, R.T., Hatcher, P.G., 2002. Biogeochemical controls on reaction of sedimentary organic matter and aqueous sulfides in holocene sediments of Mud Lake, Florida. *Geochim. Cosmochim. Acta* 66, 937-954.
- Fitzgerald, J.W., Strickland, T.C., Swank, W.T., 1982. Metabolic fate of inorganic sulphate in soil samples from undisturbed and managed forest ecosystems. *Soil Biology and Biochemistry* 14, 529-536.
- Fortin, D., Leppard, G.G., Tessier, A., 1993. Characteristics of lacustrine diagenetic iron oxyhydroxide. *Geochim. Cosmochim. Acta* 57, 4391-4404.

- 697 Francois, R., 1987. A study of sulfur enrichment in the huic fraction of marine-sediments during early
698 diagenesis. *Geochim. Cosmochim. Acta*. 51, 17-27.
- 699 Gagnon, C., Mucci, A., Pelletier, É., 1995. Anomalous accumulation of acid-volatile sulphides (AVS) in a
700 coastal marine sediment, Saguenay Fjord, Canada. *Geochimica et Cosmochimica Acta* 59, 2663-2675.
- 701 Gallon, C., Tessier, A., Gobeil, C., Alfaro-De la Torre, M.C., 2004. Modeling diagenesis of lead in
702 sediments of a Canadian Shield lake. *Geochim. Cosmochim. Acta* 68, 3531-3545.
- 703 Garmo, Ø., Skjelkvåle, B., De Wit, H.A., Colombo, L., Curtis, C., Fölster, J., Hoffmann, A., Hruška, J.,
704 Høgåsen, T., Jeffries, D., Keller, W.B., Krám, P., Majer, V., Monteith, D., Paterson, A., Rogora, M.,
705 Rzychon, D., Steingruber, S., Stoddard, J., Vuorenmaa, J., Worsztynowicz, A., 2014. Trends in Surface
706 Water Chemistry in Acidified Areas in Europe and North America from 1990 to 2008. *Water Air Soil Poll.*
707 225, 1-14.
- 708 Gun, J., Goifman, A., Shkrob, I., Kamyshny, A., Ginzburg, B., Hadas, O., Dor, I., Modestov, A.D., Lev, O.,
709 2000. Formation of Polysulfides in an Oxygen Rich Freshwater Lake and Their Role in the Production of
710 Volatile Sulfur Compounds in Aquatic Systems. *Environ. Sci. Technol.* 34, 4741-4746.
- 711 Hansel, C.M., Lentini, C.J., Tang, Y., Johnston, D.T., Wankel, S.D., Jardine, P.M., 2015. Dominance of
712 sulfur-fueled iron oxide reduction in low-sulfate freshwater sediments. *ISME J.*
- 713 Hare, L., Carignan, R., Huerta-Diaz, M.A., 1994. A field study of metal toxicity and accumulation by
714 benthic invertebrates; implications for the acid-volatile sulfide (AVS) model. *Limnol. Oceanogr.* 39, 1653-
715 1668.
- 716 Helz, G., 2014. Activity of zero-valent sulfur in sulfidic natural waters. *Geochem. Trans.* 15, 13.
- 717 Helz, G.R., Tossell, J.A., 2008. Thermodynamic model for arsenic speciation in sulfidic waters: A novel
718 use of ab initio computations. *Geochim. Cosmochim. Acta* 72, 4457-4468.
- 719 Helz, G.R., Valerio, M.S., Capps, N.E., 2002. Antimony Speciation in Alkaline Sulfide Solutions: Role of
720 Zerovalent Sulfur. *Environ. Sci. Technol.* 36, 943-948.
- 721 Holmer, M., Storkholm, P., 2001. Sulphate reduction and sulphur cycling in lake sediments: a review.
722 *Freshwater Biol.* 46, 431-451.
- 723 Hsieh, Y.P., Chung, S.W., Tsau, Y.J., Sue, C.T., 2002. Analysis of sulfides in the presence of ferric minerals
724 by diffusion methods. *Chem. Geol.* 182, 195-201.
- 725 Hsieh, Y.P., Shieh, Y.N., 1997. Analysis of reduced inorganic sulfur by diffusion methods: Improved
726 apparatus and evaluation for sulfur isotopic studies. *Chem. Geol.* 137, 255-261.
- 727 Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. *Science of The*
728 *Total Environment* 338, 3-14.
- 729 Johnston, S.G., Burton, E.D., Aaso, T., Tuckerman, G., 2014. Sulfur, iron and carbon cycling following
730 hydrological restoration of acidic freshwater wetlands. *Chemical Geology* 371, 9-26.
- 731 Johnston, S.G., Burton, E.D., Hagan, R., Aaso, T., Tuckerman, G., 2015. A revised method for determining
732 existing acidity in re-flooded acid sulfate soils. *Applied Geochemistry* 52, 16-22.
- 733 Katsev, S., Dittrich, M., 2013. Modeling of decadal scale phosphorus retention in lake sediment under
734 varying redox conditions. *Ecol. Model.* 251, 246-259.
- 735 Katsev, S., Tsandev, I., L'Heureux, I., Rancourt, D.G., 2006. Factors controlling long-term phosphorus
736 efflux from lake sediments: Exploratory reactive-transport modeling. *Chem. Geol.* 234, 127-147.
- 737 Kertesz, M.A., 2000. Riding the sulfur cycle – metabolism of sulfonates and sulfate esters in Gram-
738 negative bacteria. *FEMS Microbiology Reviews* 24, 135-175.
- 739 King, G.M., Klug, M.J., 1982. COMPARATIVE ASPECTS OF SULFUR MINERALIZATION IN SEDIMENTS OF A
740 EUTROPHIC LAKE BASIN. *App. Environ. Microbiol.* 43, 1406-1412.
- 741 Kopáček, J., Hejzlar, J., Kaňa, J., Norton, S.A., Stuchlík, E., 2015. Effects of Acidic Deposition on in-Lake
742 Phosphorus Availability: A Lesson from Lakes Recovering from Acidification. *Environmental Science &*
743 *Technology* 49, 2895-2903.

- 744 Kraal, P., Burton, E.D., Bush, R.T., 2013. Iron monosulfide accumulation and pyrite formation in
745 eutrophic estuarine sediments. *Geochim. Cosmochim. Acta.* 122, 75-88.
- 746 Lehmann, J., Solomon, D., Zhao, F.J., Mcgrath, S.P., 2008. Atmospheric So₂ Emissions Since the Late
747 1800s Change Organic Sulfur Forms in Humic Substance Extracts of Soils. *Environ. Sci. Technol.* 42, 3550-
748 3555.
- 749 Lehtoranta, J., Ekholm, P., Pitkanen, H., 2009. Coastal Eutrophication Thresholds: A Matter of Sediment
750 Microbial Processes. *AMBIO* 38, 303-308.
- 751 Likens, G.E., Driscoll, C.T., Buso, D.C., Mitchell, M.J., Lovett, G.M., Bailey, S.W., Siccama, T.G., Reiners,
752 W.A., Alewell, C., 2002. The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry* 60, 235-316.
- 753 Lindsay, M.B.J., Condon, P.D., Jambor, J.L., Lear, K.G., Blowes, D.W., Ptacek, C.J., 2009. Mineralogical,
754 geochemical, and microbial investigation of a sulfide-rich tailings deposit characterized by neutral
755 drainage. *Appl. Geochem.* 24, 2212-2221.
- 756 Liu, K., Wu, L., Couture, R.-M., Li, W., Van Cappellen, P., 2015. Iron isotope fractionation in sediments of
757 an oligotrophic freshwater lake. *Earth and Planetary Science Letters* 423, 164-172.
- 758 Losher, A.J., Kelts, K.R., 1989. Organic sulphur fixation in freshwater lake sediments and the implication
759 for US ratios. *Terra Nova* 1, 253-261.
- 760 Lynch, J.A., Bowersox, V.C., Grimm, J.W., 2000. Acid rain reduced in Eastern United States. *Environ. Sci.*
761 *Technol.* 34, 940-949.
- 762 Manceau, A., Nagy, K.L., 2012. Quantitative analysis of sulfur functional groups in natural organic matter
763 by XANES spectroscopy. *Geochim. Cosmochim. Acta* 99, 206-223.
- 764 Mandernack, K.W., Lynch, L., Krouse, H.R., Morgan, M.D., 2000. Sulfur cycling in wetland peat of the
765 New Jersey Pinelands and its effect on stream water chemistry. *Geochim. Cosmochim. Acta.* 64, 3949-
766 3964.
- 767 Matisoff, G., Holdren, G.R., 1995. A model for sulfur accumulation in soft water lake sediments. *Water*
768 *Resour. Res.* 31, 1751-1760.
- 769 Matisoff, G., Wang, X., 2000. Particle mixing by freshwater infaunal bioirrigators: Midge (Chironomidae:
770 Diptera) and mayflies (Ephemeroidea: Ephemeroptera). *J. Great Lakes Res.* 26, 174-182.
- 771 McLaren, J.W., Methven, B.A.J., Lam, J.W.H., Berman, S.S., 1995. The use of inductively coupled plasma
772 mass spectrometry in the production of environmental certified reference materials. *Mikrochim. Acta*
773 119, 287-295.
- 774 Meysman, F.J.R., Middelburg, J.J., 2005. Acid volatile sulfide (AVS) - A comment. *Mar. Chem.* 97, 206-
775 212.
- 776 Morgan, B., Burton, E.D., Rate, A.W., 2012. Iron monosulfide enrichment and the presence of
777 organosulfur in eutrophic estuarine sediments. *Chem. Geol.* 296–297, 119-130.
- 778 Morse, J.W., Luther, G.W., 1999. Chemical influences on trace metal-sulfide interactions in anoxic
779 sediments. *Geochim. Cosmochim. Acta* 63, 3373-3378.
- 780 Morse, J.W., Rickard, D., 2004. Chemical dynamics of sedimentary acid volatile sulfide. *Environ. Sci.*
781 *Technol.*, 131A-136A.
- 782 Morse, J.W., Wang, Q.W., 1997. Pyrite formation under conditions approximating those in anoxic
783 sediments .2. Influence of precursor iron minerals and organic matter. *Marine Chemistry* 57, 187-193.
- 784 Nordstrom, D., 2000. Aqueous redox chemistry and the behavior of iron in acid mine waters, in: Wilkin,
785 R.T., Ludwig, R.D., Ford, R.G. (Eds.), *Workshop on Monitoring Oxidation-Reduction Processes for*
786 *Ground-Water Restoration*. US Environmental Protection Agency-Report EPA/600/R-02/002, Cincinnati,
787 OH, pp. 43-47.
- 788 Paraska, D.W., Hipsey, M.R., Salmon, S.U., 2014. Sediment diagenesis models: Review of approaches,
789 challenges and opportunities. *Environ. Modell. Softw.* 61, 297-325.
- 790 Park, S.S., Jaffé, P.R., 1999. A Numerical Model to Estimate Sediment Oxygen Levels and Demand.
791 *Journal of Environmental Quality* 28, 1219-1226.

- 792 Peiffer, S., Gade, W., 2007. Reactivity of Ferric Oxides Toward H₂S at Low pH. *Environ. Sci. Technol.* 41,
793 3159-3164.
- 794 Poulton, S.W., Krom, M.D., Raiswell, R., 2004. A revised scheme for the reactivity of iron (oxyhydr)oxide
795 minerals towards dissolved sulfide. *Geochim. Cosmochim. Acta* 68, 3703-3715.
- 796 Prietzel, J.r., Botzaki, A., Tyufekchieva, N., Brettholle, M., Thieme, J.r., Klysubun, W., 2011. Sulfur
797 Speciation in Soil by S K-Edge XANES Spectroscopy: Comparison of Spectral Deconvolution and Linear
798 Combination Fitting. *Environ. Sci. Technol.* 45, 2878-2886.
- 799 Regnier, P., O'Kane, J.P., Steefel, C.I., Vanderborgh, J.P., 2002. Modeling complex multi-component
800 reactive-transport systems: towards a simulation environment based on the concept of a Knowledge
801 Base. *Appl. Math. Model.* 26, 913-927.
- 802 Revsbech, N.P., 1989. An oxygen microsensor with a guard cathode. *Limnol. Oceanogr.* 34, 474-478.
- 803 Rickard, D., Luther, G.W., 2007. Chemistry of iron sulfides. *Chemical Reviews* 107, 514-562.
- 804 Rickard, D., Morse, J.W., 2005. Acid volatile sulfide (AVS). *Mar. Chem.*, 141-197.
- 805 Rudd, J.W.M., Kelly, C.A., Furutani, A., 1986. The role of sulfate reduction in long-term accumulation of
806 organic and inorganic sulfur in lake sediments. *Limnol. Oceanogr.* 31, 1281-1291.
- 807 Scherer, H.W., 2009. Sulfur in soils. *Journal of Plant Nutrition and Soil Science* 172, 326-335.
- 808 Schoepfer, V.A., Bernhardt, E.S., Burgin, A.J., 2014. Iron clad wetlands: Soil iron-sulfur buffering
809 determines coastal wetland response to salt water incursion. *Journal of Geophysical Research:*
810 *Biogeosciences* 119, 2014JG002739.
- 811 Sevinç, S., S., Spycher, N.F., Ginn, T.R., Sani, R.K., Peyton, B., 2007. Biogeochemical reactive-diffusive
812 transport of heavy metals in Lake Coeur d'Alene sediments. *Appl. Geochem.* 22, 2569-2594.
- 813 Sievert, S.M., Kiene, R.P., Schulz-Vogt, H.N., 2007. The Sulfur Cycle. *Oceanography* 20, 117-123.
- 814 Sleighter, R.L., Chin, Y.-P., Arnold, W.A., Hatcher, P.G., McCabe, A.J., McAdams, B.C., Wallace, G.C., 2014.
815 Evidence of Incorporation of Abiotic S and N into Prairie Wetland Dissolved Organic Matter. *Environ. Sci.*
816 *Technol.* 1, 345-350.
- 817 Smith, S.L., Jaffé, P.R., 1998. Modeling the transport and reaction of trace metals in water-saturated
818 soils and sediments. *Water Resour. Res.* 34, 3135-3147.
- 819 Soetaert, K., Meysman, F., 2012. Reactive transport in aquatic ecosystems: Rapid model prototyping in
820 the open source software R. *Environ. Modell. Softw.* 32, 49-60.
- 821 Solomon, D., Lehmann, J., de Zaruk, K.K., Dathe, J., Kinyangi, J., Liang, B., Machado, S., 2011. Speciation
822 and Long- and Short-term Molecular-level Dynamics of Soil Organic Sulfur Studied by X-ray Absorption
823 Near-Edge Structure Spectroscopy. *J. Environ. Qual.* 40, 704-718.
- 824 Subosa, P.F., Kihara, K., Rokushika, S., Hatano, H., Murayama, T., Kubota, T., Hanaoka, Y., 1989. Ion
825 Chromatography of Inorganic Anions in Brine Samples. *J. Chromatogr. Sci.* 27, 680-684.
- 826 Sundby, B., Martinez, P., Gobeil, C., 2004. Comparative geochemistry of cadmium, rhenium, uranium,
827 and molybdenum in continental margin sediments. *Geochim. Cosmochim. Acta* 68, 2485-2493.
- 828 Thomas-Arrigo, L.K., Mikutta, C., Lohmayer, R., Planer-Friedrich, B., Kretzschmar, R., 2016. Sulfidization of
829 Organic Freshwater Flocs from a Minerotrophic Peatland: Speciation Changes of Iron, Sulfur, and
830 Arsenic. *Environmental Science & Technology* 50, 3607-3616.
- 831 Urban, N.R., Ernst, K., Bernasconi, S., 1999. Addition of sulfur to organic matter during early diagenesis
832 of lake sediments. *Geochim. Cosmochim. Acta* 63, 837-853.
- 833 Van Cappellen, P., Wang, Y., 1995. Metal cycling in surface sediments: Modeling the interplay of
834 transport and reaction, Allen, H.E. ed. Ann Arbor Press, Chelsea, MI.
- 835 Van Cappellen, P., Wang, Y., 1996. Cycling of iron and manganese in surface sediments: a general theory
836 for the coupled transport and reaction of carbon, oxygen, nitrogen, sulfur, iron, and manganese. *Am. J.*
837 *Sci.* 296, 197-243.
- 838 Van den Berg, G., Loch, J.P.G., van der Heijdt, L., Zwolsman, J.G., 2000. Redox processes in recent
839 sediments of the river Meuse, The Netherlands. *Biogeochemistry* 48, 217-235.

- Vestergren, J., Vincent, A.G., Jansson, M., Persson, P., Ilstedt, U., Gröbner, G., Giesler, R., Schleucher, J., 2012. High-Resolution Characterization of Organic Phosphorus in Soil Extracts Using 2D 1H–31P NMR Correlation Spectroscopy. *Environ. Sci. Technol.* 46, 3950-3956.
- Vet, R., Artz, R.S., Carou, S., Shaw, M., Ro, C.-U., Aas, W., Baker, A., Bowersox, V.C., Dentener, F., Galy-Lacaux, C., Hou, A., Pienaar, J.J., Gillett, R., Forti, M.C., Gromov, S., Hara, H., Khodzher, T., Mahowald, N.M., Nickovic, S., Rao, P.S.P., Reid, N.W., 2014. A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmospheric Environment* 93, 3-100.
- Wang, F., Tessier, A., 2009. Polysulfide and metal speciation in sediment porewaters of freshwater lakes. *Environ. Sci. Technol.* 43, 7252-7257.
- Wang, F., Tessier, A., Buffle, J., 1998. Voltammetric determination of elemental sulfur in pore waters. *Limnol. Oceanogr.* 43, 1353-1361.
- Weber, F.-A., Voegelin, A., Kaegi, R., Kretzschmar, R., 2009. Contaminant mobilization by metallic copper and metal sulphide colloids in flooded soil. *Nature Geosci.* 2, 267-271.
- Werne, J.P., Hollander, D.J., Lyons, T.W., Sinninghe Damsté, J.S., 2004. Organic sulfur biogeochemistry: Recent advances and future research directions. *Geo. Soc. Am. Spec. Paper* 379, 135-150.
- Werne, J.P., Lyons, T.W., Hollander, D.J., Schouten, S., Hopmans, E.C., Sinninghe Damsté, J.S., 2008. Investigating pathways of diagenetic organic matter sulfurization using compound-specific sulfur isotope analysis. *Geochim. Cosmochim. Acta* 72, 3489-3502.
- Wilkin, R.T., Ford, R.G., 2006. Arsenic solid-phase partitioning in reducing sediments of a contaminated wetland. *Chem. Geol.* 228, 156-174.
- Wright, R.F., Larssen, T., Camarero, L., Cosby, B.J., Ferrier, R.C., Helliwell, R., Forsius, M., Jenkins, A., Kopacek, J., Majer, V., Moldan, F., Posch, M., Rogora, M., Schopp, W., 2005. Recovery of acidified European surface waters. *Environ. Sci. Technol.* 39, 64A-72A.
- Xia, K., Weesner, F., Bleam, W.F., Bloom, P.R., Skjellberg, U.L., Helmke, P.A., 1998. XANES studies of oxidation states of sulfur in aquatic and soil humic substances. *Soil Sci. Soc. Am. J.* 62, 1240-1246.
- Zeng, T., Arnold, W.A., Toner, B.M., 2013. Microscale Characterization of Sulfur Speciation in Lake Sediments. *Environ. Sci. Technol.* 47, 1287-1296.
- 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: Synthesis of diagenetic modelling studies showcasing depth profiles of S species in freshwater sediments. Studies showing simulated profiles calibrated against observations are identified by solid squares (■) and those showing only simulated profiles by open squares (□). Note that modelling studies that included S in the reaction network but that did not present results on S are not listed.

Reference	System	$\text{SO}_4^{2-}(\text{aq})$	$\Sigma \text{S}^{\text{II}}(\text{aq})$	$\Sigma \text{S}^0(\text{aq})$	S_{TOT}	$\text{FeS}_{\text{m(s)}}$	$\text{FeS}_{2(\text{s})}$	$\text{S}(\alpha)_{(\text{s})}$	R-SH	R-O-SO ₃ -H	Me-S _(s)
Park and Jaffé (1999)	lake	□									
Van Cappellen and Wang (1995)	lake	□									
Katsev et al. (2006)	lake	□			□						
Bessinger et al. (2012)	lake				□	□	□				□
Van den Berg et al. (2000)	river	■									
Katsev and Dittrich (2013)	lake	■				□					
Choi et al. (2006) ^a	wetland	■				□					
Smith and Jaffé (1998)	lake	■	□								□
Dittrich et al. (2009)	lake	■	□			□					
Canavan et al. (2007)	lake	■	■								□
Sevinç et al. (2007)	lake	■	■			□					□
Couture et al. (2010c)	lake	■	■			■			□		
Canavan et al. (2006)	lake	■	■		■	■	□				
Torres et al. (2015) ^a	reservoir	■	■			■	■		□		■
This study	lake	■	■	■	■	■	■	■	■	■	

$\Sigma \text{S}^0_{(\text{aq})}$: $\text{S}^0_{(\text{aq})} + n[\text{S}^0_n \text{S}^{x-2}]$, where n, the number of zero-valent S atoms in a given polysulfide species, varies between 1 and 7, and x, the number of H atoms, varies between 0 and 2.

R-SH: Reduced S_{org} such as thiols

R-O-SO₃-H: Organosulfates

Me-S: Metal(loid) sulfides (Torres et al. 2015), As₂S₃ (Bessinger et al., 2012; Smith and Jaffé, 1998), Ni and Zn sulfides (Canavan, 2006), HgS (Bessinger et al., 2012)

a: not reviewed in Paraska et al. (2014)

Table 2: Reaction network included in the model. The corresponding rate equations and parameter values are given in Table 3 and Table 4, respectively. Two pools of degradable organic matters are considered, OM_i, with $i = 1, 2$. OM is assigned the formula CH₂O for mass balance calculations and underscores ( ) denote reverse reactions.

Primary redox reactions	Equation	#
Aerobic respiration	$OM_i + O_2 \rightarrow CO_2 + H_2O$	R1
Fe ^{III} reduction A	$OM_i + 4Fe(OH)_3 + 7CO_2 \rightarrow 4Fe_{(aq)} + 8HCO_3^- + 3H_2O$	R2
Fe ^{III} reduction B	$OM_i + 4FeOOH + H_2O + 7CO_2 \rightarrow 4Fe_{(aq)} + 8HCO_3^-$	R3
Dissimilatory sulfate reduction	$2OM_i + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	R4
Secondary reactions		
Fe ^{II} oxidation by O ₂	$Fe_{(aq)} + 0.25O_2 + 2HCO_3^- + 0.5H_2O \rightarrow Fe(OH)_3 + 2CO_2$	R5
Sulfide oxidation by O ₂	$HS^- + 2O_2 \rightarrow H^+ + SO_4^{2-}$	R6
FeS oxidation by O ₂	$4FeS_{m(s)} + 3O_2 + 2H_2O \rightarrow 4S\alpha_{(8)s} + FeOOH$	R7
Sulfide oxidation by Fe ^{III}	$HS^- + 2Fe(OH)_3 + 5H^+ \rightarrow 2Fe_{(aq)} + S^0_{(aq)} + 6H_2O$	R8
FeS precipitation	$Fe_{(aq)} + HS^- \rightarrow FeS_{m(s)} + H^+$	R9
FeS dissolution	$FeS_{m(s)} + 2H^+ \rightarrow Fe_{(aq)} + H_2S$	R_9
Pyrite precipitation, H ₂ S pathway	$FeS_{m(s)} + H_2S \rightarrow FeS_{2(s)} + H_2$	R10
Pyrite precipitation, S ⁰ pathway	$FeS_{m(s)} + S^0_{(aq)} \rightarrow FeS_{2(s)}$	R11
Elemental S precipitation	$S^0_{(aq)} \rightarrow 1/8S(\alpha)_{8(s)}$	R12
Elemental S dissolution	$1/8S(\alpha)_{8(s)} \rightarrow S^0_{(aq)}$	R_12
OM sulfidization	$OM_i + HS^- \rightarrow R-SH$	R13
Assimilatory sulfate reduction	$SO_4^{2-} \rightarrow R-SH$	R14
Organosulfate hydrolysis	$R-O-SO_3-H + H_2O \rightarrow HSO_4^- + R-OH_2$	R15

894 **Table 3:** Rate equations included in the model. Parameter values are given in Table 4.

$$\begin{aligned}
R_{C_i} &= k_{OM_i} [OM_i] \\
R_{1_i} &= R_{C_i} \times f_{O_2} \times \text{accel, where } f_{O_2} = \frac{[O_2]}{K_{O_2} + [O_2]} \\
R_{2_i} &= R_{C_i} \times f_{FeOH_3}, \text{ where } f_{FeOH_3} = \frac{[FeOH_3]}{K_{FeOH_3} + [FeOH_3]} \times \frac{\text{kin}_{O_2}}{\text{kin}_{O_2} + [O_2]} \\
R_{3_i} &= R_{C_i} \times f_{FeOOH}, \text{ where } f_{FeOOH} = \frac{[FeOOH]}{K_{FeOOH} + [FeOOH]} \times \frac{\text{kin}_{FeOH_3}}{\text{kin}_{FeOH_3} + [FeOH_3]} \times \frac{\text{kin}_{O_2}}{\text{kin}_{O_2} + [O_2]} \\
R_{4_i} &= R_{C_i} \times f_{SO_4}, \text{ where } f_{SO_4} = \frac{[SO_4^{2-}]}{K_{SO_4} + [SO_4^{2-}]} \times \frac{\text{kin}_{FeOOH}}{\text{kin}_{FeOOH} + [FeOOH]} \times \frac{\text{kin}_{FeOH_3}}{\text{kin}_{FeOH_3} + [FeOH_3]} \times \frac{\text{kin}_{O_2}}{\text{kin}_{O_2} + [O_2]} \\
R_5 &= k_{Feox} [O_2] [Fe^{2+}] \\
R_6 &= k_{tsox} [O_2] [\Sigma S^{-II}_{(aq)}] \\
R_7 &= k_{rhom} [O_2] [FeS_{m(s)}] \\
R_8 &= k_{tsfe} [Fe(OH)_3] [\Sigma S^{-II}_{(aq)}] \\
R_9 &= k_{Fepr} (\Omega_{FeSm(s)} - 1) \\
R_{_9} &= k_{Fedis} [FeS_{m(s)}] (1 - \Omega_{FeSm(s)})^a \\
R_{10} &= k_{pyrpre} [FeS_{m(s)}] [\Sigma S^{-II}_{(aq)}] \\
R_{11} &= k_{pyrpre\_ES} [FeS_{m(s)}] [\Sigma S^0_{(aq)}] \\
R_{12} &= k_{Spre} [\Sigma S^0_{(aq)}] \\
R_{_12} &= k_{Sdis} [S(\alpha)_{8(s)}] \\
R_{13} &= k_{sorg} [\Sigma S^{-II}_{(aq)}] [\Sigma OM_i] \\
R_{14} &= k_{OMS} \times (R_1 + R_2 + R_3) \\
R_{15} &= k_{omso} \times \frac{\text{Kin}_{SO_4}}{\text{Kin}_{SO_4} + [SO_4^{2-}]}
\end{aligned}$$

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895 ^a $\Omega_{FeS} = \frac{[Fe^{2+}] \times [\Sigma S^{-II}]}{[H^+]^2 \times K_{FeS}}$

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Table 4. Model parameters and boundary conditions used in the simulations. Parameter values are either constrained with the model (C), measured (M), or based on literature values (L). Literature sources are indicated within the table footnotes below.

Parameter	Value			Unit	Source
	Basin A	Basin B (oxic)	Basin B (anoxic)		
Fluxes of solids					
Organic matter pool 1	250	250	250	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	C
Organic matter pool 2	125	125	125	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	C
Organic matter pool 3	140	120	120	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
R-O-SO ₃ -H	0.56	0.21	0.21	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
R-SH	0	0	0	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
Fe oxide pool 1 (Fe(OH) ₃)	6.7	0.1	0.1	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
Fe oxide pool 2 (FeOOH)	4.6	2	2	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	C
FeS _{(m)s}	0	0	0	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
S(α) _{8(s)}	0	0	0	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
FeS _{2(s)}	0	0	0	$\mu\text{mol cm}^{-2}\text{yr}^{-1}$	M
Concentrations at boundary ^a					
O ₂	0.15	0.02	0	$\mu\text{mol cm}^{-3}$	M
SO ₄ ²⁻	3.4×10^2	1.2×10^{-2}	3.9×10^{-3}	$\mu\text{mol cm}^{-3}$	M
Fe ²⁺	0	0.2	0.5	$\mu\text{mol cm}^{-3}$	M
ΣS ^{-II} _(aq)	0	8.8×10^{-4}	2.5×10^{-3}	$\mu\text{mol cm}^{-3}$	M
ΣS ⁰ _(aq)	0	2.0×10^{-5}	1.3×10^{-3}	$\mu\text{mol cm}^{-3}$	M
Half saturation coefficients					
KO ₂	8×10^{-4}	1×10^{-4}	1×10^{-4}	$\mu\text{mol cm}^{-3}$	C
KFe(OH) ₃	0.6	2×10^3	2×10^3	$\mu\text{mol g}^{-1}$	C
KFeOOH	1.7×10^3	9×10^3	9×10^3	$\mu\text{mol g}^{-1}$	C
KSO ₄	2.9×10^{-2}	1.1×10^{-2}	1	$\mu\text{mol cm}^{-3}$	C
Inhibition coefficients					
KinO ₂	1×10^{-2}	1×10^{-2}	1×10^{-2}	$\mu\text{mol cm}^{-3}$	C
KinFe(OH) ₃	4×10^2	20	20	$\mu\text{mol g}^{-1}$	C
KinFeOOH	4.9×10^2	1.1×10^3	1.1×10^3	$\mu\text{mol g}^{-1}$	C
KinSO ₄	9.4×10^{-2}	6.3×10^{-3}	6.3×10^{-3}	$\mu\text{mol cm}^{-3}$	C
Saturation constants					
KFeS	2.5×10^3	2.6×10^4	4.9×10^4	-	L ¹ , C
Rate constants					
k _{OM1}	1	1	1	yr^{-1}	L ²
k _{OM2}	1×10^{-2}	1×10^{-2}	1×10^{-2}	yr^{-1}	L ²
k _{ts_{ox}}	1×10^3	1×10^3	1×10^3	$\text{cm}^3 \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{fe_{ox}}	1.3×10^4	5×10^3	5×10^3	$\text{cm}^3 \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{fe_{pre}}	21.3	8.6	1.5	$\mu\text{mol g}^{-1} \text{yr}^{-1}$	L ² , C
k _{fe_{dis}}	1×10^{-3}	1×10^{-3}	1×10^{-3}	yr^{-1}	L ²
k _{ts_{fe}}	2.5	2.5	2.5	$\text{cm}^3 \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{s_{org}}	7.8×10^{-2}	2.2×10^{-2}	1.6×10^{-2}	$\text{cm}^3 \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{r_{hom}}	6.5×10^3	2.9×10^5	2.9×10^5	$\text{cm}^3 \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{pyr_{pre}}	3.2	3.2	0.2	$\text{g} \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{pyr_{pre}_ES}	0.3	0.3	2×10^2	$\text{g} \mu\text{mol}^{-1} \text{yr}^{-1}$	C
k _{S_{dis}}	0.1	0.1	0.1	yr^{-1}	C
k _{S_{pre}}	2.5×10^3	6.1×10^3	3.6×10^3	$\text{cm}^3 \text{g}^{-1} \text{yr}^{-1}$	C
k _{oms_o}	0.14	0.14	0.14	$\mu\text{mol g}^{-1} \text{yr}^{-1}$	C
k _{OMS}	1×10^{-4}	1×10^{-4}	1×10^{-4}	$\text{cm}^3 \mu\text{mol}^{-1}$	C
Other parameters					
Oxygen acceleration factor	25	25	25	-	L ²
Bioturbation coefficient	6.9×10^{-2}	6.9×10^{-2}	0	$\text{cm}^2 \text{yr}^{-1}$	M, C
Burial rate ^b	0.13	0.15	0.15	cm yr^{-1}	M
Bioirrigation constant	14.4	14.4	0	yr^{-1}	M
pH	6.5	6.9	6.9	-	M
Porosity	0.9	0.9	0.9	$\text{cm}^3 \text{cm}^{-3}$	M

^a The boundary concentrations for SO₄²⁻ are the concentrations at the end of the simulation time.

^b For basin A, the burial rate is 0.095 before the year 1865.

L: (1)(Davison et al., 1999), (2)(Canavan et al., 2006)

Table 5. Predicted fluxes of dissolved species across the sediment-water interface ($\mu\text{mol cm}^{-2} \text{yr}^{-1}$) in Basin A and B prior to the increase in anthropogenic S deposition (< 1900) and at peak S deposition (1985). Positive and negative values indicate upward and downward fluxes, respectively.

	Basin A		Basin B	
	< 1900	1985	< 1900	1985
O ₂	261.0	260.9	111.0	110.0
Fe ^{II}	-6.2	-6.0	-0.9	0.8
SO ₄ ²⁻	1.8×10 ⁻²	1.6	2.3	5.9
S ⁰ _(aq)	0.0	-3.6×10 ⁻³	8.5×10 ⁻²	8.3×10 ⁻²
S ^{-II} _(aq)	-3.6×10 ⁻²	-0.5	-0.5	-0.9

Figure 1: Conceptual model of the S cycle in freshwater sediments. The reaction network and rate formulations are described in Tables 2 and 3, respectively.

Figure 2. Depth profiles of average measured concentrations ($n=3$; symbols and error-bars at $\pm 1\sigma$) and modeled profiles (lines) of sediment pore-water O_2 (upward triangles), Fe (circles), SO_4^{2-} (diamonds), total sulfide ($\Sigma S^{-II}_{(aq)}$; squares) and total zero-valent sulfur ($\Sigma S^0_{(aq)}$; downward triangles) in Basins A (upper panels a, c, e, g, i) and B (lower panels b, d, f, h, i) of Lake Tantaré. Basin B was sampled when its hypolimnion was either oxygenated (closed symbols) or anoxic (open symbols). Model fits are indicated by dashed lines for Basin A and for the oxygenated period of Basin B, and by solid lines for the anoxic period of Basin B.

Figure 3. Measured (symbols) and modelled profiles (lines) of C_{org} (circles), Fe (diamonds), total S (squares) and $C_{org}:S_{org}$ ratio (triangles) in Basins A (upper panels a, c, e, g) and B (lower panels b, d, f, h) sediments of Lake Tantaré. Modeled profiles of the C_{org} as OM1 and OM2 and of Fe as $Fe(OH)_3$ and $FeOOH$ are also exhibited.

Figure 4. Measured sedimentary concentrations of AVS (circles), CRS (diamonds) and ES (downward triangles) determined by sequential extraction and of oxidized (upward triangles) and reduced S_{org} (squares) determined by XANES using the GCF approach. Upper panels (a, c, e, g) and lower panels (b, d, f, h) are for Basins A and B sediments, respectively. Lines represent modelled profiles of $FeS_{m(s)}$, $FeS_{2(s)}$, $S(\alpha)_{8(s)}$, R-O-SO₃-H and R-SH. Error-bars represent $\pm 1\sigma$ of triplicate measurements for AVS, the interval between duplicate measurements for CRS and ES, and the uncertainty ensuing error propagation for R-SH and R-O-SO₃-H.

Figure 5. Inventories between 0 and 30 cm depth in the sediments of S species ($\mu\text{mol cm}^{-2}$ dry weight) at the two sampling sites (panel a) and comparison of the S_{org} concentrations estimated with the XANES spectra using the GCF approach and by sequential extractions in Basins A (circles) and B (triangles) sediments (panel b).

Figure 6. Relative absorbance of normalized XANES spectra at the S K-edge for Basins A and B sediment trap and sediment core samples (circles) and corresponding best fits (solid lines) obtained by the linear combination fittings approach (LCF) along with the spectra of the reference compounds used in the analysis (panel a) and the Gaussian curve fitting approach along with the individual spectra components (panel b). The depths in the cores of the sediment samples analyzed are indicated above each line. On panel b the approximate oxidation state of the associated S species is given on the far right while the energy of each GCF component appears beside the peaks.

Figure 7. Model-predicted reaction rates of SO_4^{2-} reduction, $\text{FeS}_{\text{m(s)}}$ dissolution, $\text{FeS}_{\text{m(s)}}$ precipitation and organic matter sulfidization as a function of depth in the sediments (0-10 cm) and over the time-period 1925-2000 in the perennially oxygenated Basin A (panels a-d) and seasonally anoxic Basin B (panels e-h).