The role of sediments in the phosphorus cycle in Lake Lugano. II. Seasonal and spatial variability of microbiological processes at the sediment-water interface

Maja A. Lazzaretti and Kurt W. Hanselmann in collaboration with Helmut Brandl, Daniel Span[1], Reinhard Bachofen

Institute of Plant Biology/Microbiology, University of Zürich, Zollikerstr. 107, CH-8008 Zürich, Switzerland
[1] Institute F.-A. Forel, University of Geneva, 10 route de Suisse, CH-1290 Versoix, Switzerland

ABSTRACT

P, Fe, Mn, and S species were analyzed in water samples from the sediment-water interface collected at four seasonally different times during the course of a year at two sampling sites in the southern basin of Lake Lugano (Lago di Lugano). The results reveal the strong influence of the biogeochemical processes in the sediment on the chemical composition of the lake water above. Consumption of oxygen and nitrate under oxic to microoxic conditions in the water column as well as sequential release of reduced manganese and iron under anoxic conditions was observed as a direct or indirect consequence of microbially mediated degradation of organic matter. The seasonal pattern observed for the release and the retainment of dissolved reduced iron and manganese correlates well with the one for dissolved phosphate. Iron, manganese and phosphorus cycling are coupled tightly in these sediments. Both sediment types act as sinks for hydrogen sulfide and sulfate. An inner-sedimentary sulfur cycle is proposed to couple iron, manganese and phosphorus cycling with the degradation of organic matter. Nutrient cycling at the sediment-water interface might thus be driven by a microbially regulated "electron pumping" mechanism. The results contribute to a better understanding of the role of sediment processes in the lake's internal phosphorus cycle and its seasonal dynamics.

1. Introduction

The southern basin of Lake Lugano has been eutrophic for more than 20 years. Intensive primary production in the photic zone results in high sedimentation rates of organic material (Polli and Simona, this issue; Polli et al., 1990). Considerable numbers and various types of heterotrophic microorganisms were isolated from the sediment surface layers near Agno (Peduzzi et al., this issue) indicating a large potential for biodegradation. Microbial decomposition of the organic matter releases

nutrients, such as phosphate, into the sediment pore water. The degradation products react with each other or with certain solid phases which form part of the sediment matrix, or they diffuse back into the lake water. *In situ* studies of indicative compounds which are present as dissolved species in the interstitial water can lead to qualitative and quantitative estimates of the microbial processes and activities occurring at the sediment-water interface (Brandl et al., 1990; Hanselmann, 1989). With the aid of dialysis pore water samplers (Brandl and Hanselmann, 1991) such studies were carried out at two sites in the southern basin of Lake Lugano. Due to elevated Fe and Mn concentrations at the two sites they are well suited for studies on the microbially mediated coupling between Fe, Mn, P and S cycling. We followed interstitial concentrations of mineralization products as the oxidation conditions at the sediment-water interface changed from anoxic to oxic. Here we report on microbial mineralization processes which, affect metal (Fe, Mn) and phosphorus exchanges and their regulation by seasonally changing redox conditions. A model is derived which links sedimentary phosphorus cycling to microbially driven electron exchange reactions between C, S, Mn and Fe cycles.

2. Sampling and analytical methods

Pore water samples and samples from bottom water near the sediment were collected from two different sites in the deeper part of the southern basin of Lake Lugano, one located south east of Melide in 85 m depth, the other north west of Figino in 95 m depth. Span et al. (this issue) investigated the structure and the geochemical composition of the sediments at the same sites. The two locations are used regularly for monitoring purposes by the Commissione Internazionale per la protezione delle acque italo-svizzere (Barbieri and Polli, this issue), whose findings about stratification and chemical composition of the lake water are in part presented by Barbieri and Mosello (this issue).

Samples from the sediment-water interface were collected four times during one annual cycle between May 1989 and March 1990. One experiment at the site Figino was lost because of poor visibility at the sampling site at the time of retrieval (December 1989). For the collection of interstitial water we employed the equilibrium diffusion technique, with dialysis pore water samplers (DPS) having a vertical resolution of 1.5 cm. The sampler compartments were covered with a cellulose dialysis membrane (Union Carbide) (Brandl, 1987; Brandl and Hanselmann, 1991). The samplers were positioned and retrieved with the aid of the manned submarine F. A. Forel and allowed to equilibrate for 17 to 21 days. During retrieval and transport of the pore water samplers to the nearby field laboratory they were kept in a protective casing to prevent excessive contamination and exposure to air (Brandl and Hanselmann, 1991; Brandl et al., 1992).

Samples for the determination of total dissolved hydrogen sulfide were immediately fixed with zinc acetate (4% w/v in 2% v/v acetic acid), while particle free samples for the determination of nitrate and sulfate were preserved in formalin (1% v/v; Brandl and Hanselmann, 1991). Due to the high iron and manganese contents of the sediments in the south basin it became necessary to acidify the samples for the

determination of total dissolved iron, manganese and phosphate in the dialysis compartments prior to sampling in order to prevent changes in the concentration of these components caused by oxidation, precipitation or adsorption. The samples were acidified with nitric acid for iron and manganese determinations (0.55 M final concentration in the dialysis compartment), those for phosphate determinations with sulfuric acid (0.04 M final concentration in the compartment). All samples of two dialysis plates were fixed within 120 min after the retrieval of the samplers from the sediment. The sampling sequence which is suggested in the paper by Brandl and Hanselmann (1991) is essential.

Phosphate was quantified colorimetrically with the molybdenum blue method immediately after fixation (method modified after Murphy and Riley, 1962). Nitrate and sulfate were determined by ion chromatography, iron and manganese by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Sulfide was quantified colorimetrically with the methylene blue method (Gilboa-Garber, 1971) and the values were corrected for diffusive losses during retrieval of the samplers according to an experimentally derived equation (Brandl, 1987, Brandl and Hanselmann, 1991).

3. Results

3.1. Consumption of dissolved oxidants (oxygen and nitrate) during seasonal redox changes at the sediment-water interface

The southern basin of Lake Lugano is holomictic (Barbieri and Polli, this issue). In 1989 complete mixing occurred between January and March. At the end of the mixing period, oxygen concentrations of approximately 5 mg/l were determined in the water column near the sediment surface at both sites (Laboratorio Studi Ambientali (LSA), 1991). In June, during the development of thermal stratification, the oxygen concentrations must have decreased to less than 0.1 mg/l, which follows from extrapolations of the oxygen-gradients in the water column to the sediment surface. Completely anoxic conditions were maintained for the period between June 1989 and January 1990. Destratification of the water column between January and March lead to reoxygenation of the water overlying the sediment surface. Oxygen concentrations of approximately 2 and 4 mg/l were determined near the sediment surface at the Figino site and the Melide site respectively in March 1990 (Laboratorio Studi Ambientali (LSA), 1991).

In June 1989, nitrate concentrations above the sediment surface were 8 to 10 μM, while 6 to 7 μM were determined in the pore water at both sampling sites. No clear gradient across the sediment-water interface was observed at that time. In March 1990, after complete mixing of the water column had occurred, concentrations of 80 μM were detected 1 to 3 cm above the sediment. The concentrations decreased to 6 to 8 μM in the top 2 cm of the sediment.
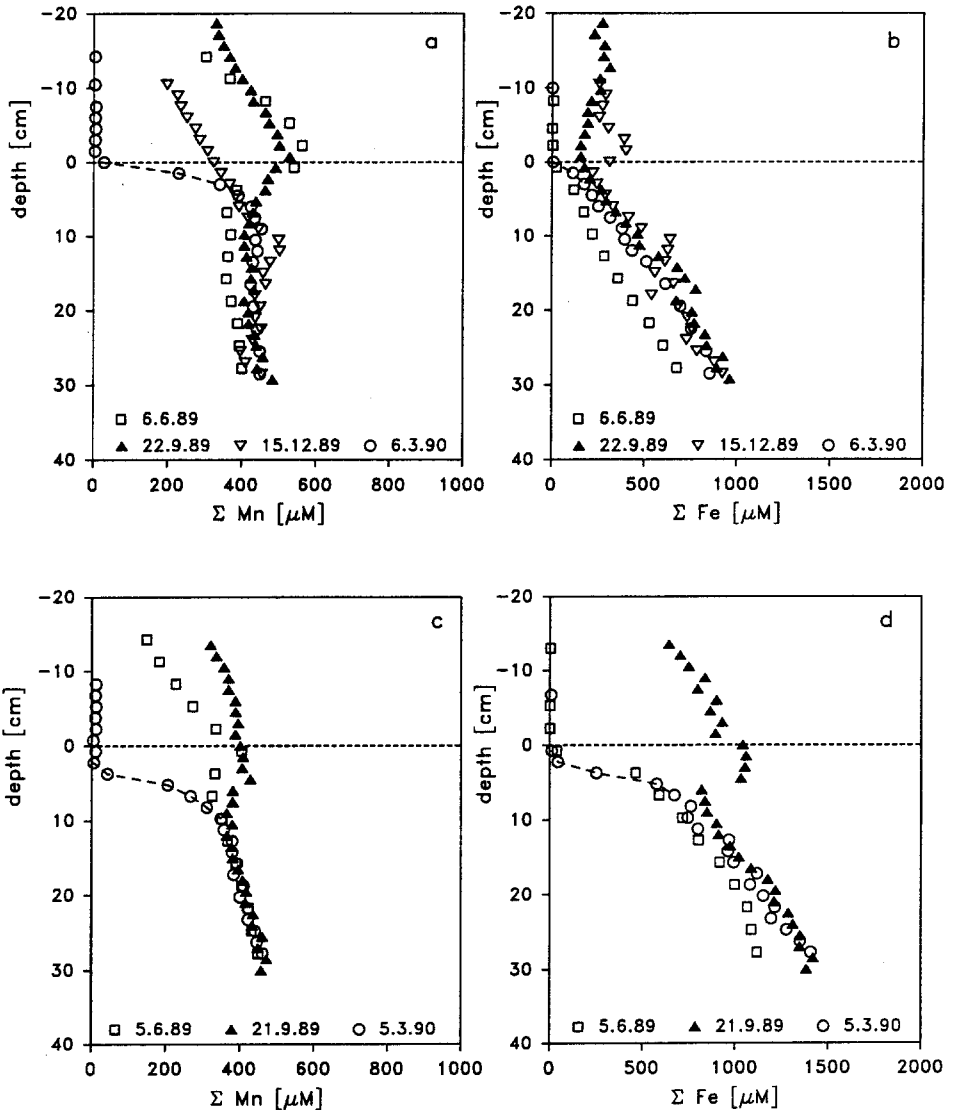
Figure 1. Seasonal development of the concentration of total dissolved manganese and total dissolved iron at the sediment-water interface at the sampling sites Melide (a, b) and Figino (c, d) respectively. Dates refer to time of retrieval of samplers

3.2. Seasonal development of manganese and iron release and precipitation at the sediment-water interface

Dissolved reduced manganese was detected in high concentrations above the sediment surface in June 1989 at both sampling sites (Fig. 1 a, c). The slope of the gradients indicate intense release of manganese at the sediment surface. Con-

centrations reached 450 μM to 400 μM at 28 cm depth at the Figino and Melide site respectively.

The release of manganese at the sediment-water interface did not change significantly at the Melide site between June and September 1989, whereas it slowed down at the Figino site. No manganese was released from the sediment surface from either site in March 1990. The sink where precipitation of manganese took place was located in the top few cm of the sediment.

The concentrations of dissolved reduced iron were below 8 μM above the sediment surface at both sampling sites in June 1989 (Fig. 1 b, d). Release of dissolved reduced iron increased with progressing anaerobiosis at the sediment surface. Concentrations below the sediment-water interface increased to 1400 μM and 960 μM at 29 cm depth at Figino and Melide respectively. Both gradients indicate almost constant release of reduced iron from deeper sediment layers. Under oxic conditions (March 1990) oxidation and precipitation of the upwards diffusing reduced iron species took place near the sediment surface.

3.3. Seasonal evolution of phosphate gradients at the sediment-water interface

During anaerobiosis (September and December 1989) intensive release of phosphate from the top sediment layers led to diffusion into the overlaying water and into deeper sediment strata at the Melide sampling site (Fig. 2a). At the Figino site a phosphate flux occurred from the water column into the sediment (September 1989) (Fig. 2b).

After complete mixing of the water column (March 1990) a steep gradient immediately below the sediment surface was observed at both sampling sites. The concentration of dissolved phosphate decreased from 140 μM and 110 μM measured at 3 cm depth in Melide and Figino sediments respectively to 5 μM at the sediment surface at both sampling sites. A sink for dissolved phosphate was thus localized just below the sediment surface. Phosphate concentrations in sediment strata deeper than 8 cm increased from December to March at the Melide site, whereas they decreased from September to March at the Figino site.

3.4. Hydrogen sulfide evolution and sulfate consumption at the sediment-water interface

Free hydrogen sulfide could be detected during microoxic and anoxic conditions (June to December 1989) at the sediment surface at the sampling site Melide only (Fig. 3a). Concentrations in the sediment near bottom water (0 to 20 cm above the sediment surface) were up to 60 μM (December 1989), but decreased rapidly towards the sediment-water interface. In sediment layers below 15 cm depth the free hydrogen sulfide concentration never exceeded 5 μM.

During the whole period of investigation no free hydrogen sulfide was detected at the sampling site Figino. Concentrations in the pore water as well as in the water directly above the sediment surface were always below 1 μM (= detection limit corrected for diffusive losses during sampling).
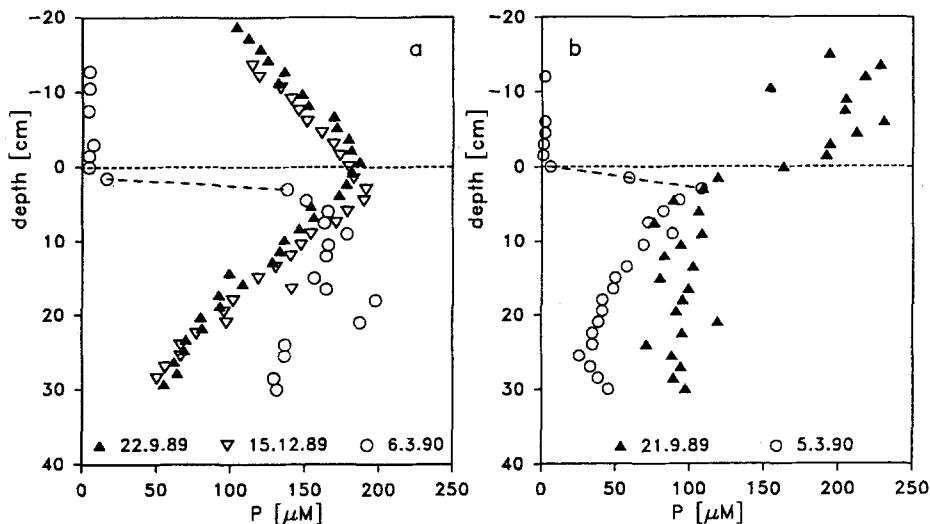
Figure 2. Seasonal development of phosphate gradients at the sediment-water interface of the sampling sites Melide (a) and Figino (b) respectively. Dates refer to time of retrieval of samplers

Sulfate concentrations which were approximately 160 µM at the sediment surface at both sampling sites under oxic conditions decreased to 5 µM within the top 5 cm sediment depth (Fig. 3 b, c). Deeper sediment layers contained only small amounts of free sulfate. The horizon of sulfate consumption moved into the overlaying water during development of anoxia but the sediments remained sinks for S species during the entire year.

4. Discussion

4.1. Consumption of oxidants during seasonal redox changes at the sediment-water interface

TOC contents average 10 % (d.w./d.w.) in the surficial sediment layers and decrease slightly to about 4 to 5 % in 30 cm depth (Niessen, 1987; Span et al., this issue). Microbial metabolisms can thus be supported by ample amounts of oxidizable organic matter in the whole sediment column. Suitable oxidants which are supplied through the water column in dissolved (O_2, NO_3^-, SO_4^{2-}) or solid (MnO_2, $MnO(OH)$, $FeO(OH)$, Fe_2O_3) form are used by different types of microbes in a thermodynamically determined sequence (Hanselmann, 1986). Oxygen and nitrate, the most energy-efficient electron acceptors, are consumed in the top few millimeters of an organic-rich sediment (Brandl, 1987). This leads to spatial as well as temporal segregation of the different mineralization processes. Microbially mediated mineralization of sedimentary organic matter may also be responsible for the rapid
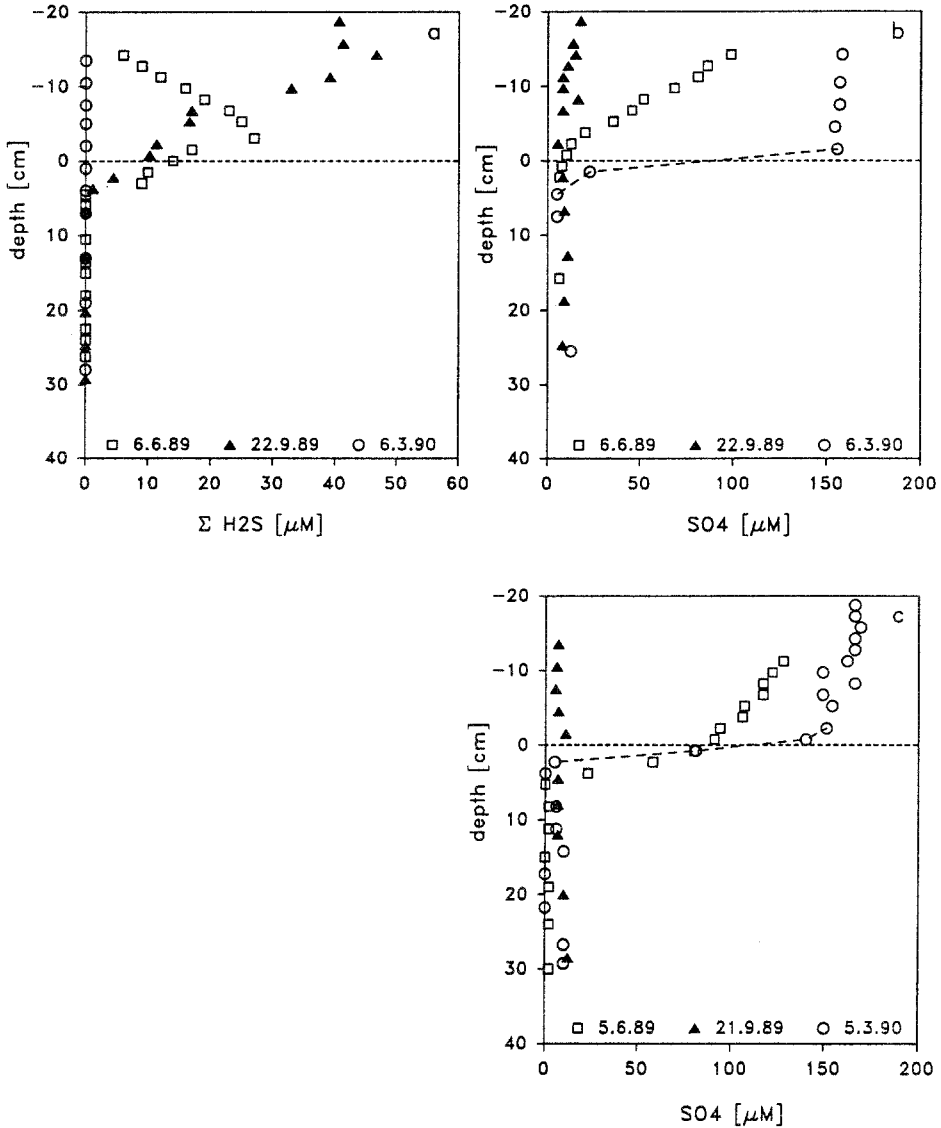
Figure 3. Concentration of total dissolved hydrogen sulfide (H_2S, HS^- and S^{2-}) and sulfate at the sediment-water interface at sampling site Melide (a, b) and Figino (c) respectively at the dates indicated. At the site Melide, at depths below 6 cm, values for $\sum H_2S$ were $< 1\ \mu M$ (detection limit corrected for diffusive losses). No dissolved hydrogen sulfide could ever be detected at the Figino site

consumption of oxygen and nitrate in the deeper hypolimnetic water layers between March and June 1989.

4.2. Microbial mediation of metal(hydr)oxide reduction

Redox reactions accounting for the release of Mn^{2+} and Fe^{2+} species were observed at the sediment-water interface as well as in deeper sediment strata (Fig. 1). At both sampling sites the appearance of reduced manganese preceeded the appearance of reduced iron at the sediment surface. There was already active Mn(hydr)oxide reduction in June while Fe(hydr)oxides seemed to remain stable under the then prevailing conditions. Alternatively Mn oxide could have been reduced by Fe^{2+} in the top sediment layers according to the process proposed by Myers and Nealson (1988): $Mn^{4+} + 2\,Fe^{2+} \rightarrow Mn^{2+} + 2\,Fe^{3+}$. There was a large upward flux of dissolved Fe^{2+} species in June (Fig. 1b, d) but none was released into the water column. The Fe^{2+} was trapped while Mn^{2+} was released. The rate of Fe^{2+} oxidation in this zone might have been faster than its reduction and the rate of its supply from deeper layers. Under the more reducing conditions in September, Mn and Fe(hydr)oxides were released simultaneously from the sediment surface into the water column. Once the Mn oxides were sufficiently depleted, the rate of Fe^{2+} oxidation could have become slower than the rate of Fe^{3+} reduction and Fe^{2+} could then have been released into the overlaying water. In deeper strata where solid Fe and Mn species account for 2 to 6% (d.w.) of the sediment matrix (Span et al., this issue) the release processes were practically unaffected by the seasonal redox changes at the sediment surface. Calculation of the saturation indices of rhodochrosite, $MnCO_3$, which could be the source of Mn^{2+} in deeper sediment strata, showed supersaturation of the pore waters with respect to this mineral. Microscopic analysis of Lake Greifen sediments by Wersin et al. (1991) has indicated that poorly crystalline Fe oxides can be present in anoxic freshwater sediments. Microbially mediated electron transfer between organic carbon and oxidized metal(hydr)oxides may thus be responsible for the continued release of Fe^{2+} and Mn^{2+} species in deeper sediment strata.

Microorganisms capable of obtaining energy for growth from the oxidation of organic compounds with Mn(IV) or Fe(III) as the sole electron acceptor have only recently been isolated (Lovley et al., 1987; Lovley and Phillips, 1988a). Their quantitative importance for the reduction of Mn- and Fe(hydr)oxides in sediment environments remains to be determined (Lovley, 1991). Purely chemical reactions with biogenic compounds as reducing agents for metal(hydr)oxides must also be considered. The reduced biogenic compounds (e.g. H_2S, S^0, oxalate, pyruvate, quinones and other metabolites in the case of Mn oxides) which couple chemical and biological processes are produced by microorganisms, and the low redox potentials which are necessary for the reactions to occur have to be maintained through metabolic activities (Hanselmann, 1989). Microorganisms which are involved in the mineralization of organic matter in the sediment environment thus mediate, directly or indirectly, the reduction of Mn- and Fe(hydr)oxides.

4.3. Seasonal evolution of phosphate gradients at the sediment-water interface

For the sampling site *Melide* the seasonal pattern describing release and retainment of dissolved phosphate at the sediment surface agrees well with the corresponding variations observed for dissolved iron and manganese.

Reductive dissolution of Mn(hydr)oxides (September 1989) began as soon as sufficiently reducing conditions had developed at the sediment-water interface. It was followed by Fe(hydr)oxide release under more stringent reducing conditions (December 1989). The release of phosphate took place concomitantly. Under oxic conditions at the sediment surface (March 1990), the topmost sediment layers became sinks for iron, manganese and phosphate. The reduced metal species were oxidized and precipitated as metal(hydr)oxides.

Surfaces of inorganic iron(hydr)oxides have a high adsorption capacity for dissolved anions under neutral pH conditions (Stumm and Morgan, 1981). They preferentially adsorb dissolved phosphate (Sigg and Stumm, 1989; Zinder and Stumm, 1985). Under oxic conditions they could thus be able to serve as a chemical barrier against phosphate transport across the sediment-water interface. Baccini (1985) suggested that with increasing atomic ratio of dissolved iron to dissolved phosphorus in the pore water of the reduced sediment zone the capacity of a sediment to form a phosphate scavenging iron(hydr)oxide barrier under oxic conditions would be enhanced. Calculations carried out with our data lead to values higher than 1 at all sediment depths (Fig. 4 b, December 1989). Corresponding calculations made for the dissolved manganese to dissolved phosphate ratio show a similar pattern (Fig. 4a). Manganese(hydr)oxides having high specific surface areas (up to about 100 $m^2 \cdot g^{-1}$; Sigg and Stumm, 1989) may play an analogous role as the iron(hydr)oxides in this particular sediment environment. Phosphate could be bound to these and other amorphous inorganic complexants (non apatite inorganic phosphorus, NAIP) or it could be included in phosphate containing minerals (e.g. apatite). In the surficial sediment layers the NAIP phase follows seasonal variations (Span et al., this issue) which correspond to the patterns of dissolved species.

The contents of solid iron and manganese are even higher in the top 10 cm of the sediment at the sampling site *Figino* (Span et al., this issue). Fe^{2+}/PO_4^{3-} ratios reach more than 6 (September 1989), and Mn^{2+}/PO_4^{3-} ratios more than 2 in the uppermost sediment layers (Fig. 4 d, c). The sediment seems to be able to act as a sink for phosphate even under anoxic conditions (Fig. 2 b, September) when unusually high concentrations of phosphate are found in the sediment-near hypolimnion water. Active microbial mineralization and methanogenesis (Hanselmann et al., 1990) in the apparently stagnant water layer above the sediment surface may lead to this local accumulation of phosphate. The large phosphate binding capacity of the sediment might also explain the decrease of the phosphate concentration in deeper sediment layers between September and March.

The seasonal dynamics of metal(hydr)oxide-contents and phosphorus release and retainment are tightly coupled and mediated by microbial electron transfer from organic matter oxidation. Besides being involved in phosphate cycling through direct or indirect mediation of iron and manganese(hydr)oxide reduction, microorganisms are also influencing the P cycle through growth and lysis at the sediment-water
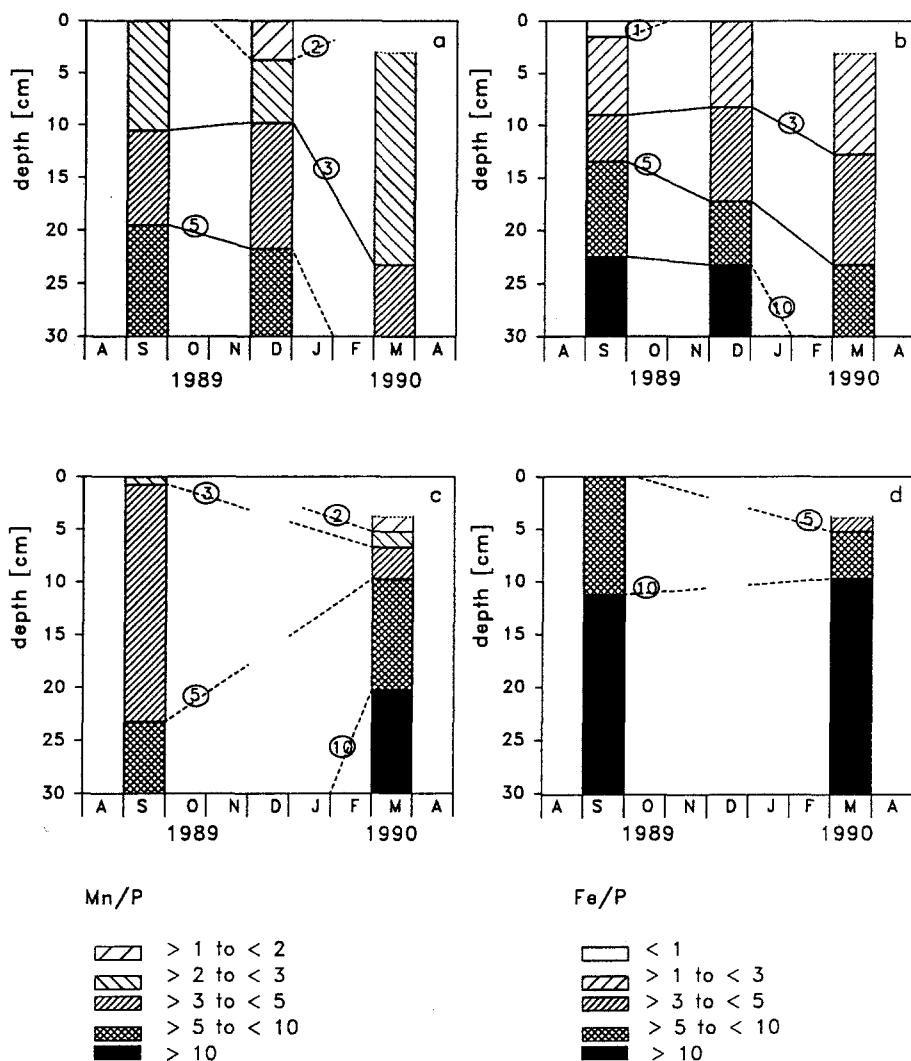
Mn/P

⊞	> 1 to < 2
⊠	> 2 to < 3
▨	> 3 to < 5
▦	> 5 to < 10
■	> 10

Fe/P

☐	< 1
⊞	> 1 to < 3
▨	> 3 to < 5
▦	> 5 to < 10
■	> 10

Figure 4. Comparison of seasonal and spatial variations of total dissolved manganese to dissolved phosphate ratios $\sum Mn/P$ (a, c) and total dissolved iron to dissolved phosphate ratios $\sum Fe/P$ (b, d) (atomic ratios = numbers on the connecting lines) in the pore water of sampling site Melide (a, b) and Figino (c, d) respectively

interface. Gächter (1987; Gächter et al., 1988) proposed that sediment microorganisms would store large amounts of phosphate intracellularly under oxic conditions which they would release under anoxic ones. The large amounts of NAIP (Span et al., this issue) and its variation in the sediment surface layers at the site Melide as well as the capacity of the sediment at the site Figino to act as a sink for phosphate under anoxic conditions indicate however, that adsorptive processes are dominating at both sites. Mass developments of *Beggiatoa* mats which could serve as an effective

biological sink for nutrients at the sediment surface were not observed. The frequently changing redox conditions do not allow for the establishment of stable populations of these microaerobic organisms. At the two sites, microbial assimilation and release of phosphate probably play quantitatively minor roles in the regulation of the phosphorus cycle.

4.4. Interactions with the sulfur cycle

At both sites, the sediments act as a sink for sulfate and hydrogen sulfide (H_2S, HS^- and S^{2-}, Fig. 3). At the sampling site Melide, a distinct flux of total dissolved hydrogen sulfide from the anoxic bottom water into the sediment was observed during times of thermal stratification (Fig. 3a). Also sulfate fluxes were always directed into the sediment (Fig. 3b). No free hydrogen sulfide was observed in measurable amounts in the pore water and in sediment near bottom water at the metal-rich sampling site Figino. Since anaerobic mineralization of organic matter will lead to the production of sulfide (Nedwell, 1982) and since sulfate will be reduced by sulfate reducing bacteria, a permanent sink for sulfur compounds has to be assumed within the sediment. The high concentrations of dissolved reduced iron and dissolved reduced manganese favors the precipitation of sulfide minerals thermody-namically (Berner, 1980). Also manganese and iron(hydr)oxides can interact with free hydrogen sulfide and form certain metal sulfide precipitates. In laboratory studies MnO_2 (Burdige and Nealson, 1986) and $FeOOH$ (Rickard, 1974) were abiologically reduced with hydrogensulfide. The elemental sulfur thus formed could serve as electron acceptor for sulfur reducing bacteria like *Desulfuromonas acetoxidans*, certain *Desulfovibrio species* and a few other sulfur reducing sulfidogens likely to be present in anoxic lake sediments. Investigations in marine intertidal sediments suggested the complete oxidation of sulfide to sulfate by MnO_2 (King, 1990). The presence of sulfate- and sulfur reducing microorganisms together with utilizable organic substrates (acetate and propionate have been detected) could thus support a sedimentary sulfur cycle. It might function as the electron transfer link between organic matter degradation and NAIP-associated metal and phosphate cycling.

5. Conclusions

The two sediment types which we studied in the southern basin of Lake Lugano influence the chemical composition of the hypolimnetic water decisively. Microbial degradation of the organic material consumed all of the dissolved suitable oxidizing agents at the sediment-water interface. With progressing stagnation, the hypolimnetic bottom water was depleted of oxidized species (O_2, NO_3^-, SO_4^{2-}), and became enriched with reduced compounds (Mn^{2+}, Fe^{2+}, H_2S).

Seasonal variations in the content of dissolved reduced manganese and iron at the sediment-water interface at the sampling site Melide correlated with the seasonal patterns observed for the release and the retainment of dissolved phosphate.
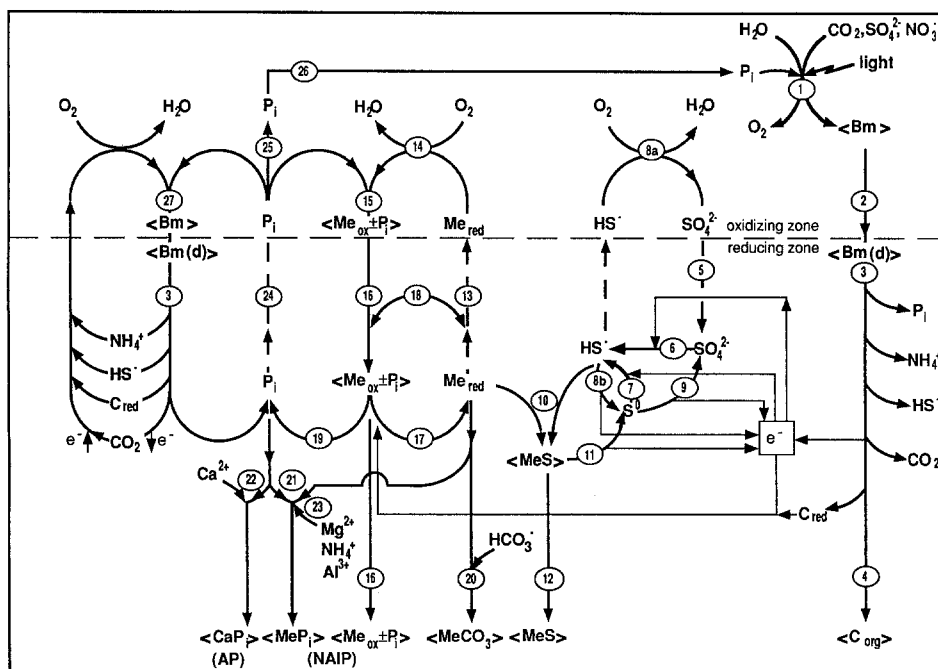
Figure 5. A mechanistic model summarizing phosphorus cycling and sinks in the studied sediments of the southern basin of Lake Lugano. The coupling of the iron and manganese cycles with the phosphorus cycle and the role of the sulfur cycle functioning as electron-transfer mediator are described with the reaction equations listed in table 1.

Abbreviations: $\langle\rangle$ particulate forms; without $\langle\rangle$ dissolved forms; $\langle Bm\rangle$ biomass; $\langle Bm(d)\rangle$ organic detritus, dead biomass still containing organically bound phosphorus (OP); e^- electron; C_{red} reduced organic carbon; $\langle C_{org}\rangle$ not degraded organic carbon, partially recalcitrant under the conditions in deeper sediment strata; $\langle MeS\rangle$ reactive metal sulfide; Me_{red} dissolved, mobile, reduced metal species (Fe^{2+}, Mn^{2+}); $\langle Me_{ox}\rangle$ precipitated, oxidized metal(hydr)oxide; $\langle Me \pm P_i\rangle$ metal(hydr)oxide with or without adsorbed phosphate, forms part of the non-apatite inorganic phosphorus (NAIP); P_i inorganic phosphate (soluble reactive phosphorus: SRP); $\langle MeP_i\rangle$ metal-phosphate mineral (NAIP); $\langle CaP_i\rangle$ apatite phosphorus (AP); $\langle MgP_i\rangle$ struvite; $\langle AlP_i\rangle$ variscite; $\langle MeCO_3\rangle$ metal-carbonate mineral

The high retention capacity for phosphate of sediment from the Figino site seems to be due to the high iron and manganese content present in all sediment layers. Even under the anoxic conditions in the deeper layers, the solid metal phases probably are present as oxidized forms. With respect to phosphate the Figino sediments seem to be able to act as a sink; retention and uptake processes thus should dominate the phosphorus cycle under all conditions. The same mechanisms seem to take place at both sites, the difference lying only in the quantitative importance of the various processes.

Microorganisms which aerobically or anaerobically degrade organic material drive the cycling of Mn, Fe and P directly or indirectly. They may also play an important role in innersedimentary sulfur cycling, thus interfering with the metal

Table 1. Reaction equations describing the processes of the meachanistic model presented in Fig. 5. Numbers correspond to circled numbers in Fig. 5

No.	reaction

 1 Biomass formation through oxic photosynthesis by planktonic algae: $a\ CO_2 + z\ H_2O + y\ H^+ + d\ NO_3^- + e\ HPO_4^{2-} + f\ SO_4^{2-} \to \langle C_aH_bO_cN_dP_eS_f \rangle + v\ O_2$, yielding OP

 2 Sedimentation and lysis of dead biomass

 3 Degradation of organic matter by chemoorganoheterotrophic microorganisms employing a variety of oxidants (Hanselmann, 1991): $\langle C_aH_bO_cN_dP_eS_f \rangle + z\ H_2O \to a\ CO_2 + y\ H^+ + x\ e^- + d\ NH_4^+ + e\ HPO_4^{2-} + f\ HS^-$, leading to the production of SRP and reduced inorganic and eventually organic compounds (e.g. C_{red} = formate)

 4 Burial of still oxidizable organic matter

 5 Diffusion-limited supply of sulfate as oxidant

 6 Sulfate reduction by chemoheterotrophic and chemomixotrophic sulfidogens, e.g. *Desulfovibrio* spp.: $8\ e^- + SO_4^{2-} + 9\ H^+ \to HS^- + 4\ H_2O$

 7 Sulfur reduction by chemoheterotrophic sulfidogens, e.g. *Desulfuromonas acetoxidans:* $2\ e^- + S^0 + H^+ \to HS^-$

 8 Sulfide oxidation in the absence of light by a) aerobic Thiobacilli: $S^{2-} + 2\ O_2 \to SO_4^{2-}$, or by b) anaerobic Thiobacilli; e.g. *Thiobacillus denitrificans:* $2\ HS^- + 2\ H^+ + 2\ NO \to N_2 + 2\ S^0 + 2\ H_2O$, or through sulfidation of Goethite (Rickard, 1974): $2\ \langle FeO(OH) \rangle + 3\ H^+ + 3\ HS^- \to 2\ \langle FeS \rangle + \langle S^0 \rangle + 4\ H_2O$ and possibly Manganite $(MnO(OH))$

 9 Sulfur oxidation in the absence of light by anaerobic Thiobacilli (see **8**): $\langle S^0 \rangle + 2\ NO_2^- \to SO_4^{2-} + N_2$ or through sulfuration of metal(hydr)oxides (Manganite): $6\ \langle MnO(OH) \rangle + \langle S^0 \rangle + 10\ H^+ \to 6\ Mn^{2+} + SO_4^{2-} + 8\ H_2O$

10 Precipitation of metal-sulfides, e.g. Pyrrhotite: $HS^- + Fe(OH)^+ \to \langle FeS \rangle + H_2O$

11 Sulfidation of metal(hydr)oxides, e.g.: $2\ \langle MnO(OH) \rangle + \langle FeS \rangle + 5\ H^+ \to 2\ Mn^{2+} + Fe(OH)^+ + \langle S^0 \rangle + 3\ H_2O$

12 Burial and diagenesis of metal sulfides, e.g. Pyrite-formation: $\langle FeS \rangle + \langle S^0 \rangle \to \langle FeS_2 \rangle$

13 Diffusive transport of dissolved, reduced metal species

14 Chemical or biologically mediated oxidation of reduced metal species under oxic conditions; e.g. by *Hyphomicrobium spp.*: $2\ Mn^{2+} + O_2 + 2\ H_2O \to 2\ \langle MnO_2 \rangle + 4\ H^+$, or by *Siderocapsa spp.*: $4\ Fe(OH)^+ + O_2 + 2\ H_2O \to 4\ \langle FeO(OH) \rangle + 4\ H^+$

15 Adsorption of phosphate onto metal(hydr)oxide surfaces, e.g.: $\langle Me-O-OH_2^+ \rangle + H_2PO_4^- \to \langle Me-O-PO_4H^- \rangle + H^+ + H_2O$ (NAIP; formal stoichiometry Stumm and Morgan, 1981)

16 Burial of metal(hydr)oxides with and without adsorbed phosphate

17 Reductive dissolution of metal(hydr)oxides, directly as by strain GS-15 (Lovley and Phillips, 1988 a) or indirectly, mediated by microbial electron transfer compounds: $\langle MnO_2 \rangle + 4\ H^+ + 2\ e^- \to Mn^{2+} + 2\ H_2O$, or: $\langle FeO(OH) \rangle + 2\ H^+ + 1\ e^- \to Fe(OH)^+ + H_2O$. The electrons may stem from sulfurogenic hydrogensulfide oxidation, from sulfurotrophic sulfate production, from sulfurogenic pyrrhotite oxidation or from the degradation of certain organic compounds

18 Reduction of Mn^{4+} by Fe^{2+} (Myers and Nealson, 1988; Lovley and Phillips, 1988 b): $Mn^{4+} + 2\ Fe^{2+} \to Mn^{2+} + 2\ Fe^{3+}$

19 Release of phosphate associated with reductive metal(hydr)oxide dissolution (formal equation): $\langle Me-O-PO_4H^- \rangle + e^- + 3\ H^+ \to Me^{2+} + H_2PO_4^- + H_2O$ (four source of e^- see **18**)

20 Precipitation of reduced metal-carbonate minerals (siderite, rhodochrosite); e.g.: $Fe(OH)^+ + HCO_3^- \to \langle FeCO_3 \rangle + H_2O$ and $Mn^{2+} + HCO_3^- \to \langle MnCO_3 \rangle + H^+$

21 Precipitation of reduced metal-phosphate minerals (NAIP, e.g. vivianite): $3\ Fe(OH)^+ + 2\ H_2PO_4^- + 5\ H_2O \to \langle Fe_3(PO_4)_2 \cdot 8\ H_2O \rangle + H^+$

22 Precipitation of calcium-phosphate minerals (AP); e.g. carbonate-apatite: $10\ Ca^{2+} + 4\ H_2PO_4^- + 3\ HCO_3^- + 2\ H_2O \to \langle Ca_{10}(PO_4)_4(CO_3)_3(OH)_2 \rangle + 13\ H^+$, or octacalcium: $4\ Ca^{2+} + 3\ H_2PO_4^- + 2\ \tfrac{1}{2}\ H_2O \to \langle Ca_4H(PO_4)_3 \cdot 2\ \tfrac{1}{2}\ H_2O \rangle + 5\ H^+$

23 Precipitation of other phosphate minerals like struvite: $Mg^{2+} + NH_4^+ + H_2PO_4^- \to \langle MgNH_4PO_4 \rangle + 2\ H^+$, or variscite: $Al^{3+} + H_2PO_4^- + 2\ H_2O \to \langle AlPO_4 \cdot 2\ H_2O \rangle + 2\ H^+$

24 Diffusive transport of dissolved phosphate (SRP)

25 Release of free phosphate stemming from anaerobic or aerobic mineralization processes and from desorption from metal(hydr)oxide surfaces

26 Transport of phosphate into the photic zone where it can be used for **1**

27 Phosphate assimilation for chemotrophic biomass synthesis in the absence of light (Gächter, 1987; Gächter et al. 1988), e.g. *Beggiatoa spp.* forming nutrient barrier at the redoxcline

cycles on the level of metal sulfide precipitation. A model for the coupling of the various material cycles at the sediment-water interface is depicted in Fig. 5. It summarizes our findings and links them to known geo-biochemical processes at the sediment-water interface.

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