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Phosphate exchange across the sediment-water interface when shifting from anoxic to oxic conditions – an experimental comparison of freshwater and brackish-marine systems

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Abstract. Comparative, experimental studies on sediment cores from freshwater and brackish-marine conditions reveal major differences in the benthic exchange of phosphate across the sediment-water interface when shifting from anoxic to oxic conditions. The flux of phosphate to the sediment during this shift was found to be mediated mainly by scavenging from newly formed colloidal ferric oxohydroxide. The capacity of the iron-rich particles to scavenge phosphorus depended on the stoichiometric ratio between dissolved iron and phosphorus built up in the supernatant water during reducing conditions. The freshwater system was characterized by high iron to phosphorus ratios in the dissolved phase and thus most of the phosphate was incorporated into the colloidal iron oxohydroxide during the oxygenation. In contrast, the marine systems reached lower iron to phosphorus ratios during the anoxic period which resulted in less efficient phosphate scavenging. Consequently, significant amounts of phosphate remained dissolved in the marine systems after the change to oxic conditions, possibly increasing the proportion of phosphate recycled to the euphotic zone. Manganese showed a consistent redox-dependent behaviour in all the investigated systems, but interacted neither with phosphate nor with iron.

Introduction

The classic model for redox-related phosphorus exchange across the sediment-water interface originates from studies performed in freshwater systems (Einsele 1936, 1938; Mortimer 1941, 1942) and is based on an intimate coupling to the cycling of iron. Today, this view still seems relevant (Davison & Tipping 1984), but also appears to be an over-simplification. Studies in the 1980s addressed release and uptake of phosphorus by benthic biota as an overlooked mechanism affecting the sediment-water dynamics of phosphorus (reviewed by Boström et al. 1988; Gächter & Meyer 1993). Caraco et al. (1989) claim that the sulphate concentration of the overlying water rather than the redox conditions is a crucial factor controlling the release of phosphorus from sediments. A recent study on suspended matter from the

Baltic Sea (Ingri et al. 1991) infers phosphorus to be scavenged chiefly by a manganese rich phase when turning from anoxic to oxic conditions, i.e. positive redox-turnover. This latter study contrasts to the common view that the abiotic flux of phosphorus to the sediment after an anoxic period is mediated mainly by precipitating ferric oxohydroxide (e.g. Mortimer 1942; Mayer et al. 1982; Lean et al. 1986; McQueen et al. 1986; Ellis-Evans & Lemon 1989).

Neither the relative importance of different processes in governing the benthic dynamics of phosphorus, nor the relevance of freshwater models to marine systems is yet fully understood, even though phosphorus is an essential nutrient in all aquatic ecosystems (Kuhl 1974; Nalewajko & Lean 1980). Several experimental studies have examined redox-related benthic phosphorus exchange in the marine environment (Hallberg et al. 1976; Holm 1978; Balzer 1980, 1984; Balzer et al. 1983; Sundby et al. 1986), but we have found none comparing freshwater and marine environments. We report here on an experimental study of the exchange of phosphorus, iron and manganese across the sediment-water interface during positive redox-turnover at freshwater and marine stations. Our findings suggest fundamental differences in the exchange dynamics between these two environments, with implications for nutrient limitation.

Study Area

The study area (Figure 1) is situated south of Stockholm, Sweden. Sediment-water samples from three stations were used for incubation experiments. One station (Lake MB) was located in freshwater in Lake Mälaren (Södra Björkfjärden), one of the World's large lakes (Herdendorf 1982), and the other two were marine stations located in Himmerfjärden (Bay H5) and Yttre Hållsfjärden (Coastal C) of the adjoining brackish Baltic Sea (Figure 1). The geomorphology of the study area is basically controlled by fault lineaments. The Precambrian basement, dominated by sedimentary gneisses and granitoids (Stålhös 1968, 1979, 1982, 1984), is to a large extent covered by unconsolidated Quaternary drift (Möller 1969; Persson 1977; Björnbom 1981, 1985). Coniferous forest is the principal vegetation, but certain areas are also arable land. There are two towns in the area, Södertälje (60,000 inhabitants) and Trosa (4,000 inhabitants), respectively.

A modern tertiary sewage treatment plant located at the head of Himmerfjärden serves the town of Södertälje and southwestern parts of Stockholm (Cronström 1988). In 1989, this plant treated sewage water from 234,000 people (A-G. Dahlberg pers. comm.), plus urban surface runoff and waste waters from approximately 500 mostly small industries (Hellström & Knutsson 1983). Its effluent water creates a gradient of eutrophication in the receiving

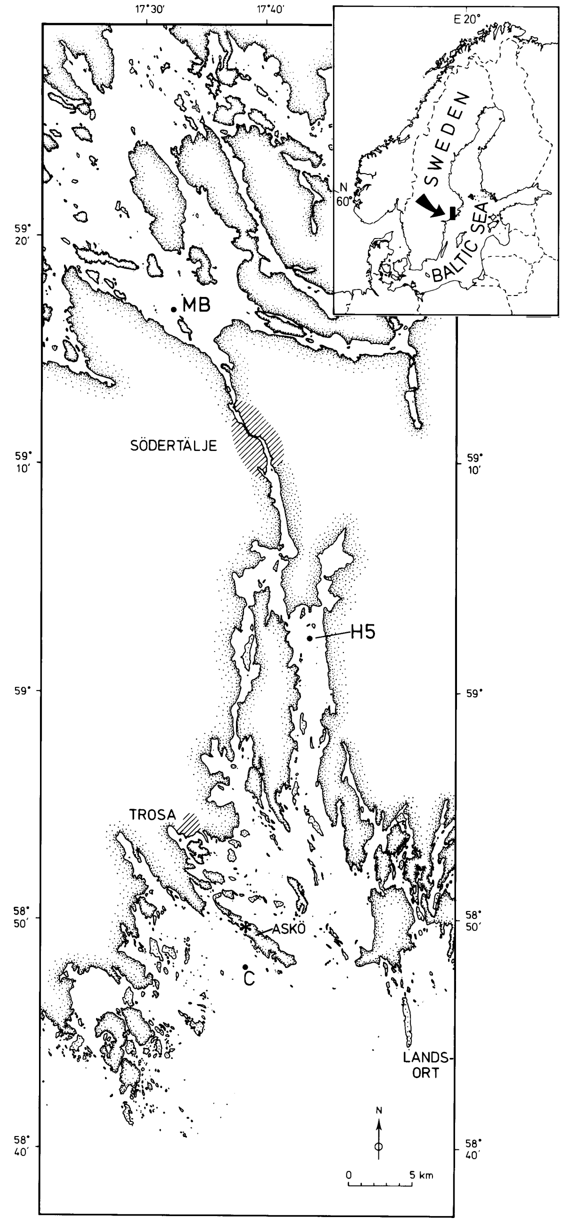

Figure 1. Study area and the position of the three sampling stations (MB = Lake MB, H5 = Bay H5 and C = Coastal C). The field laboratory at the island of Askö is denoted by an asterisk.

area, with an almost double annual primary productivity (Larsson & Hagström 1982) and a significantly increased crop of rotifer and cladoceran zooplankton (Johansson 1983; Johansson et al. 1992) in the inner part of Himmerfjärden, compared to station Coastal C outside the bay.

The annual salinity range of the brackish area is 5 to 8‰ whereas Lake Mälaren is a dimictic freshwater lake. As a rule, the water columns are stratified during summer and early autumn, with a thermocline located 10 to 15 m below the water surface. The water exchange of the brackish bay area is mainly governed by two baroclinic modes, one caused by density variations in the southern boarder sounds and one by the regular estuarine circulation. The barotropic influences are less important (Engqvist & Omstedt 1992). The tide range is $<$ 5 cm in this part of the Baltic Sea (Magaard 1974). Lake Mälaren is connected to the Baltic by a locked canal at the town of Södertälje. No river enters the study area and no bottom trawling occurs.

Stations

All three stations (Figure 1) have soft bottoms, rich in organic matter in the upper layers with more argillaceous mud beneath, but they differ with respect to salinity and biotic conditions. At the freshwater station, Lake MB, (water depth 43 m) the surface layer of the sediment was pale yellow-brown and the underlying argillaceous mud light grey. This part of Lake Mälaren is well oxygenated and the benthic community comprises various species of oligochetes, chironomids, mussels of the genus *Pisidium*, and the crustacean *Monoporeia affinis* (Milbrink et al. 1974; Wiederholm 1978; Willén et al. 1990), giving no indication of local pollution. Concentrations of toxic metals in the sediments are fairly low (Persson 1991).

The sediment at Coastal C station (37 m) is visually similar to station Lake MB. Here, the meiofauna is dominated by nematodes and ostracods, whereas the macrobenthos consists basically of a priapulid, *Halicryptus spinulosus*, a polychaete, *Harmothoe sarsi*, an isopod *Saduria entomon*, two deposit feeding haustoriid amphipods, *Monoporeia affinis* and *Pontoporeia femorata*, and a tellinid clam *Macoma balthica* (Ankar & Elmgren 1975, 1976; Cederwall 1990). Considering the vertical distribution of live *Bosmina* resting eggs, bioturbation seems to be a significant process down to a depth of at least 4 cm (Kankaala 1983).

At station Bay H5 (27 m) the sediment is euxinic, black to the top and characteristically laminated (Schaffner et al. 1992). Recurring oxygen deficiency during summer and early autumn has led to depletion of the benthic fauna (Larsson et al. 1991). At the date of sampling, the oxygen concentration was 0.4 ppm in the bottom waters and whitish, mat-forming colonies of sulphur-oxidizing bacteria were the only visible organisms.

Methods

Sample collection

In late July to mid-August 1989, five sediment cores were collected at each station, by careful sampling with a Kajak-type gravity corer (Blomqvist & Abrahamsson 1985). By using cylindrical Plexiglas (polyacryl amide) coring tubes with an internal diameter of 80 mm, at least the upper 50 mm of the sediment bed is reliably sampled (Blomqvist 1985). The sediment cores obtained were about 25 cm high, with an overlying water column of approximately the same height. Sealing at the top and at the bottom was provided by stoppers of polyvinyl chloride (PVC) (Blomqvist & Abrahamsson 1985). Likewise, water from 1–2 m above the bottom was collected with a Ruttner-type sampler. During transport from the sampling stations to the field laboratory at the island of Askö (Figure 1), the sediment cores were kept vertical and chilled in dark boxes.

At the laboratory, the top stoppers were equipped with upward bent pipes of Plexiglas, connected to narrow PVC-tubes (Figure 2). This arrangement made it possible to sample and exchange supernatant water without resuspending the sediment. A magnetic stirring bar at the top of each of five coring tubes was propelled by a common water-driven central unit (Figure 2). This permitted gentle stirring and mixing (Hjellström 1987) of the overlying water throughout the anoxic part of the incubation. To avoid errors from high concentrations of nutrients in the supernatant water, which might develop during transport of sediment cores (Elderfield et al. 1981), four-fifths of the overlying water was replaced by new bottom water before the incubation started. During incubation, the cores were placed in a water bath (9 ± 2 °C) and kept in a dark constant temperature room (10 ± 3 °C). Anoxic conditions were generated either by having the tubes tightly capped or by careful N_2-bubbling (Figure 2). The anoxic period was interrupted by air-bubbling, inducing a positive redox-turnover. Manipulations of the iron content were made by addition of dissolved $Fe(NO_3)_2$ to two cores from station Bay H5.

Analytical methods

Throughout the experiments dissolved oxygen, pH and temperature of the supernatant waters were measured frequently. Also, the cores were inspected for colour changes, precipitates, odors, etc. Temperature and dissolved oxygen were recorded with a WTW (Wissenschaftlich-Technische Werkstätten, Weilheim, F.R.G.) OXI 96 instrument, equipped with an EO 96 OXO electrode, calibrated against water saturated air, and pH was measured with a WTW pH meter, pH 95, calibrated against WTW technical buffer solutions

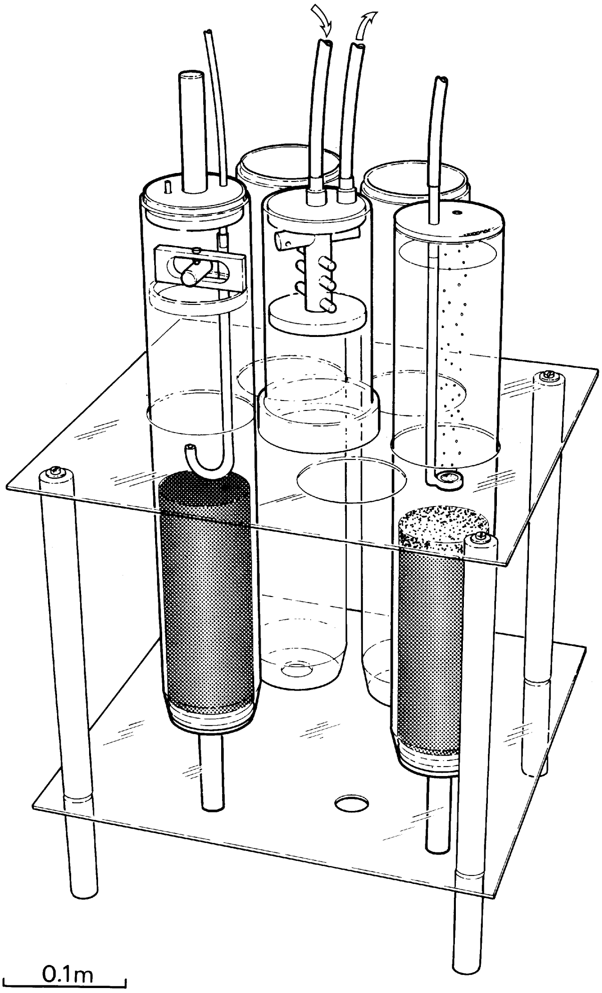

Figure 2. Incubation arrangement. The left sediment core (anoxic) is equipped with a magnet spin bar and an upward bent pipe for replacement of supernatant water. The right core (oxic) has a gas distributor for supply of N_2-gas or air.

pH 4.01 and 7.00. Water samples were taken with Millipore syringes. Half of each sample was filtered through a series of 10.0, 1.0 and 0.2 μm Nucleopore filters, using in-line filter holders, fitted directly onto the syringe. 5–10 ml of the aliquot was squeezed through the filters before the collection of filtrate started. Filters and filter holders were pre-washed in 1 M HNO_3 for at least 24 h (Batley & Gardner 1977; Truitt & Weber 1979) and then thoroughly rinsed with reagent grade water from an Elga Spectrum RO1 System (Elga, High Wycombe, UK). Syringes were soaked in HCl 1:1 before being rinsed as above. Unless otherwise stated, filtered samples are referred to as dissolved species (PO_4-diss, Fe-diss and Mn-diss) and the difference between unfiltered and filtered concentrations are referred to as particulate forms (PO_4-part, Fe-part and Mn-part). Phosphate was determined with a phosphoantimonylmolybdenum blue method (Koroleff 1983). As a precautionary action to minimize interferences, the concentrated samples were diluted (2–5 times) prior to addition of reagents (Blomqvist et al. 1993) and the absorbance read after 20 minutes of reaction time, using a Spectronic 1001, UV-VIS spectrophotometer (Bausch & Lomb, New York, USA). Samples for metal determinations were preserved by addition of concentrated p.a. HNO_3 (E. Merck, Darmstadt, FRG), to a final concentration of 1 ml HNO_3 litre^{-1} (Magnusson & Westerlund 1980), and stored in polyethylene bottles, cleaned according to Borg et al. (1984). Approximately four months later, iron and manganese were determined by atomic emission spectroscopy, using an inductively coupled plasma source (ARL 3580, Applied Research Laboratories, Lausanne, Switzerland).

Results

Stations with oxidized benthic conditions

After eight days of incubation the supernatant water of cores from station Lake MB and Coastal C became depleted in oxygen (Figure 3a-b). About 5 days later, black patches started to appear on the originally brownish sediment surface. During oxic conditions the pH for Lake MB was 8.0 ± 0.1 (arithmetic mean ± 1 S.D.) and Coastal C 8.1 ± 0.05, but declined to the lower values of 7.1 ± 0.3 and 7.3 ± 0.3 for Lake MB and Coastal C, respectively, during the anoxic period. The environmental conditions are described in greater detail elsewere (Gunnars 1990). Dissolved species of phosphate, iron and manganese were mobilized within the sediments during the anoxic incubation, and released into the supernatant water (Figure 3a-b). These enhanced fluxes of phosphorus, iron and manganese out of the sediment during negative redox-turnover agree with previous observations in lakes (e.g. Einsele & Vetter 1938; Mortimer 1941, 1942; Mayer et al. 1982; Ellis-Evans & Lemon 1989) and from incubation studies with benthic chambers in freshwater (Gächter et al. 1988) and marine environments (e.g. Hallberg et al. 1976; Balzer 1982, 1984; Balzer et al. 1983; Sundby et al. 1986). The average concentrations of PO_4-diss, Fe-diss and Mn-diss at the end of the anoxic incubation were 17, 40 and 84 μmol litre^{-1}, respectively, for Lake MB. A PO_4-diss mean amounting to 22 μmol litre^{-1} for Coastal C cores compares well to Lake MB, whereas the concentration of Fe-diss (21 μmol litre^{-1}) and Mn-diss (57 μmol litre^{-1}) for this brackish-marine station were significantly lower than recorded for the freshwater station.

When the positive redox-turnover was induced, the surficial sediments started to grow lighter in colour within a few hours, and concomitantly PO_4-diss fell rapidly, whereas a corresponding increase of PO_4-part was recorded. Simultaneously, iron-rich colloidal particles were formed, and after 15–20 h of air-bubbling almost all iron had been converted from dissolved to particulate form (Figure 3a-b). The particles were not visible to the naked eye, but were to a large degree retained by 1 and 0.2 μm filters. The quick change in species distribution of phosphorus presumably was due to scavenging by precipitated ferric oxohydroxide.

The scavenging process differed in effectiveness in the freshwater and brackish-marine cores. At station Lake MB, the removal of phosphorus from the dissolved phase was more or less complete after the positive redox-turnover (Figure 3a), while about 7 μmol litre^{-1} of the phosphate remained dissolved for the Coastal C station (Figure 3b). In the freshwater of Lake MB the concentration of PO_4-part and Fe-part decreased only slowly (Figure 3a) with an approximate turn-over time of 830 h (sensu Bolin & Rodhe 1973), whilst the rate of decline was faster (estimated turn-over time of 120 h) for the Coastal C station.

In contrast to iron and phosphorus, the species distribution of manganese was dominated by dissolved forms throughout the anoxic as well as the oxic period. Mn-diss decreased slowly, but no increase of Mn-part corresponding to the decline in the dissolved phase was found (Figure 3a-b), though, a very small, rapid increase in Mn-part was recorded at the positive redox-turnover.

The euxinic brackish-marine station Bay H5

The concentration of oxygen decreased rapidly in cores from Bay H5 (Figure 4a). The whitish surface colonies of sulphur-oxidizing bacteria disappeared within two days. The anoxic incubation, by means of N_2-bubbling, resulted in an increase in pH from 7.1 ± 0.06 to 8.0 ± 0.7, thus suggesting that the gas-purging not only removed O_2, but also expelled CO_2 from the supernatant water. During the re-aeration the pH was 8.05 ± 0.06. Initially, the concentration of PO_4-diss increased considerably, culminating at an average of 15 μmol litre^{-1} at the end of the anoxic phase (Figure 4a). On the other hand, Fe-diss showed a minor increase only and remained low (<0.5 μmol litre^{-1}) throughout the experiment. The total concentration of iron even decreased during the anoxic incubation.

The average concentration of Mn-diss in the supernatant water rose slowly up to 6 μmol litre^{-1} during the first 300 h of incubation (Figure 4a) even though oxidized conditions had started to develop in the surficial sediments

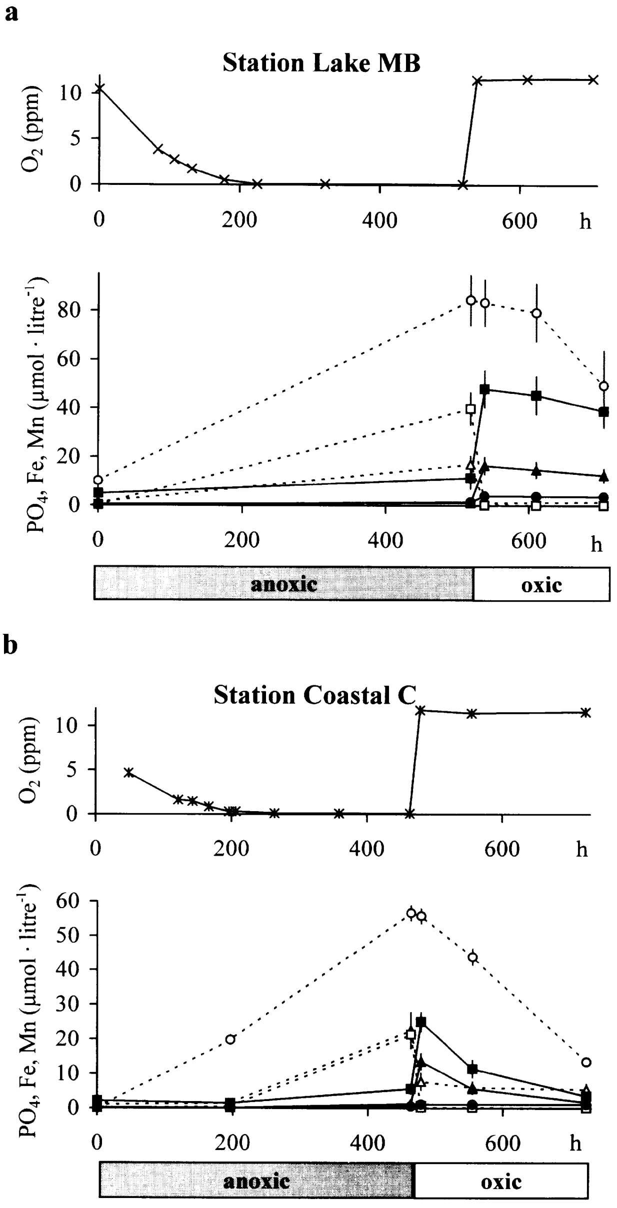

Figure 3. Time course of dissolved (open symbol) and particulate (filled symbol) phosphate (- -△- - diss; –▲– part), iron (- -□- - diss; –■– part) and manganese (- -○- - diss; –●– part) concentrations in the supernatant water of the freshwater station Lake MB (*a*) and the brackish marine station Coastal C (*b*), during a shift from anoxic to oxic conditions. Initially, the surficial sediment of these stations were oxic. Vertical bars denote ± 1 S.E. (standard error of the mean), *n* = 5 for both stations. Time unit: hours.

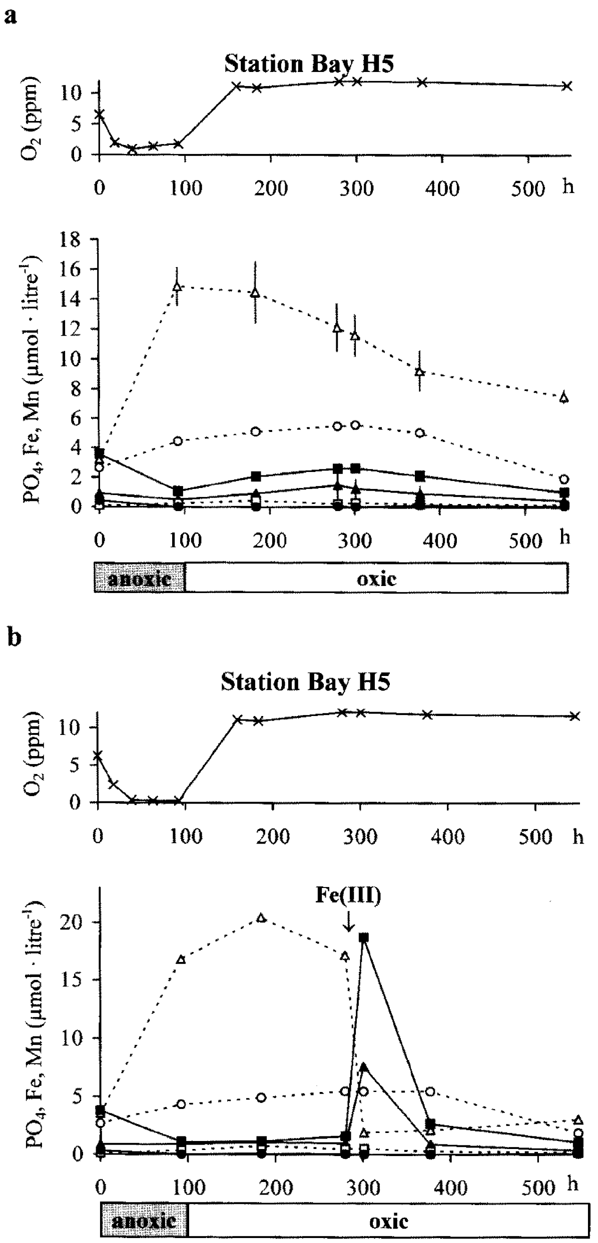

Figure 4. Time course of dissolved (open symbol) and particulate (filled symbol) phosphate (- -△- - diss; –▲– part), iron (- -□- - diss; –■– part) and manganese (- -○- - diss; –●– part) concentrations in the supernatant water of the euxinic brackish-marine station Bay H5 (*a*, *b*), during a shift from anoxic to oxic conditions. The sediment of this station was black at the top already at the start of the incubation. Vertical bars of panel *a* denote ± 1 S.E., $n = 3$. In panel *b*, $n = 1$, the arrow shows the addition of ferric iron to the supernatant water to a total concentration of 36 μmol liter^{-1}. Time unit: hours.

at 160 h. Manganese in dissolved form was the dominating species throughout the experiment. A general feature of station Bay H5 compared to Lake MB and Coastal C was low concentrations of both iron and manganese.

During the positive redox-turnover in cores from station Bay H5, no sudden shifts from dissolved to particulate species were recorded for phosphorus, iron or manganese (Figure 4a). Instead, PO_4-diss remained in solution. However, a slow decline started after about three days of air-bubbling, probably due to adsorption by the sediment surface, on which oxidized brown patches started to appear at this time.

In another set of experiments, ferric iron was added to the supernatant water of two cores from station Bay H5 (final concentration 18 and 36 μmol Fe(III) litre^{-1}, respectively). This resulted in a drastic decrease in PO_4-diss (Figure 4b), probably due to scavenging by the precipitating ferric oxohydroxide. The precipitate consisted of rather large, visible particles which rapidly settled to the bottom, and Fe-part returned within three days to concentrations in level with starting values (Figure 4b). Manganese was not affected by the addition of iron. The second core (not shown in Figure 4b), with less iron added (18 μmol Fe(III) litre^{-1}), behaved similarly (Gunnars 1990).

Discussion

Our experiments suggest fundamental differences in the phosphorus exchange dynamics between marine and freshwater systems, controlled by the availability of iron. During the anoxic period, the euxinic brackish-marine station (Bay H5) released phosphorus, but little or no iron. At the onset of oxic conditions, the phosphate remained dissolved in the supernatant water (Figure 4a). This behaviour contrasts with the commonly held view of how the dynamics of phosphate is governed across the sediment-water interface. With respect to phosphate as well as iron, the freshwater station, Lake MB, served in this context as a reference and corresponded well to the classic model (Figure 3a). Finally, station Coastal C appeared as an intermediate between stations Bay H5 and Lake MB (Figure 3b). The amount of iron released at station Coastal C was much higher than at station Bay H5, but not enough to remove all the dissolved phosphate in the supernatant water after the positive redox-turnover. In fact, these findings imply that the classic model for redox-related benthic phosphorus dynamics originating from studies conducted in freshwater environments does not apply directly to marine systems.

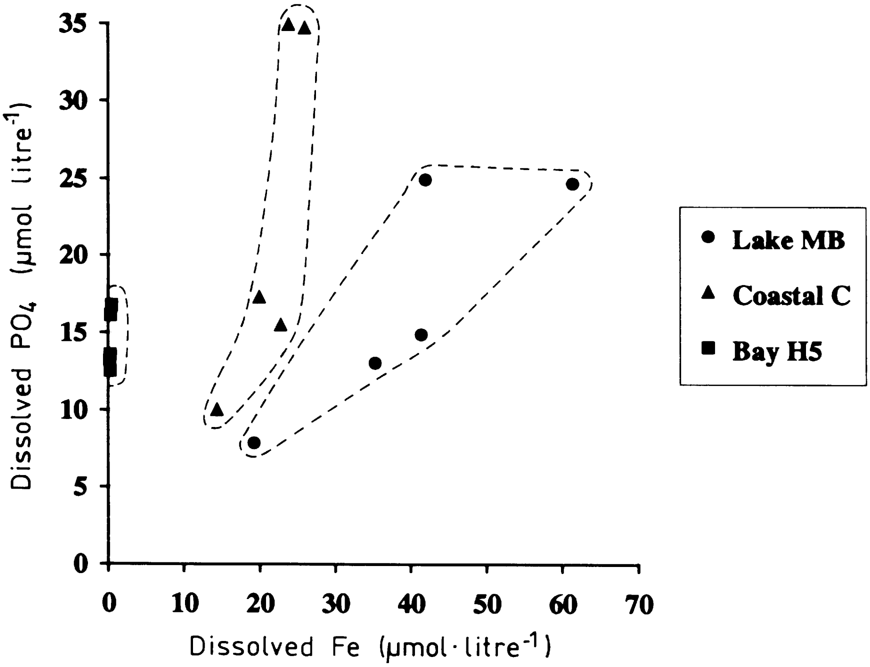

Figure 5. Concentrations of dissolved phosphate versus dissolved iron at the end of the anoxic incubations. The three populations differ in location (Kruskal-Wallis test, H = 12.5, $p < 0.01$). Envelops are drawn around data to emphasize spatial patterns.

Release ratios

The contrasting phosphorus and iron dynamics under freshwater and marine conditions are demonstrated by the molar ratio between Fe-diss and PO_4-diss at the end of the anoxic incubation (from here on called the Fe/P release ratio). During the anoxic period the three stations reached different Fe/P release ratios (Figure 5). The amount of phosphorus released was of the same order of magnitude for all stations, while the quantity of iron liberated varied considerably. Due to lower iron concentrations, the marine stations (Coastal C and Bay H5) attained lower ratios compared to the freshwater station, Lake MB (Figure 5). The sediments of Bay H5 released only small amounts of iron, culminating in a Fe/P ratio of about 0.02, whereas Coastal C reached a Fe/P ratio close to 1. Finally, the sediments of Lake MB liberated more iron than phosphorus, with a Fe/P ratio of about 2 at the end of the anoxic incubation. The marine sediments thus released a smaller proportion of iron to phosphorus, resulting in lower Fe/P ratios, and the difference was more pronounced when the marine surficial sediment was euxinic.

We have summarized Fe/P ratios during negative redox-turnover from the literature (Table 1), and the figures appear consistent with our results, i.e. marine systems have lower Fe/P ratios during anoxic conditions. A more comprehensive comparison requires more data, and should perhaps also further distinguish studies on the basis of biological-chemical conditions and geological settings (Boström et al. 1982, 1988), as well as differences in experimental approaches and techniques employed. However, in Table 1 studies of calcareous lake sediments have not been included, because in such lakes further chemical factors than goes into the present concept might affect the exchange of phosphorus and iron across the sediment-water interface (Stumm & Leckie 1971; Staudinger et al. 1990).

In the present study, the stations were situated within a small, geologically uniform area. The basic differences were related to salinity and sedimentary redox conditions. Also, the study was performed as parallel running experiments. Thus, it appears likely that our observed divergences in Fe/P ratios are related to fundamental differences between the freshwater and marine systems in the phosphorus-iron dynamics across the sediment-water interface. The lower Fe/P ratio at the end of the anoxic period for the marine stations is presumably a result of a richer supply of sulphide (Capone & Kiene 1988) which binds a greater portion of the iron, as iron sulphides (Morse et al. 1987), than applies to the freshwater environment. Marine systems are characterized by high concentrations of sulphate, which can serve as a source for sulphide production during reduced conditions, provided that metabolizeable organic substrate is present in good supply. The solubility product of both crystalline iron sulphides (mackinawite, greigite and pyrite) and amorphous iron sulphide is usually exceeded in organic-rich marine sediments, and considerable quantities of precipitated iron sulphides are reported (Berner 1984). Precipitation of iron sulphides traps iron in a solid phase resulting in a low concentration of dissolved iron and, thus, a low Fe/P release ratio. In freshwater systems, on the other hand, the low sulphate content limits the formation of sulphide, so that the concentration does not become sufficient to precipitate significant amounts of the accessible iron (Lidén 1983; Davison & Tipping 1984). Consequently, the Fe/P release ratio can be expected to be high in freshwater systems, provided the supply of dissolved sulphur from the local catchment area or from anthropogenic sources is not considerable (Stauffer 1987; Caraco et al. 1991, 1993).

Immobilization of phosphorus

A close relationship was revealed between the Fe/P release ratio and the subsequent effectiveness of scavenging by ferric oxohydroxide immediately after the positive redox-turnover (Figure 6). In systems with high Fe/P release

Table 1. A comparison of studies reporting dissolved Fe/P molar ratios in supernatant water during anoxic conditions, involving sampling of hypolimnion or bottom water and of incubations of benthic chambers and sediment cores. Studies of calcareous lake sediments have not been included.

	Fe/P ratio	**Area**	**Remark**	**Reference**
Marine system	0.2–1.1	Coastal Baltic proper, Sweden	Chamber	Holm & Lindström 1978
	0.2–0.4	Open Baltic proper	Bottom water	Kremling 1983
	0.6	Coastal Skagerrak, Sweden	Chamber	Sundby et al. 1986
	0.1	Lake Hamana, Japan	Bottom water	Ichinose et al. 1988
	0.05–0.008	Open Black Sea	Bottom water	Kempe et al. 1991
	1.1, 0.02	Coastal Baltic proper, Sweden	Sediment core	This study
Freshwater systems	3–9	Lake Schleinsee, FRG	Bottom water	Einsele 1936; Einsele & Vetter 1938
	10–280	Estwaite Water, England, UK	Bottom water	Mortimer 1942; Heaney et al. 1986
	4	Lake Ursee,	Bottom water	Tessenow 1973
	60–210	Lake Feldsee, FRG	Bottom water	Tessenow 1975
	2	Lake Constance,	Sediment core	Frevert 1979
	30	Lake Titisee, FRG	Sediment core	Frevert 1979
	3–4	Shagawa Lake, Minnesota, USA	Bottom water	Larsen et al. 1981; Stauffer & Armstrong 1986
	4	Lake Sebasticook, Maine, USA	Hypolimnetic water	Mayer et al. 1982
	12	Sombre Lake, Antarctica	Bottom water	Gallagher 1985
	2	Heywood Lake, Antarctica	Bottom water	Gallagher 1985
	1.3	Lake Sempach, Switzerland	Chamber	Gächter et al. 1988
	0.7	Amos Lake, Antarctica	Bottom water	Ellis-Evans & Lemon 1989
	15	Sombre Lake, Antarctica	Bottom water	Ellis-Evans & Lemon 1989
	2.4	Lake Mälaren, Sweden	Sediment core	This study

ratios the removal of PO_4-diss is more effective than in systems with lower Fe/P release ratios. For Fe/P ratios lower than ≈ 2 the available iron is in too short supply to bind all dissolved phosphate (Figure 6). For station C, where the concentration of iron was just a little too low to scavenge all phosphorus, the particles formed at the redox-turnover had a Fe/P ratio of 2.0 ± 0.3 (arithmetic mean ± 1 SD). Particles formed under conditions with excess of iron, i.e. station H5 when supplemented with iron and station Lake MB, had Fe/P ratios of 2.6 ± 0.2 and 3.1 ± 0.5, respectively. These findings agree with experimental studies by Tessenow (1974), implying that the Fe/P ratio in particles formed in situ have a lower limiting value around 2. Empirical data (Tessenow 1974), isotope exchange studies (Atkinson et al. 1972), infrared spectroscopic evidence (Atkinson et al. 1974; Parfitt et al. 1975; Parfitt & Atkinson 1976; Weiner et al. 1984; Tejedor-Tejedor & Anderson 1990), and inference based on adsorption isotherms (Lijklema 1980; Von Gunten & Schneider 1991; Golterman 1995a), suggests that the predominant Fe/P surface complexation ratio of ferric hydroxide is 2. It is worth noting that all the marine studies referred in Table 1 reported Fe/P ratios below 2 in the dissolved phase, whereas the freshwater lakes, with two exceptions (Lake Sempach: Fe/P = 1.3 and Amos Lake: Fe/P = 0.7; both eutrophic), had Fe/P release ratios of ≥ 2.

Within a pH range of 3 to 9, the incorporation of phosphate into iron oxohydroxides is known to increase with decreasing pH (Lijklema 1980; Sigg & Stumm 1981; Tejedor-Tejedor & Anderson 1990; Golterman 1995b), but decrease with increasing humic acid concentration and be rather insensitive to variations in ionic strength caused by monovalent ions (Hawke et al. 1989). Stations Lake MB and Coastal C had similar pH values in the supernatant water throughout the experiments, so it is reasonable to infer that the observed difference in iron-phosphorus interaction between the two stations is not pH-related. Results from separate incubation experiments with water from station Lake MB and Coastal C, in which both salinity and Fe/P ratio were varied, have demonstrated that a given Fe/P ratio yields about the same scavenging effect, independent of salinity in the range 0–33 ‰ (Johansson 1993). Taken together, these results strongly suggest that it is basically the Fe/P ratio of the dissolved phase which governs the fate of phosphorus immediately after a positive redox-turnover in our systems. This would not be expected if the dynamics of phosphorus was controlled primarily by biotic processes (cf. Gächter et al. 1988).

Manganese dynamics

The dissolved forms dominated the manganese speciation throughout the experiments. In all the investigated systems the concentration of Mn-diss

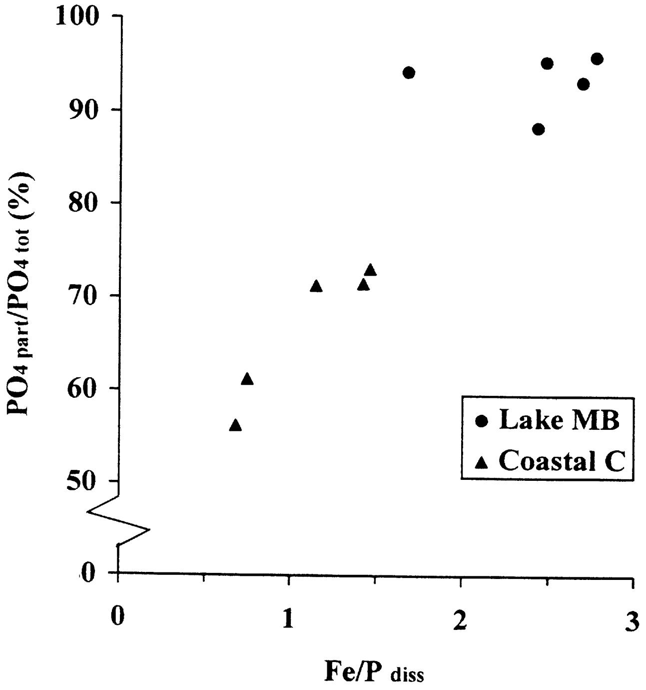

Figure 6. Percentage of phosphorus in particulate phase immediately after the positive redox-turnover versus the Fe/P molar ratio of the dissolved phase in the supernatant water at the the end of the anoxic incubations. No precipitate was formed in cores from station Bay H5. The relation is statistically significant (Spearman rank correlation coefficient 0.94, $p < 0.001$).

declined after the onset of oxic conditions. At the rapid formation of colloidal iron, which scavenged dissolved phosphate, no corresponding dramatic change in manganese speciation was observed, even though data for Lake MB and Coastal C showed a very small increase of Mn-part at the positive redox-turnover. In the present study, almost no manganese was recovered in the particulate phase (Figures 3 and 4), not even after the addition of ferric iron (Figure 4b). The average Mn-part/Fe-part ratios 0.04 and 0.08 for Coastal C and Lake MB, respectively, were low.

Our data do not show how Mn-diss was removed from the water. However, the abiotic oxidation of manganeous manganese in the absence of catalysts is a very slow process requiring years (Morgan 1967; Diem & Stumm 1984). This contrasts with ferrous iron which is oxidized within minutes or hours (Davison & Seed 1983; Millero et al. 1987; King et al. 1995). The very low concentration of suspended particulate manganese recorded (Figures 3 and 4) suggests that surface adsorption and microbial oxidation (Nealson et al. 1988) in the sediment (Nealson & Ford 1980; Ehrlich 1982) are the most probable mechanisms for the observed removal. Still, several days were needed for a concentration reduction by a factor of two in the studied systems (Figure 3).

A redox-related interaction between manganese and phosphate in the water has been considered since the 1930's (Ohle 1937; Einsele 1938). Still, there is no consensus concerning the influence of manganese on phosphorus cycling. Particles rich in manganese oxide/hydroxide from both marine and freshwater are known to contain phosphorus (Davison & Tipping 1984; Ingri et al. 1991). The latter authors reported that in the Landsort Deep, Baltic proper, most of the phosphate was scavenged by suspended manganese, with approximately 70% of the particulate phosphate found in the Mn-rich phase. Shaffer (1986) suggested that observed phosphate anomalies in the Black Sea cannot explained solely by the behaviour of iron, but that a manganese shuttle consisting of precipitating and dissolving manganese oxohydroxides at the redox boundary also must be considered. However, in our experiments we found no significant interaction between phosphate and manganese dynamics (Figures 3 and 4). Experimental data by Gächter et al. (1988) agree with our findings.

One might expect manganese to act as a phosphorus scavenger in iron deficient systems such as station Bay H5. However, the concentration of Mn_{diss} was low and the Mn_{part} content was very low in cores from station Bay H5 (Figure 4). Also, what might be most crucial for the lack of interaction between phosphorus and manganese in our experiments was that no significant formation of particulate manganese took place in the supernatant water under the conditions of study. This might reflect a short supply in quantity or quality of suspended particles and bacteria needed for effective removal of dissolved manganese (Morris & Bale 1979; Chapnik et al. 1982; Diem & Stumm 1984). Further investigations are needed to clarify under what conditions phosphate may be scavenged by manganese.

Implications

Strong consistency in the cycling of iron and phosphorus in freshwater lakes has previously been demonstrated in various studies (Einsele 1936; Mortimer 1941, 1942; Tessenow 1975; Mayer et al. 1982; Gallagher 1985; Ellis-Evans & Lemon 1989). In our experiments, the removal of phosphorus after the positive redox-turnover seemed to be controlled by the availability of precipitating iron in both freshwater and marine systems. The similarity in interaction patterns of phosphorus and iron (Figure 3a-b) suggests that the two elements were components of the same solid phase. The iron deficient system, station Bay H5, obviously lacked an efficient scavenging mechanism for phosphorus (Figure 4a), but addition of iron to the system caused rapid removal of phosphorus (Figure 4b). This contrasts with station Lake MB (Figure 3a), where the scavenging mechanism was most effective, even without addition of iron. At station Coastal C, the amount of iron appear to be in too short supply to precipitate all phosphate liberated, since some remained dissolved in the supernatant water (Figure 3b).

The implications of a differentiation in Fe/P release ratio can be significant. When proportionally less iron than phosphorus is supplied to the bottom water, as for marine systems (Table 1, Figure 5), the scavenging process will be less effective (Figure 6). This will affect the cycling of phosphorus. Studies in freshwater systems have shown that the scavenging of phosphorus by precipitating ferric oxohydroxides can effectively prevent phosphorus from entering the euphotic surface layer of the water body (Tessenow 1975; Mayer et al. 1982; Gallagher 1985; Ellis-Evans & Lemon 1989). Our data indicate that the marine systems, after a positive redox-turnover, tend to show higher concentrations of dissolved phosphorus (Figures 3 and 4). This finding is of particular interest in connection with reports that phosphorus immobilization in sediments with overlaying oxic water is less effective in coastal marine and brackish systems than in freshwater lakes (Caraco et al. 1990). Together, these findings suggest enhanced availability of phosphate in marine and brackish water as a contributory explanation of why, in contrast to lakes, the net primary production of coastal marine environments in the temperate zone today is usually limited by nitrogen (Caraco 1988; Hecky & Kilham 1988; Howarth 1988; Källqvist 1988; Vitousek & Howarth 1991). Also, differences in the benthic conditions may help to explain reported variations in limiting nutrients within a single sea area, such as the Baltic (Larsson 1988; Granéli et al. 1990). Reduction of organic supply in marine areas which are limited by nitrogen might result in potentially higher sedimentary Fe/P release ratios, and then favour a shift to phosphorus limitation (cf. Howarth et al. 1995), unless compensatory changes in nitrogen cycling occur simultaneously.

Concluding remarks

The comparative approach employed in the present study provides experimental evidence that there are clear differences in the exchange of phosphate across the sediment-water interface of freshwater and marine environments during positive redox-turnover. The marine systems reach lower Fe/P release ratios in the dissolved phase during anoxic conditions, due to a shortage of dissolved iron in the sulphide rich marine environment. The dissolved Fe/P ratio before a positive redox-turnover controls the phosphorus scavenging capacity of the particulate ferric oxohydroxide rapidly formed at the onset of oxic conditions. Marine waters tend to show higher remaining concentrations of dissolved phosphorus after a positive redox-turnover than freshwaters. Manganese was not found to interact significantly with iron or phosphate.

The ecological implications of our findings warrant further studies on this biogeochemical topic.

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