

Why the limiting nutrient differs between temperate coastal seas and freshwater lakes: A matter of salt

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Abstract

Comparison of bottom-water chemistry in the marine–limnic habitat gradient shows greater phosphorus availability in marine waters, primarily because of enhanced iron sequestration by sulfide. In the oxidative hydrolysis of iron and the concomitant precipitation of phosphate, a minimum of two iron atoms are needed to precipitate one phosphate molecule (Fe:P = 2). However, dissolved Fe:P < 2 predominates in anoxic marine waters, therefore leaving some phosphate in solution after oxygenation because of a shortage of dissolved iron for phosphate coprecipitation by iron oxyhydroxide. In contrast, anoxic bottom waters in most freshwater lakes show Fe:P > 2, allowing almost complete phosphate removal on oxygenation. This difference is a consequence of the high sulfate content of sea salt, and a main reason why nitrogen normally limits net primary production in temperate coastal waters, in contrast to the predominant phosphorus limitation of near-neutral lakes.

Phytoplankton biomass in near-neutral freshwater lakes is often phosphorus-limited, whereas nitrogen is commonly the limiting macronutrient in temperate coastal seas (Ryther and Dunstan 1971; Schindler 1977; Hecky and Kilham 1988). This contrast is fundamental for understanding production dynamics in these ecosystems and when taking action to combat eutrophication. Previously, this disparity has been explained mainly by differences between habitats in the cycling of nitrogen (Schindler 1981; Howarth et al. 1988, 1999; Vitousek and Howarth 1991). Higher rates of nitrogen fixation in freshwater lakes (Howarth et al. 1988) and larger nitrogen recycling losses (including denitrification) in shallow marine ecosystems (Nixon 1981; Schindler 1981) have been invoked as biogeochemical mechanisms. Both of these mechanisms predict a tendency toward nitrogen deficiency in coastal marine systems. However, a greater supply of phosphorus in coastal marine areas, or a relative depletion of bioavailable phosphorus in freshwater lakes, will also contribute to this difference in nutrient limitation (Caraco et al. 1990; Gunnars and Blomqvist 1997).

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The transformation of dissolved phosphate into particulate form (biological uptake, chemical precipitation, and adsorption) is a critical process for understanding phosphorus concentrations in natural waters (Nedwell et al. 1999; Benitez-Nelson 2000; Reynolds and Davies 2001). The stoichiometric Fe:P ratio can govern the efficiency of phosphate precipitation in waters subjected to a shift from anoxic to oxic conditions (Gunnars and Blomqvist 1997; Gunnars et al. 2002), such as bottom and pore waters. The ecological relevance of this ratio has not been evaluated thoroughly for a wide range of aquatic habitats. The most extensive published data evaluation reported a negative relationship between the bottom-water Fe:P ratio and the surface-water sulfate concentration from 51 seasonally anoxic freshwater lakes in North America (Caraco et al. 1993). Here, we present data on a biogeochemical mechanism tied to salinity, which makes phosphorus more available in coastal marine waters than in freshwater systems and, hence, promotes marine nitrogen limitation. We have focused our analysis on coastal marine and near-neutral limnic environments (pH 6–8) and therefore exclude freshwater lakes with acidic water or calcareous sediments and likewise leave out most tropical environments. In the tropics, as well as in calcareous lakes, sequestering by carbonate is often a significant control on the cycling of phosphorus (Howarth et al. 1995; Wetzel 2001).

We report results from critical experiments, water column measurements, and a comparison of dissolved molar Fe:P ratios from a wide range of marine and freshwater anoxic bottom waters, which taken together, explain why net primary production is usually limited by phosphorus in freshwater habitats but by nitrogen in the temperate coastal marine zone, except for low-salinity estuarine waters, which

likewise often appear phosphorus-limited (e.g., Myers and Iverson 1981; Caraco 1988; Andersson et al. 1996).

Materials and methods

Our field sampling was conducted in the brackish north-western Baltic Sea proper and the adjoining freshwater Lake Mälaren of Sweden, which offer favorable opportunities for comparative studies of brackish marine and limnic conditions. We incubated natural sediment cores with supernatant water (Gunnars and Blomqvist 1997; Isaksson 1997) and carboys with water (Gunnars et al. 2002) and followed the scavenging of phosphate during oxidative hydrolysis of Fe(II) after oxygenation of anoxic water by gentle bubbling with air. The natural concentration of dissolved iron and phosphate in the sampled water varied, and further variation was caused by differences in benthic release from anoxic sediments in the core incubations. In some cases, we added Fe(II) to study the effect of the initial Fe:P ratio on phosphate scavenging. All experiments were run in the dark at 6–9°C, approximating the deep water in our study areas. Acid-washed equipment and reagent-grade chemicals were used. Further details on the study areas, field sampling procedures, and experimental design are given elsewhere (Gunnars and Blomqvist 1997; Isaksson 1997; Gunnars et al. 2002).

The salinity (S = practical salinity scale) was 4–6 in samples from the Baltic and <0.05 from Lake Mälaren, and all had near-neutral pH (7.3–8.1). In addition, the salinity of some water samples was adjusted by adding artificial seawater salt (i.e., salinity of water from Lake Mälaren was increased to 6 and Baltic seawater to 15 and 33; Gunnars et al. 2002).

Wet chemical analyses—Dissolved and particulate phosphate and iron species were defined by serial membrane filtration (0.45- and 0.2- μm Millipore filters), ultracentrifugation ($100,000 \times g$, 15 min), or dialysis (molecular mass cutoff, 100,000). Phosphate was analyzed according to Koroleff (1983a), whereas samples for iron determination (preserved with 1 μl of concentrated HNO_3 ml^{-1}) were read by inductively coupled plasma atomic emission spectrometry, following the modified Swedish Environmental Protection Agency method 200.7 or, alternatively, colorimetrically following Koroleff (1983b). Particulate fractions were calculated as the difference between total and dissolved concentrations. Oxygen concentration was determined by Winkler titration or with an electrode oxygen meter (YSI 54A or WTW Oxi 320) calibrated against water-saturated air at the experimental temperature. Salinity and pH were measured with electrodes (YSI 33 S-C-T-meter and WTW pH 95 or WTW pH 320, respectively). National Bureau of Standards buffer solutions were used to calibrate the pH instruments.

Scanning electron microscopy—Particles were collected on 0.2- μm Nuclepore filters and analyzed with a Jeol 880 scanning electron microscope (SEM) equipped with a Link 5929 energy-dispersive spectrometer (EDS; acceleration voltages 15 and 20 kV) for study of elemental composition of the precipitated matter.

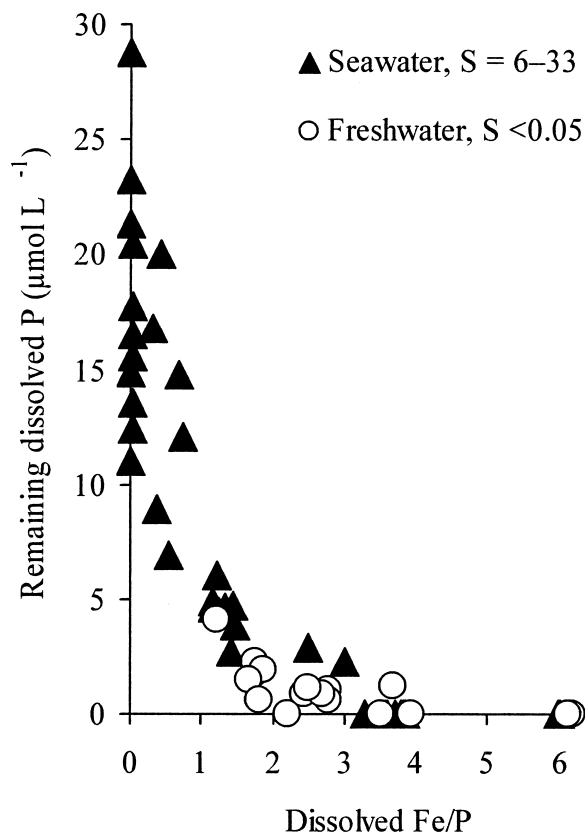


Fig. 1. Experimental oxygenation of anoxic water, showing that little phosphate remains available for plant production after air bubbling of water with an initial dissolved molar ratio of Fe:P > 2, irrespective of salinity. For Fe:P < 2, the efficiency of the dissolved phosphate removal is related to the relative proportion of Fe(II) present. Data are from incubations of cores of natural sediment, with overlying freshwater from Lake Mälaren and brackish water from the adjoining Baltic Sea proper, and from carboy water systems of these water areas.

Results and discussion

With a salinity range of 0–33, our experiments (Fig. 1) demonstrate that the dissolved Fe:P ratio is a critical control on the precipitation of phosphate in waters subjected to a shift from anoxic to oxic conditions. In systems with an initial Fe:P > 2, dissolved phosphate is efficiently bound into particulate form and removed (residual $\text{P} < 1 \mu\text{mol L}^{-1}$ in most cases), whereas the precipitation of phosphate is incomplete at Fe:P < 2, regardless of salinity (Fig. 1). These findings are consistent with the formation of a discrete iron-phosphate phase with a lower limiting Fe:P stoichiometry close to 2 (Gunnars et al. 2002). A likely mechanism is that complexation with phosphate at an early stage of iron hydrolysis (Rose et al. 1996, 1997) generates basic subunits consisting of one iron dimer and one phosphate molecule (i.e., Fe:P = 2), which subsequently aggregate into larger entities of Fe(III) oxyhydroxide phosphate (Maison et al. 1997a,b).

The formation of an iron-phosphate phase when dissolved Fe(II) is oxidized is illustrated by in situ chemical depth

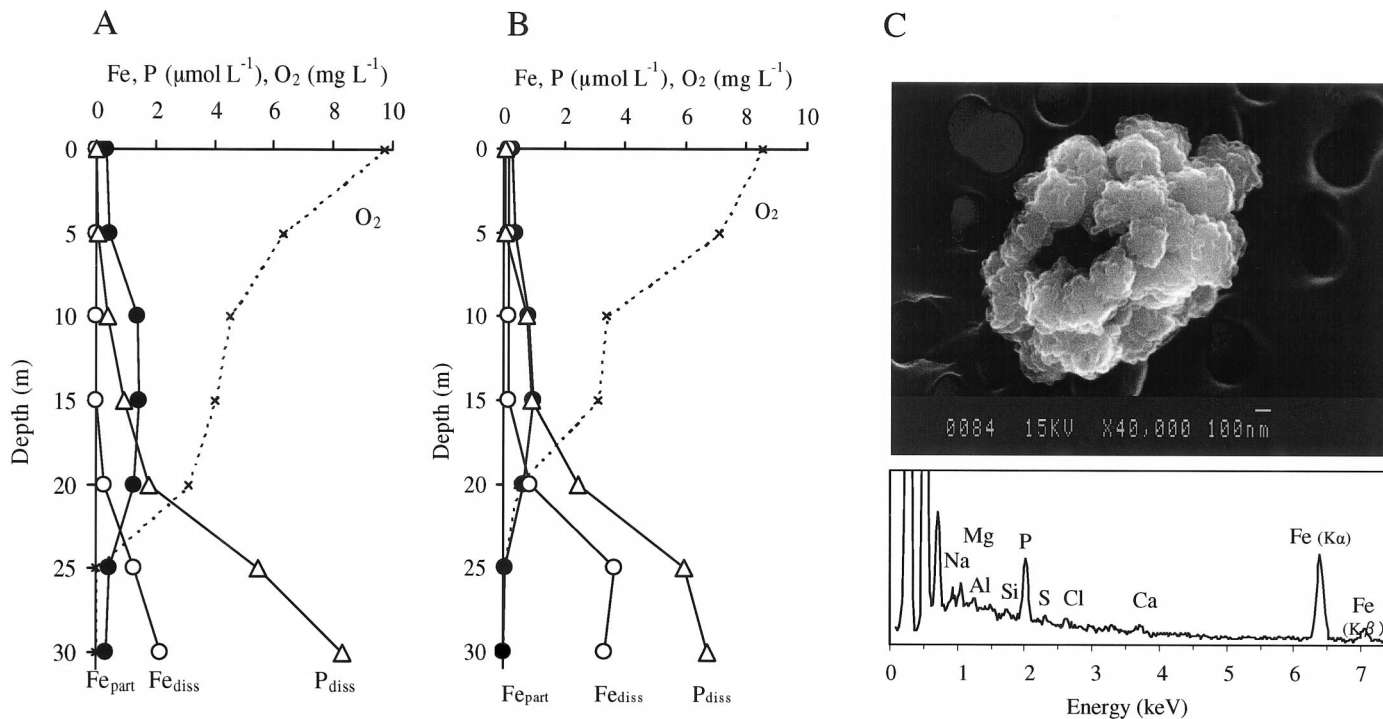


Fig. 2. (A, B) Evidence of vertical transport of dissolved iron and phosphate from anoxic bottom water of Fe:P < 2 upward into a suboxic water column, where particulate iron oxyhydroxide precipitates some phosphate, allowing the rest to reach the upper oxic layer. These vertical concentration profiles were collected in the brackish ($S = 4\text{--}6$) Hallsfjärden Bay (Sta. H7: $59^{\circ}07'12''\text{N}$, $17^{\circ}41'42''\text{E}$), north-western Baltic Sea proper, on (A) 13 August 1998 and (B) 5 August 1999. (C) Scanning electron micrograph and elemental composition of a colloidal iron-phosphate particle, apparently formed through oxygenation at the oxic–anoxic boundary, in Hallsfjärden Bay collected 5 August 1999 at 25 m depth and retained on a $0.2\text{-}\mu\text{m}$ Nuclepore filter. Scale bar = 100 nm. Lower panel shows EDS spectra of the particle, demonstrating the presence of phosphorus and iron.

profiles (Fig. 2) from the water column of Hallsfjärden Bay in the Baltic. These are a natural analog of our experimental oxygen incubations, with an additional photosynthetic sink for phosphate. The profiles show that the concentration of dissolved iron present in this brackish water is not sufficient to sequester completely the dissolved phosphate, some of which escapes precipitation at the oxic–anoxic boundary. A significant fraction of the dissolved phosphate released from soft bottom sediments can thus be mixed up into the overlying oxic water and can reach primary producers in the euphotic zone of coastal marine systems. This is in contrast to chemical depth profiles from freshwater lakes with anoxic water, in which phosphate is generally almost completely precipitated by iron before reaching the oxic upper mixed layer (Sholkovitz and Copeland 1982; Gallagher 1985; Stauffer and Armstrong 1986).

Data from the literature on the dissolved Fe:P molar ratio in anoxic bottom waters of a wide range of marine and near-neutral freshwater environments show a systematic salinity-related trend (Fig. 3). Water samples of marine origin all have Fe:P < 2, whereas most freshwater lakes have Fe:P > 2, suggesting why the immobilization of phosphate (Fig. 1) on oxygenation is more effective in freshwater. Moreover, within each of these two main groups, the Fe:P ratios cluster further into two subgroups. Fe:P < 0.1 are mostly from persistently anoxic marine basins, whereas most coastal ma-

rine stations (predominantly Baltic records) fall in the Fe:P = 0.1–2 range. Three exceptions in the latter range were from eutrophic freshwater lakes (Lake Sampach, 1.2; Amos Lake, 0.7; Lake Lugano, 0.3). In eutrophic and mesotrophic freshwater lakes, Fe:P = 2–5 are typical, whereas Fe:P > 10 predominate in the bottom waters of oligotrophic lakes, indicating a negative relationship between lake trophic status and the Fe:P ratio. The Fe:P ratio of 265 from the eutrophic freshwater lake Esthwaite Water in 1940 (Mortimer 1942) deviates from this overall trend, but with further eutrophication, the ratio had fallen to 11 (Fig. 3, arrow) by 1972 (Heaney et al. 1986), further confirming the inverse relationship.

The Fe:P ratio can be influenced by changes in availability of both iron and phosphorus (Fig. 3). However, our cross-system comparison shows that systematic marine–freshwater variation in Fe:P ratios appears to be related primarily to large differences found in the concentration of iron. In fact, records of dissolved iron under anoxic conditions tend to separate into a marine cluster with low concentrations and a freshwater cluster of high concentrations (Fig. 4A), whereas no such pattern is found for phosphorus (Fig. 4B). In addition, the range in dissolved concentration is much wider for iron (six orders of magnitude) than for phosphorus (four orders of magnitude).

This marine–freshwater trend in iron availability (Fig. 4A)

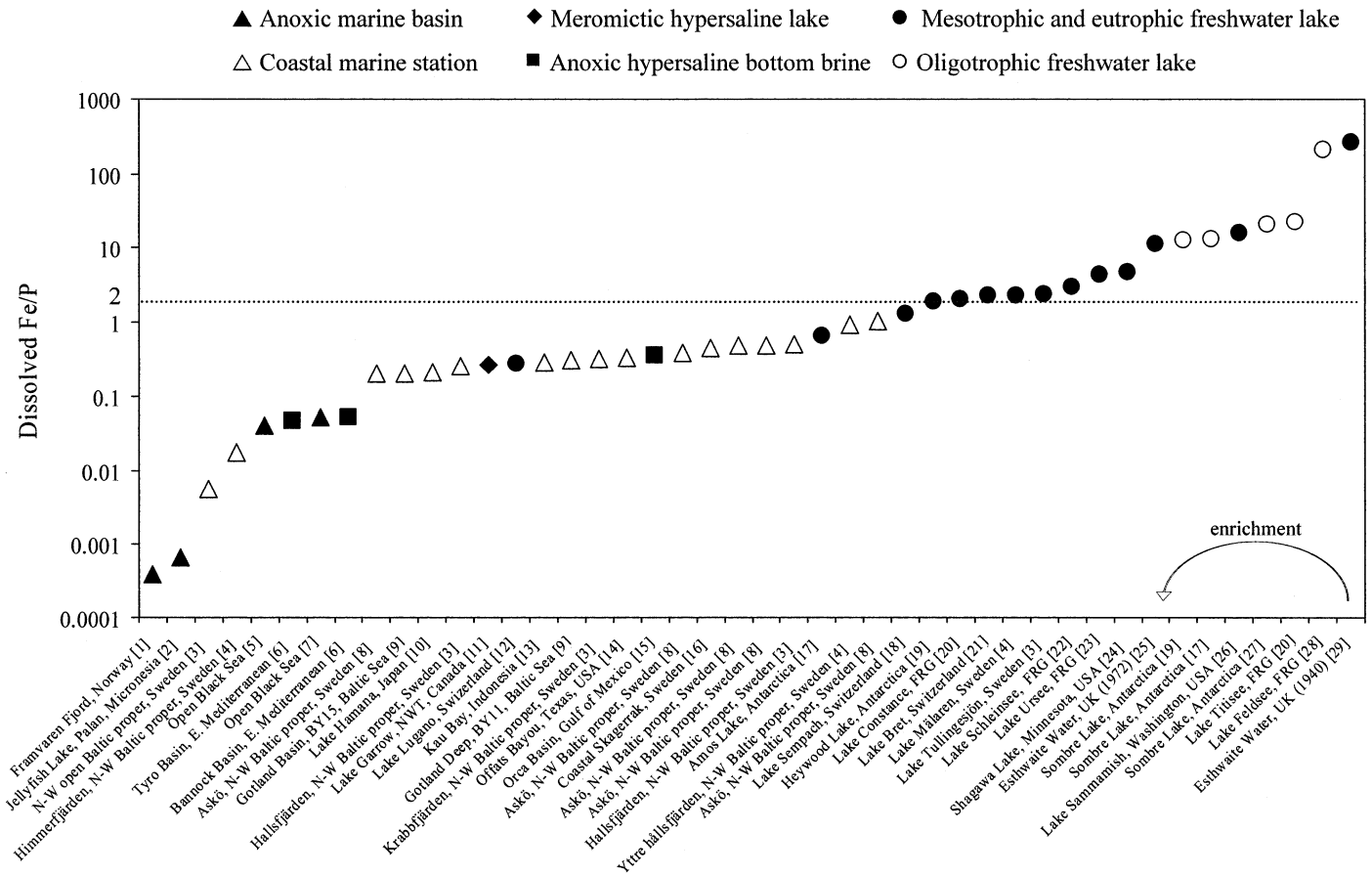


Fig. 3. Diagram showing dissolved molar Fe:P ratios in anoxic bottom waters of a wide range of marine–saline systems (squares, triangles, and diamonds) and near-neutral (pH 6–8) freshwater lakes (circles); acid and calcareous lakes have been excluded. Arrow describes change in Fe:P ratio following nutrient enrichment of lake Esthwaite Water from 1940 to 1972 (Mortimer 1942; Heaney et al. 1986). For sources 1–29, see Web Appendix 1 at http://www.aslo.org/lo/toc/vol49/issue_6/2236a1.pdf.

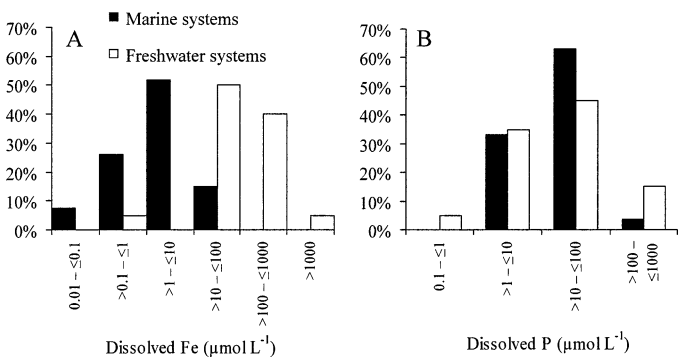


Fig. 4. Distributions of dissolved concentration of (A) iron and (B) phosphate in the anoxic bottom waters represented in Fig. 3. The concentrations of dissolved iron (A) are typically $\leq 10 \mu\text{mol L}^{-1}$ in marine systems and $> 10 \mu\text{mol L}^{-1}$ in freshwater, and these distributions are separated statistically ($p < 0.00003$), whereas the concentrations of dissolved phosphate (B) are more evenly distributed, and do not differ significantly ($p > 0.4$) across the marine–freshwater spectrum (Mann–Whitney U -tests: $U_{\text{Fe}} = 517$ and $U_{\text{P}} = 265$, $n_{\text{lake}} = 20$ and $n_{\text{sea}} = 27$).

is related to the supply of sulfide (Fig. 5), which precipitates Fe(II) as sulfides (Morse et al. 1987). The sulfide needed in this reaction is readily formed from sulfate by bacterial reduction under anaerobic conditions (Postgate 1984). Sulfate is a major constituent of sea salt (Wilson 1975) and is found

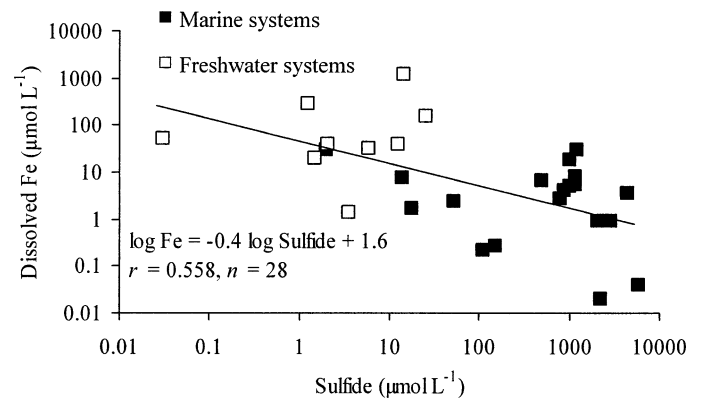


Fig. 5. Negative log-log correlation between the concentrations of dissolved iron versus sulfide in anoxic bottom waters represented in Fig. 3.

in seawater at 100–1,000 times higher dissolved concentrations than in freshwater (Livingstone 1963; Urban 1994). Anoxic marine bottom and pore waters therefore have a richer supply of sulfide than corresponding freshwater environments (Capone and Kiene 1988). Furthermore, eutrophic freshwater lakes have a richer supply of sulfide than oligotrophic lakes (Holmer and Storkholm 2001). The stronger iron sequestration by sulfide in marine environments compared with limnic systems (Gerritse 1999) and in eutrophic freshwater lakes compared with oligotrophic ones (Holmer and Storkholm 2001) reduces the Fe:P ratio and hence the capacity for removal of phosphate. Thus, because of the lower Fe:P ratio (Fig. 3), more phosphate tends to remain dissolved after oxygenation (Fig. 1) in coastal marine environments than in lakes (Fig. 2). In freshwater, a tendency toward lower Fe:P ratios is seen in eutrophic lakes (Fig. 3).

The idea of a disparity in the availability of phosphate between freshwaters and coastal marine waters is further supported by empirical records of lower phosphorus immobilization in marine sediments with overlying oxic water, and hence a proportionally greater release of phosphorus than in corresponding freshwater sediments (Caraco et al. 1990). Likewise, experimental studies simulating estuarine mixing have reported conservative chemical behavior of dissolved phosphate, or only limited removal, because of a shortage of iron (Smith and Longmore 1980). A further increase in the availability of phosphate in marine environments might be caused by a more rapid coagulation and deposition of iron-rich colloids in seawater than in freshwater (Gunnars et al. 2002), giving a shorter exposure time for surface adsorption of phosphate.

The contrast between predominant limitation by nitrogen in temperate marine waters and by phosphorus in near-neutral freshwaters appears to be reinforced by differences in the phosphorus requirements of their metazoan zooplankton. The particularly low N:P ratio of the herbivorous cladocerans, which are often dominant in freshwater lakes (Wetzel 2001), might accentuate lake phosphorus limitation by selectively sequestering this element in zooplankton biomass (Elser and Hassett 1994). Differences in feeding and excretion mechanisms might also influence the availability of nitrogen. Unlike cladocerans, the copepods, which often dominate marine neritic zooplankton biomass (Longhurst 1985), tend to feed selectively on nitrogen-rich food (Cowles 1989) and produce pellets that rapidly sink out of the euphotic zone (Turner 2002), thus depleting the water mass of nitrogen and reinforcing phytoplankton nitrogen limitation, a mechanism that should be more significant in deeper waters.

There are essential differences between marine and freshwater ecosystems also in the primarily biologically regulated nitrogen cycle. Two main circumstances could reduce nitrogen availability in coastal seas (*see also* NRC 2000): namely, lower cyanobacterial nitrogen fixation (e.g., through inhibition by sulfate in seawater; Howarth and Cole 1985; Stal et al. 1999; Marino et al. 2002, 2003) and higher absolute rates of denitrification in nearshore marine and estuarine systems (Seitzinger 1990), leading to a higher ratio of denitrification to nitrogen fixation in coastal marine areas than in freshwater lakes (Seitzinger 1988). That these circumstances are less

prevalent in near-neutral freshwater lakes is also a factor strengthening their phosphorus limitation.

We report observations of several types, all of which indicate that phosphate is more available in coastal marine waters than in freshwater. This fundamental, salinity-dependent difference in phosphorus availability promotes nitrogen limitation in coastal seas, unlike in freshwater lakes and in dilute estuarine waters, where phosphorus is normally the primary limiting macronutrient. These natural tendencies can, of course, be modified locally by anthropogenic loads or special circumstances. The divergence in phosphorus availability is basically an effect of the sulfate content of sea salt, which results in more extensive sequestering of iron by sulfides, and therefore less efficient coprecipitation of phosphate by iron oxyhydroxide in marine systems, a mechanism first proposed by Caraco et al. (1989) from studies in lakes of varying sulfate concentrations. These findings make it clear that measures to mitigate the effects of nutrient enrichment might have to differ between freshwater and coastal marine environments.

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