

NOTES

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Why the phosphorus retention of lakes does not necessarily depend on the oxygen supply to their sediment surface

Abstract—In order to improve the trophic state of Lake Sempach, a eutrophied lake in central Switzerland, its external phosphorus (P) load has been decreased and its hypolimnion has been artificially oxygenated to lower the lake-internal P recycling. Based on more than 15 yr of experience, we conclude that the reduction of the external P load resulted in a corresponding decrease of the lake's P concentration. However, contrary to initial expectations, increased hypolimnetic dissolved oxygen concentrations neither (1) reduced the P release from sediments during summer nor (2) resulted in an increased permanent P retention. These observations warrant a reevaluation of the well-accepted management strategy of decreasing the lake internal P cycling by maintaining an aerobic hypolimnion and sediment surface. We hypothesize that oxygenation only results in an increased permanent benthic P burial if, because of the depressed sulfide production, more ferrous phosphate (e.g., vivianite) and less FeS is deposited in the anoxic sediment. Hence, it is not the oxic sediment surface that directly affects the permanent redox-dependent sediment P retention but the molar ratio of the available reactive Fe(II): S²⁻:PO₄ in the anoxic sediment. This ratio is driven by the settling rate and the nature of organic matter and particulate iron, as well as the supply of oxygen, nitrate, and sulfate to the sediment.

It is well known and generally accepted that oxic lake sediments retain phosphorus (P) more efficiently than anoxic sediments; that is, formerly oxic sediments release vast amounts of phosphate when they become anoxic. Based on such observations, Einsele (1936a) and Mortimer (1941, 1971) developed the classical concept of the coupled cycling of iron (Fe) and P. According to that concept, under oxic conditions and at about neutral pH, iron precipitates as a trivalent iron oxyhydroxide that has a large capacity to coprecipitate and/or adsorb phosphate. Under anoxic conditions, the reductive dissolution of the solid Fe(III) oxyhydroxide results in a parallel dissolution of the previously bound phosphate. More recently, it has been proposed that benthic bacteria can supplement this abiotic redox-dependent fixation and release of P (Gächter and Meyer 1993; Hupfer et al. 1995). In the presence of O₂, some facultative aerobic bacteria deposit P as polyphosphate in their cells but release it as ortho-P under anoxic conditions. Advanced wastewater treatment technology profits from both processes to enhance P removal from wastewater.

At first glance, this traditional concept of aquatic sediment P biogeochemistry suggests lower P release rates from the sediment and hence lower P concentrations in the water column, provided that oxic conditions are permanently main-

tained at the sediment surface. However, based on their experience with artificial hypolimnetic oxygenation of Lake Sempach for more than 15 yr, Gächter and Wehrli (1998) concluded that artificial maintenance of oxic conditions in the hypolimnion did not affect P cycling at the sediment-water interface (Fig. 1). These results obtained from long-term, large-scale experiments, as well as considerable older literature showing that anoxia does not necessarily result in P release from sediments (e.g., Schindler et al. 1973, 1977; Levine et al. 1986), suggest that a modified concept of the redox-controlled P retention in lake sediments is needed.

To our knowledge, Einsele (1936a) was the first to describe an interesting relation between the iron and P cycles in eutrophic lakes. In essence, ferrous iron (Fe²⁺) and phosphate accumulate simultaneously in the anoxic hypolimnion during stagnation periods. However, during the next turnover (when O₂ is introduced) a “ferric phosphate” is precipitated. According to Tessenow (1974) and Gunnars et al. (2002) this “ferric phosphate” is a Fe(III) oxyhydroxide that coprecipitates phosphate. The minimum molar stoichiometric Fe:P ratio of this solid is about 2. Thus, if in the anoxic hypolimnion the ratio Fe²⁺/(HPO₄²⁻ + H₂PO₄⁻) ≥ 2, Fe as well as phosphate precipitate nearly quantitatively after a sufficient amount of O₂ is introduced to oxidize and precipitate all the iron. If the ratio Fe²⁺/(HPO₄²⁻ + H₂PO₄⁻) < 2, the excess phosphate remains in solution (Gunnars et al. 2002).

In Mortimer's (1941, 1971) classic laboratory experiments on Fe and P cycling in water-sediment systems, sedimentation of organic material was stopped and the sediment overlying water was maintained permanently oxic. Under these conditions, ferric (hydr)oxides formed in the uppermost sediment and trapped the P. If a eutrophic lake behaved similarly, similar processes should occur at its sediment-water interface. However, as sketched in Fig. 2, real lakes differ from such laboratory experiments because the oxic sediment surface at any specified time will eventually be buried by settling material. Thus, during further anoxic diagenesis, the precipitated “ferric phosphate” will be reduced in the buried sediment. Contrary to the situation at the anoxic sediment surface, the resulting Fe²⁺ and HPO₄²⁻/H₂PO₄⁻ ions will not be diluted quickly into a vast hypolimnion. The newly formed concentration maximum in the pore-water profile causes P and Fe(II) to diffuse in the sediment upward, downward, or both according to the respective concentration gradients. In such a narrow production zone of Fe²⁺ and HPO₄²⁻/H₂PO₄⁻, the solubility product of a ferrous phosphate can be exceeded, leading to the precipi-

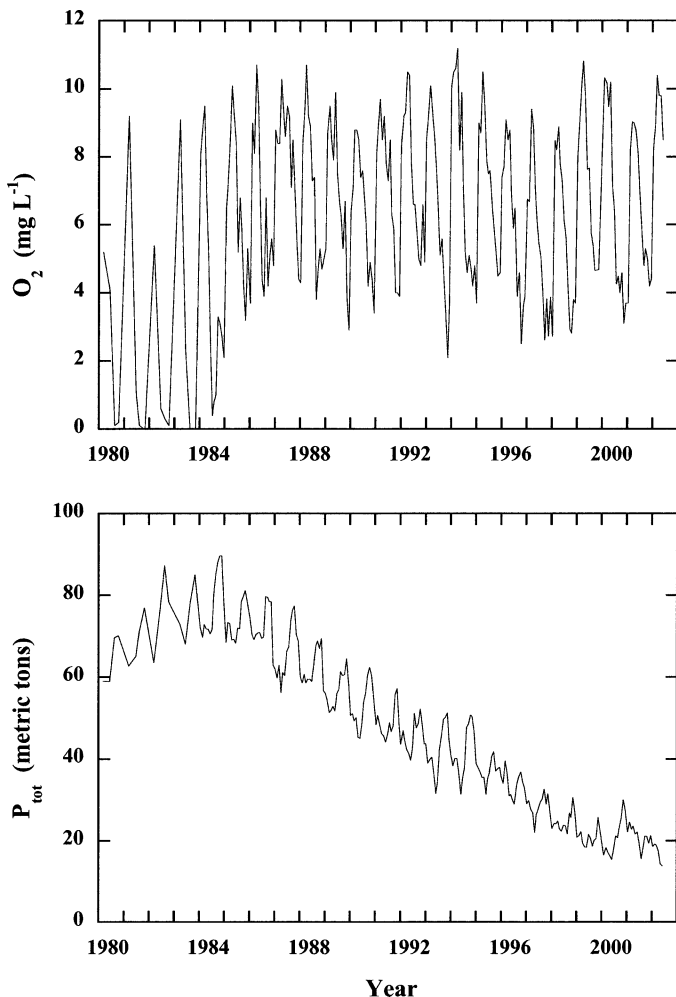


Fig. 1. Seasonal variation of dissolved oxygen concentration close to the lake bottom (sampling depth 85 m) and changes of the hypolimnetic ($z > 20$ m) P content in Lake Sempach (according to Ernst Butscher unpubl. data).

tation of, for example, vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (Tessenow 1974; Emerson and Widmer 1978; Manning et al. 1999). If the redox potential decreases further and sulfate reduction eventually occurs, part of the Fe^{2+} accumulated in the pore water precipitates as FeS. Because at lower Fe^{2+} concentrations, higher PO_4^{3-} concentrations are required to exceed the solubility product of vivianite, sulfate reduction results in a concomitant dissolution of vivianite (Eq. 1). As a result, the higher phosphate concentration in the sediment pore water enhances the diffusive phosphate efflux out of the sediment.



In natural lake sediments, this reaction is irreversible because the dissolved PO_4 diffuses toward the sediment surface, whereas the iron remains seized in the anoxic sediment as FeS that can convert into pyrite (FeS_2) during further diagenesis (Berner 1970; Peiffer 1994). FeS and FeS_2 are terminal sinks for Fe in sulfidic sediments because (1) at their low, solubility products Fe^{2+} equilibrium concentrations are too low to allow steep Fe(II) concentration gradients in the

sediment and hence considerable dissolution and (2) oxygenation of Fe(II) to Fe(III), the rate limiting step of pyrite oxidation, a surface-controlled reaction mediated by dissolved Fe(III) (Luther 1990), does not occur in sulfidic sediments. Consequently, Fe is permanently removed as a reactive partner from the Fe-P-S system. Because sulfide does not only reduce Fe(III) oxyhydroxide (Peiffer 1994) but also precipitates Fe^{2+} as FeS, it lowers the availability of iron to bind P either in a ferric or a ferrous solid. Thus, diagenetic sulfate reduction and subsequent formation of FeS might decrease the permanent burial of P in lake sediments and accelerate eutrophication as suggested by, for example, Einsele (1936b), Mortimer (1941), Hasler and Einsele (1948), Ohle (1954), Curtis (1991), Caraco et al. (1993), Smolders and Roelofs (1993), Goltermann (1995), Giordani et al. (1996), and Roden and Edmonds (1997).

Because in eutrophic lakes the benthic diagenesis of the settled material is not completed within the uppermost oxic sediment layer, we assume conceptually that after burial of a formerly oxic sediment surface, phosphates recycled from the remaining organic matter and released from reductively dissolved ferric phosphates precipitate first as a solid ferrous phosphate (e.g., vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$]), whereas excess Fe(II) can precipitate in alkaline, eutrophic lake sediments as a $(\text{Ca}_x\text{Fe}_{1-x})\text{CO}_3$ species (Spadini et al. pers. comm). If, as a consequence of additional burial, the redox potential decreases further to allow sulfate reduction, then FeS will precipitate as an additional Fe(II) mineral.

For the sake of an example, we will assume that, in the anoxic but not yet sulfidogenic layer, vivianite is the only iron mineral. Based on the solubility product of vivianite ($\log K_{s_0} = 36$), total dissolved phosphate and Fe(II) concentrations in the pore water at pH 7 is $1.02 \times 10^{-5} \text{ mol L}^{-1}$ and $1.53 \times 10^{-5} \text{ mol L}^{-1}$, respectively. If vivianite and a Fe(II) carbonate mineral (e.g. siderite) coexisted, then because of the higher solubility of the siderite ($\log K_{s_0} = 10.9$), the equilibrium concentration of Fe(II) would increase to $1.87 \times 10^{-4} \text{ mol L}^{-1}$ and the total inorganic phosphate concentration would decrease to $3.12 \times 10^{-7} \text{ mol L}^{-1}$. Hence, if in the anoxic sediment the Fe:P ratio exceeds 3:2 and sulfide formation does not occur, then an increase in the dissolved iron concentration further depresses the concentration of dissolved inorganic phosphate. Therefore, it is likely that in lake sediments, the permanent P retention increases with an increasing Fe:P ratio of the settling material.

If we allow sulfate reduction to occur, the siderite, having a higher Fe(II) solubility than vivianite protects the vivianite from being attacked by the sulfide (Fig. 2); that is, the sulfide reacts preferentially with the siderite to form FeS and carbonic acid, as indicated in Eq. 2



and does not lead to phosphate dissolution (Eq. 1). Only after all siderite is transformed into FeS will each additional mole of generated sulfide result in the dissolution of 0.67 mole of phosphate (Eq. 1). When eventually all vivianite is converted into FeS, phosphate dissolution stops and H_2S starts to accumulate in the pore water.

Organic matter deposited at an oxic sediment surface and then buried in anoxic layers is sequentially decomposed by

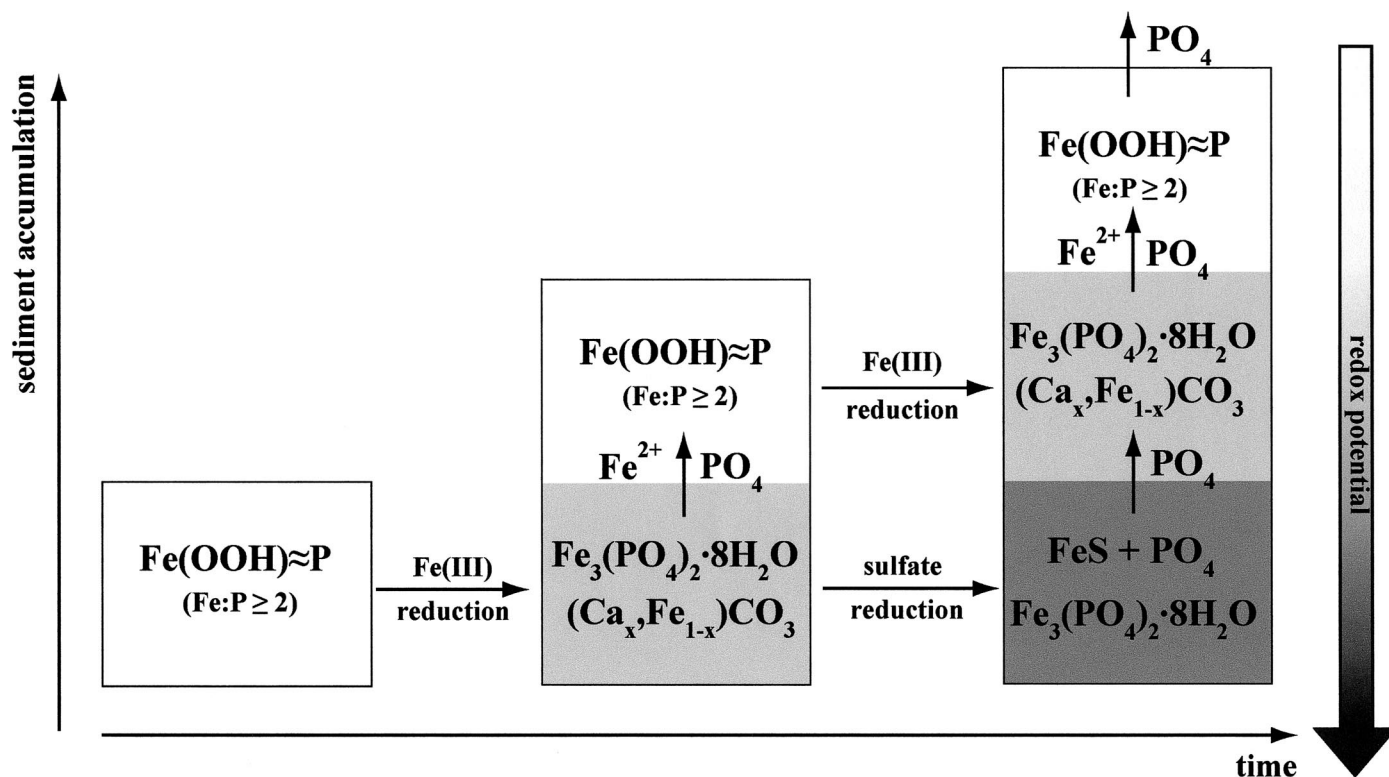


Fig. 2. Dynamic concept of redox-dependent P retention in lake sediments. An average one-dimensional redox gradient is sketched, although on a microscale (i.e., within microzones), the local redox potential might deviate from this average.

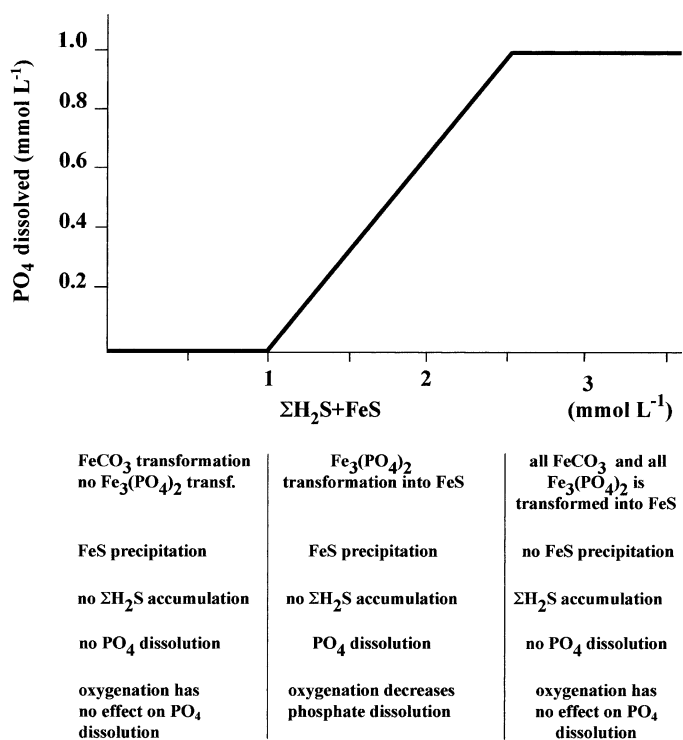


Fig. 3. Titration of a model pore water containing 1 mmol L⁻¹ FeCO₃ (solid) and 0.5 mmol L⁻¹ Fe₃(PO₄)₂·8H₂O (solid) with H₂S at pH 7 in a 1 mmol L⁻¹ solution of CaCO₃ + Ca(HCO₃)₂. ΣH₂S is used for total dissolved reduced S.

a variety of oxidation processes using O₂, NO₃⁻, Mn(IV)/(III), Fe(III), and SO₄²⁻ as inorganic oxidizing agents. The remaining, nonrefractory organic matter is then further decomposed by fermentation to CO₂ and methane (CH₄) that diffuses upward, where the CH₄ eventually will be oxidized by methanotrophs to CO₂. Hence, very likely at a given settling rate of organic material to the sediment, an increased availability of O₂ will result in a decreased sulfate reduction rate. However, as illustrated in Fig. 3, this does not necessarily imply an increased permanent P burial rate: Increased O₂ availability (less sulfide production) has no effect on P retention as long as (1) the remaining sulfide production rate still exceeds the production rate of reactive Fe(II); that is, all reactive Fe(II) precipitates as FeS, and excess dissolved sulfide accumulates in the pore water, and (2) the previous sulfide production rate still permits the formation of siderite; that is, the formation of vivianite is limited by the availability of P but not by the availability of Fe(II). Positively expressed, depressed sulfide production can only lead to an increased permanent P retention in the sediment if more vivianite and less FeS is produced; that is, if prior to oxygenation, the vivianite formation is limited by the availability of reactive Fe(II).

Scientists tend to simplify nature to the extent that they can describe complex processes with simple conceptual models. Thus, although the model sketched in Fig. 3 assumes that in sulfate-reducing sediments the three well-defined minerals vivianite, siderite, and FeS control the concentration of P and Fe(II) in the pore water, the existence of

exactly these mineral phases in sediments is not an absolute necessity. In principle, vivianite can be replaced by any solid ferrous phosphate, and siderite can be substituted by any ferrous mineral as long as the Fe solubility of the latter exceeds that of the ferrous phosphate. The model then still qualitatively explains why, depending on the ratio of reactive Fe to reactive P and the sulfide production, that (1) anoxia does not necessarily result in benthic P release in lakes with high iron but low sulfate concentration, (2) increased gross sedimentation of reactive iron might increase its P retention, (3) increased sulfide production could induce increased P release, and (4) artificial oxygenation might or might not increase P retention.

Vivianite as well as Fe(III) oxyhydroxides found in recent anoxic sediments indicate that transformation of these components to FeS are slow or that sediments are strongly heterogeneous systems. Because the suggested redox model is one-dimensional and based on thermodynamic equilibria, it cannot explain such patchy or sluggish reactions. However, dissolution and transformation kinetics, as well as possible less stable precursor precipitates of vivianite, have not been considered because (1) such data are not yet available and (2) in geological timescales, thermodynamic equilibria will eventually be attained.

Oxic formation and reductive dissolution of Fe(III) oxyhydroxide enriched with phosphate are reversible processes as long as all Fe and P resulting from reductive dissolution remain in solution. If, however, in anoxic sediment layers, because of a high demand for electron acceptors, sulfate reduction occurs, the resulting sulfide (S^{2-}) can dissolve ferrous phosphates and precipitate the Fe(II) as iron sulfide (FeS). Hence, FeS formation could increase the phosphate concentration and prevent association of Fe^{2+} with phosphate in the anoxic sediment pore water: Because the Fe(II) is blocked as solid FeS in the sulfidic layer, it is no longer available for eventual reoxidation and entrapment of the migrating phosphate.

Thus, in eutrophic lakes, the ultimate release of P from sediments does not only depend on hypolimnetic dissolved oxygen concentration, but on the balance between the gross sedimentation of organic matter, P, Fe, and the sulfide production driven by diagenetic processes in the sediment. As indicated in Fig. 3, hypolimnetic oxygenation has only a positive effect on the benthic P retention if, because of a depressed sulfide production, less solid ferrous phosphates are transformed into solid FeS.

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Nutrient limitation on a planktonic rotifer: Life history consequences and starvation resistance

Abstract—Nutrient content of plants is low relative to that of herbivores. Dietary nutrients can limit the growth and reproduction of herbivores. We studied life history consequences and starvation resistance for a common planktonic rotifer, *Keratella cochlearis*, feeding on algae grown on nutrient-limited media. A strain of *Cryptomonas* was grown on three types of growth medium with nitrogen (N) and phosphorus (P) adjusted to produce N-limiting, P-limiting, and nutrient-sufficient conditions. The analysis of nutrient content of *Cryptomonas* cells grown on nutrient-limited conditions showed that those algae exhibited higher P content than algae growing on a nutrient-sufficient medium. However, *Cryptomonas* reached lower densities in nutrient-limited media. The life history responses of *Keratella* to food quality were examined with low and high food availability. Our study showed that the interaction of food quantity and quality had a significant effect on rotifer growth rates. We observed, at low food levels, that *Keratella* growth rates were highest when the algae were grown under P limitation. The lowest rotifer growth rates were obtained when the rotifer fed on *Cryptomonas* grown in nutrient-sufficient conditions. Our study also showed that starvation resistance was higher for those rotifers fed on N-limited *Cryptomonas*. In natural situations, rotifers could even grow better under nutrient-limited conditions if this group of algae is dominant in the phytoplankton community. Moreover, differences in starvation resistance could be critical in determining competitive outcome and community structure in nutrient-variable environments.

Like higher plants, algae have relatively high ratios of C : P and C : N, and under N or P limitation, the C : N : P ratio of phytoplankton varies considerably (Goldman et al. 1979; Moal et al. 1987). Numerous studies have shown that N limitation, and particularly P limitation, reduce the quality of algae as food for zooplankton (Sommer 1992; Sterner et al. 1993; Rothhaupt 1995; Lüring and Van Donk 1997; DeMott 1998; DeMott et al. 1998; Schulz and Sterner 1999; Conde-Porcuna 2000; DeMott et al. 2001; Plath and Boersma 2001; Villar-Argaiz and Sterner 2002). Traditionally in these experiments, N- or P-limited media have been used to alter the elemental ratios of algal food and to exploit this

feature to create food supplies of differing quality for zooplankton. Most of these studies have focused largely on crustacean zooplankton (usually *Daphnia*) feeding on a single species of green algae (usually *Scenedesmus*). The extrapolation of these results to actual field conditions is quite limited because natural populations are usually made up of a variety of crustacean and noncrustacean zooplankton that feed on an algal community made up of a frequently diverse array of algae. However, few experimental studies have examined nutrient limitation for rotifer species (Rothhaupt 1995; Conde-Porcuna 2000), and/or nutrient limitation for zooplankton using nongreen algal species as food resources (Lüring and Van Donk 1997; Boersma 2000). There is no a priori reason to assume that *Scenedesmus*, a relatively rare alga in the wild, is generally representative of all other algae that zooplankton are likely to feed on in natural lakes (Brett et al. 2000). Therefore, more studies that examine how nutrient availability affects the elemental composition of non-green algal food items and their quality as food for different zooplankton are clearly necessary.

Rotifer species are more susceptible than *Daphnia* or copepods to nutrient limitation, especially P limitation (Morales-Baquero and Conde-Porcuna 2000; Conde-Porcuna et al. 2002). Conde-Porcuna et al. (2002) observed that the abundances of some rotifer species were not correlated with food availability but showed a strong dependence on P availability in a reservoir. Different susceptibilities of zooplankton species to nutrient limitation could be important in explaining the dynamics of these organisms in natural situations. Rothhaupt (1995) and Conde-Porcuna (2000) showed that P limitation significantly reduces the growth rates of the rotifers *Brachionus* and *Anuraeopsis*. Rothhaupt (1995) also showed that N-limited *Scenedesmus* allowed similar rotifer growth rates at low to moderate concentrations of food, but maximum growth rates at high food concentration were significantly reduced. However, no attempt has been made on life history consequences for rotifers feeding on nutrient-limited phytoplankton.

Starvation resistance reflects the ability of a species to store energy and control its allocation during periods of extreme