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Controlling phosphate release from phosphate-enriched sediments by adding various iron compounds

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Abstract In a laboratory experiment, different iron salts ($FeCl_2$, $FeCl_3$, $FeSO_4$) and Fe_2O_3 were added to a phosphate enriched silty loam sediment in order to study their effect on phosphate mobilisation. Phosphate concentrations in sediment pore water were not reduced by the addition of Fe_2O_3. Addition of both iron chlorides, however, resulted in a strong decrease of phosphate levels in sediment pore water. A similar but less pronounced effect was caused by the addition of iron as iron(II) sulphate. Sulphate appears to counteract the immobilisation of phosphate brought about by iron(II). Phosphate release from the sediment appeared to be determined by the iron/phosphate ratio in the sediment pore water. The addition of Fe_2O_3 barely affected the phosphate release from the sediment whereas the addition of iron salts was effective in preventing phosphate release. Increased amounts of iron added to the sediment resulted in a decreased phosphate release.

Introduction

At present, eutrophication of surface waters is a serious problem in many parts of the world. Decreasing the external nutrient load is one of the most implemented measures to combat eutrophication. However, reduction of the external phosphorus load does not always lead to a satisfactory reduction of phosphate levels in the water layer (Cullen & Forsberg 1988; Redshaw et al. 1990; Boers 1991). Owing to the internal loading of phosphorus from the sediment, the phosphorus concentration of the water layer frequently remains higher than is to be expected following the reduction of the external load.

If the phosphorus release from the sediment is sufficiently high to maintain an unacceptable degree of eutrophication of the water layer, additional measures are required. Dredging of lake sediments, for instance, is usually highly successful (Bjork 1988; Roelofs et al. 1996) but is costly, also because at present most sediments have (technically) to be considered as chemical waste. Alternatively, precipitation and immobilisation of phosphorus by the addition of iron salts to the sediment, may be a valuable technique (Boers 1991; Smolders et al. 1995).

In an enclosure experiment, Smolders et al. (1995), were able to prevent eutrophication of the water layer during one season by adding iron(II) chloride to the sediment of a eutrophied ditch. Boers (1991) found that the addition of iron(III) chloride to the upper sediment layer of a shallow lake, resulted in a significant improvement of the water quality for a period of three months. Already, in 1958, Sperber described how the addition of iron oxide (Fe_2O_3) could reduce the mobility of phosphate in waterlogged siliceous soils.

Although iron addition has already been shown to be a potentially valuable technique, little information exists about which iron compound is most suitable to diminish phosphate release from wetland sediments. In this article we present the results of a laboratory experiment which compared the ability of three different iron salts (i.e. iron(II) chloride, iron(III) chloride, iron(II) sulphate) and iron(III) oxide to impair the release of phosphate from a phosphate enriched sediment.

Materials and methods

Experimental design

Sediment was collected from a ditch in 'De Bruuk', a small nature reserve in the Netherlands, and transported to the laboratory in airtight bags. The sediment is characterised as a silty loam (1.7% clay; 78.9% silt and 19.4% sand) with an organic matter content of 6.0% (g/g). Iron concentrations in sediment pore water are very low and do not exceed 20 μmol.l^{-1} (Smolders et al. 1995).

Under hypoxic conditions in the laboratory, the sediment was mixed and distributed among glass containers with a volume of 850 ml. In each container, 750 g of fresh sediment was mixed with 190 mg of Na_2HPO_4. Next, different amounts of iron were mixed with the sediments: either 112.5, 375 or 1125 mg of iron was added as $FeCl_2$, $FeCl_3$, $FeSO_4$ or Fe_2O_3 (corresponding with 150, 500 and 1500 mg per kg of sediment). Thus, exactly the same amount of iron was added in each treatment, for each iron chemical. The experiment was carried out in triplicate. In three glass containers, serving as controls, no iron was added. To enable sampling of sediment pore water, an inert (ceramic) porous cup was installed in each container. After this, 200 ml of demineralised water was poured very carefully (without disturbing the sediment) on the sediment. The glass containers were kept in the dark at a constant temperature of 16 °C.

At days 1, 8, 35, 61 and 89, sediment pore water samples (30 ml) were taken from the sediment for analysis. At days 8, 35, 61 and 89 the water layer was carefully removed (by suction) from the sediment for analysis, after which 200 ml of demineralised water was again poured on the sediment.

Analyses

Al and Fe were measured with an Inductively Coupled Plasmaspectrophotometer, type IL Plasma 200. The following were determined colorimetrically using a Technicon AAI-system (Technicon Corporation 1969); NH_4^+ according to Grasshoff and Johannsen (1977), Cl^- according to O'Brien (1962), SO_4^{2-} according to Technicon Auto Analyzer Methodology (1981) and PO_4^{3-} according to Henriksen (1965). Alkalinity was determined by titrating 15 ml down to pH 4.2.

Results

Compared to the control treatment, addition of iron(II) and iron(III) chlorides resulted in a strong decrease in the phosphate concentrations in sediment pore water (Figure 1), the effect being stronger with increasing amounts of iron chloride. The addition of iron(II) sulphate also decreased phosphate concentrations in the sediment pore water. However, the decreases were less than those brought about by the addition of equal amounts of iron chlorides. Contrastingly, in the case of Fe_2O_3, only the addition of 150 $mg.kg^{-1}$ resulted in slightly lower phosphate concentrations in sediment pore water compared to the control treatment.

As expected, the iron/phosphate ratio in sediment pore water increased upon the addition of iron salts (Figure 1). Addition of iron sulphate, however, resulted in (much) lower iron/phosphate ratios than did the addition of equal amounts of iron chlorides. Iron/phosphate ratios remained low upon the addition of iron oxide for all doses (Figure 1).

The addition of the iron salts led to a clear decrease of phosphate release to the water layer (Figure 1, note that water was refreshed with P-free water after each sampling point). The release of phosphate was negatively correlated with the amount of iron salt added although the major part of the decrease was reached already at the lowest dose. Addition of 150 mg iron(II) sulphate, however, resulted in a considerably higher phosphate release than did the addition of the equivalent amount of iron chloride (Figure 1). The addition

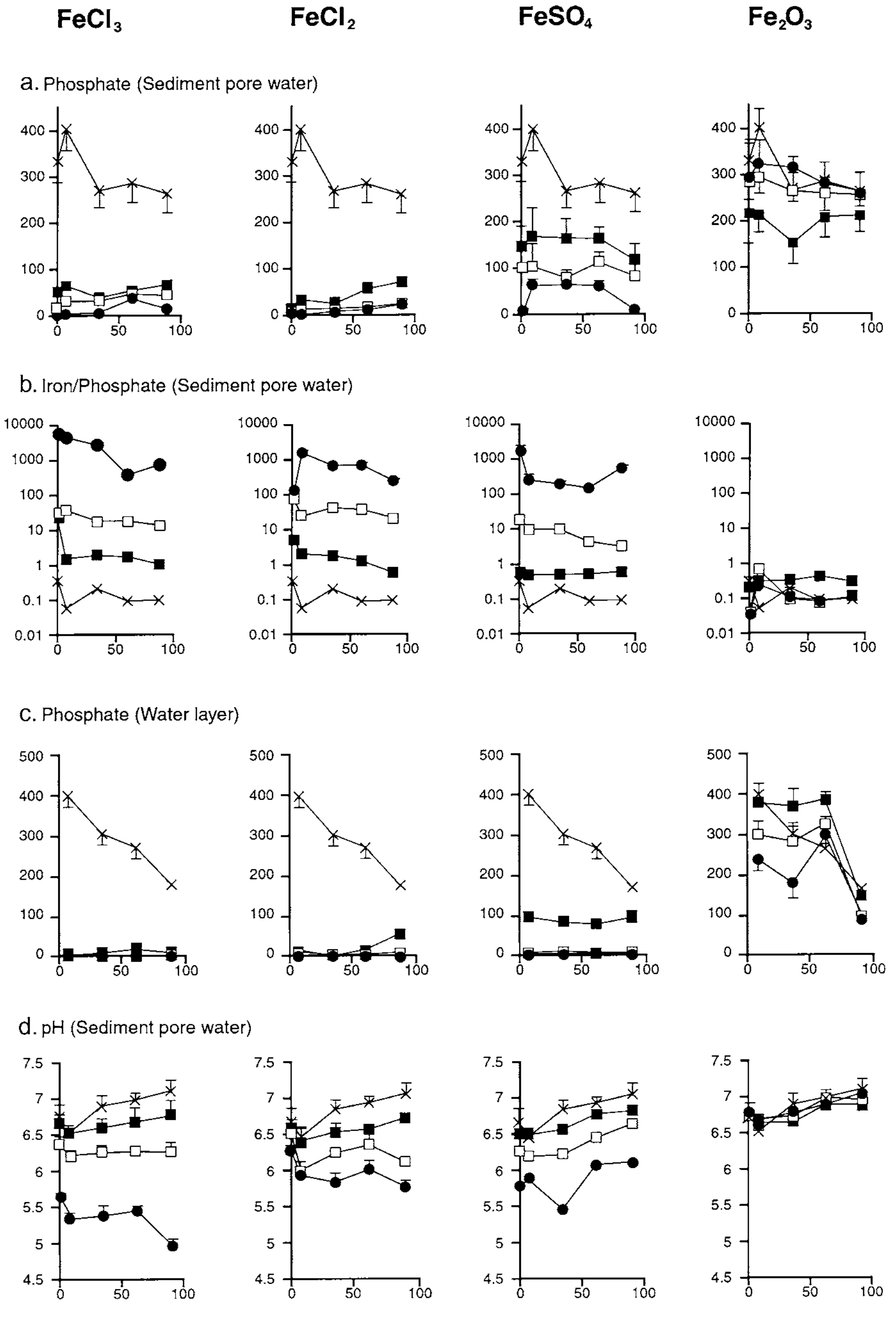


Figure 1. Phosphate levels, iron/phosphate ratios and pH in sediment pore water and phosphate levels in the water layer after the addition of different amounts of iron chemicals. All values, except pH and iron/phosphate (μmol/μmol), are given in μmol.l^{-1} and are means of triplicates. The bars represent the SD. ■ represents the 150 mg.kg^{-1} treatment; □ the 500 mg.kg^{-1} treatment, ● the 1500 mg.kg^{-1} and × the control treatment.

of iron oxide did not cause a clear decrease in phosphate release from the sediment (Figure 1).

pH and alkalinity (Figures 1 and 2) decreased after the addition of iron salts. However, after the addition of iron(II) sulphate, in the 150 and 500 mg kg^{-1} treatments, alkalinity showed a gradual increase during the experiment (Figure 2). Addition of iron oxide barely altered the pH and alkalinity of sediment pore water (Figures 1 and 2), and there were no differences between doses.

Unsurprisingly, the addition of iron salts led to a strong increase of chloride (iron chloride additions) and sulphate levels (iron(II) sulphate addition) in sediment pore water (Figure 2). The sulphate levels in the iron(II) sulphate treatments, however, showed a strong decrease during the experiment (Figure 2). The concentrations of aluminium and ammonium in sediment pore water increased with increasing levels of iron salts added. In general, however, the addition of iron(III) chloride resulted in a stronger increase of aluminium and ammonium levels than did the addition of similar amounts of iron(II) salts. The addition of iron oxide had little effect on the aluminium and ammonium concentrations of sediment pore water (Figure 2).

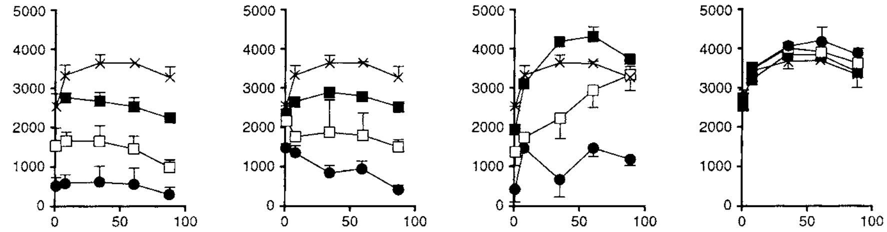
Discussion

The decrease of the phosphate levels in sediment pore water after the addition of Fe(II) and Fe(III) salts can be ascribed to the precipitation of iron(II) and iron(III) phosphates in the sediment (Boström et al. 1982; Roden & Edmonds 1997). Therefore, the remaining phosphate levels in sediment pore water were negatively related to the amounts of iron added. Compared to iron(II) chloride, iron(II) sulphate addition did not lead to a similar reduction of phosphate concentrations in sediment pore water. Apparently, sulphate counteracts the net-immobilisation of phosphate brought about by iron (II).

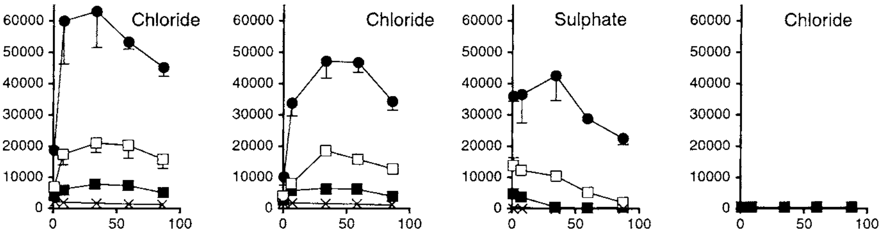
The strong decrease of sulphate concentrations in the sediment pore water during the experiment (Figure 2) indicates that an important part of the added sulphate was biogeochemically reduced to sulphide and/or gradually adsorbed to sediment particles. High amounts of sulphate may cause phosphate release due to the competition between sulphate and phosphate for anion adsorption sites (Caraco et al. 1989; Beltman et al. 2000). Furthermore, due to iron(II) sulphide precipitation, a fraction of the added iron will be immobilized in the sediment (Giblin et al. 1990; Smolders & Roelofs 1993; Smolders et al. 1995; Roden & Edmonds 1997) and thus will be unavailable for phosphate immobilisation. Sulphate reduction also increases alkalinity (Schindler et al. 1986; Curtis 1989) as was illustrated by the gradual increase of alkalinity during the experiment in the iron(II) sulphate treated

$FeCl_3$ $FeCl_2$ $FeSO_4$ Fe_2O_3

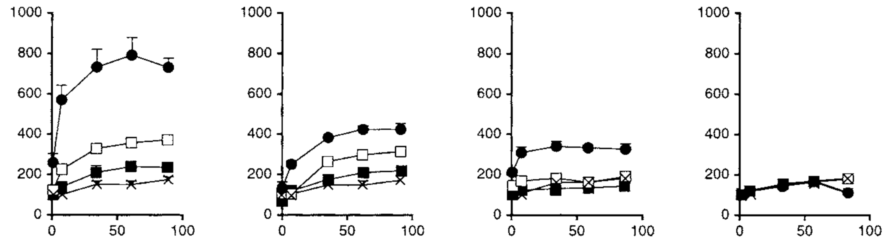
a. Alkalinity (Sediment pore water)



b. Chloride/Sulphate (Sediment pore water)



c. Ammonium (Sediment pore water)



d. Aluminium (Sediment pore water)

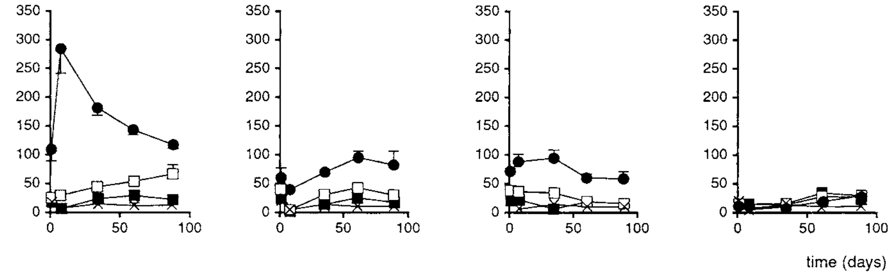


Figure 2. Alkalinity, chloride, sulphate, ammonium and aluminium in sediment pore water after the addition of different amounts of iron chemicals. All values, except alkalinity (μeq.l^{-1}), are given in μmol.l^{-1} and are means of triplicates. The bars represent the SD. ■ represents the 150 mg.kg^{-1} treatment; □ the 500 mg.kg^{-1} treatment, ● the 1500 mg.kg^{-1} and × the control treatment.

sediments. A higher alkalinity may also increase phosphate mobility (Curtis 1989; Roelofs 1991; Smolders & Roelofs 1995).

Figure 3 shows the relationship between the release of phosphate to the water layer and the iron/phosphate ratio in sediment pore water. The net phosphate release to the water layer in a certain period was negatively correlated with the mean iron/phosphate ratio in sediment pore water during the same period. The release of phosphate appears to increase strongly when iron/phosphate ratios drop below a value of 1. Thus the release of phosphate to the water layer seems to depend on the iron/phosphate ratio in sediment pore water. This result strongly supports the classical theory which states that the interaction between the iron and the phosphorus cycles plays an important role in the exchange of phosphate between the sediment and the water layer (Mortimer 1941; Baccini 1985; Curtis 1989). According to this theory, diffusion of iron(II) towards the water layer will result in oxidation of iron(II) to insoluble iron(III) (hydr)oxides in the oxygenated boundary layer between the sediment and the water layer. In this boundary layer phosphate will co-precipitate with the iron(hydr)oxides. In this way, the release of phosphate to the water layer should diminish when iron/phosphate ratios of the sediment pore water increase (Baccini 1985; Smolders & Roelofs 1993); which is exactly what we found in our experiments (Figure 3). It should be noted, however, that this mechanism would be especially important if phosphate release from the sediment is predominantly determined by diffusion.

The observed increases of ammonium and aluminium levels in the iron treatments are due to the exchange between iron and cations at the cation exchange sites of the sediment particles (Ponnamperuma 1972), and the exchange against protons produced by acid generating reactions, such as the formation of iron carbonates (Davison 1993; Smolders et al. 1995) and the hydrolysis of water by iron (Davison 1993). Increased aluminium and ammonium levels might cause aluminium toxicity in aquatic organisms and have implications for waters in which N is (co-)limiting. However, it should be realized that in the field situation the observed increases of these ions in the sediment pore water will only be temporary due to the diffusion of ions to deeper sediment layers and to the overlaying water column (Smolders et al. 1995). Compared to the addition of iron salts, iron oxide was not very effective in decreasing the phosphate release from the sediment. In contrast with the findings of Sperber (1958) it can be concluded that the adsorption of phosphate in the sediment was not improved significantly. In general, iron oxide addition did little to alter the sediment pore water chemistry.

The use of iron sulphate seems to have some disadvantages compared with the use of iron chlorides. First, at lower addition levels iron(II) sulphate is much less efficient than iron chlorides in counteracting the exchange of phos-

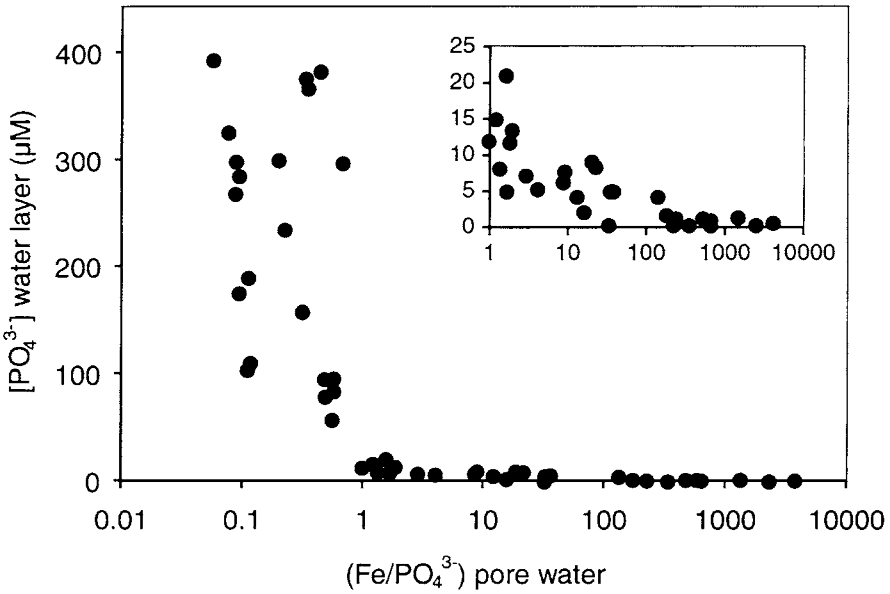


Figure 3. Relationship between the logarithm of the mean iron/phosphate (mol/mol) ratio in the sediment during the preceding period (the mean of the ratios on the sample date and the preceding sample date) and the amount of phosphate encountered in the water layer on the sample date.

phate to the water layer. Next, iron(II) sulphate does not reduce the phosphate levels in sediment pore water to the same extent as do the iron chlorides. This will be a disadvantage, particularly when turbulence plays a significant role in the release of phosphate from the sediment. In shallow lakes, for instance, turbulence due to wind action plays an important role in the exchange of phosphate (Boström et al. 1982; Roelofs 1991; Portielje & Lijklema 1999). When turbulence is of importance, phosphate might escape co-precipitation with iron(hydr)oxide. Under such circumstances phosphate exchange may instead be determined by the dissolved phosphate levels in sediment pore water. Another disadvantage of iron sulphate salts might be that the release of sulphate enriched water may have adverse effects on neighbouring systems. Sulphate reduction in sediments with low iron contents can lead to iron limitation, sulphide toxicity and internal eutrophication (Smolders & Roelofs 1993; Smolders & Roelofs 1995; Lamers et al. 1998; Lamers et al. 2001). Finally, sulphate reduction and the consequential iron sulphide precipitation will lead to a more rapid exhaustion of the iron added to the sediment.

Our experiment confirms that the addition of iron salts can make a substantial contribution to the decrease of the internal phosphorus loading of surface waters. However, the addition of iron salts does have some drawbacks.

When phosphate concentrations in the sediment are high (as was the case in our experiment), large amounts of iron are necessary to prevent phosphate exchange to the water layer. In the phosphate enriched sediment from ‘De Bruuk’, for instance, 300 kg ha^{-1} of Fe (as $FeCl_2$ or Fe Cl_3) would have to be injected in the upper 10 cm of the sediment in order to prevent phosphate release to the water layer.

The adverse effects of the addition of such high amounts of iron salts, might make application of the method undesirable. Furthermore, experiments in the field reveal that the beneficial effects of iron addition are only temporary (Boers 1991; Smolders et al. 1995) and, hence, iron addition has to be repeated frequently in order to maintain a lasting decrease of the internal phosphate loading. At the same time the costs involved in treating whole lakes can be substantial (Boers 1991). If, however, the addition of iron salts is being considered in combating phosphate mobilisation from the sediment, the use of iron chlorides has to be recommended.

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