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The role of the ironhydroxide-phosphate-sulphide system in the phosphate exchange between sediments and overlying water

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This article is dedicated to the memory of Dr Kees de Groot, who died on 21 September 1994. He was a young enthusiastic, promising scientist who will be missed by all who have known him.

Key words: phosphate, ironhydroxide, sulphide, apatite, sediments

Abstract

The accumulation of inorganic phosphate in lake sediments and a possible following release is due to the adsorption of phosphate onto Fe(OOH) and, especially in hard waters, to the precipitation of apatite. Attempts are made to quantify both processes.

For the quantification of the P adsorbed, P_{ads}, onto Fe(OOH) the Freundlich adsorption isotherm, P_{ads}=A(o-P)^B, gave good results. The constants A and B could be quantified. Constant A appeared to depend on the pH and the Ca^{2+} and Mg^{2+} concentrations in the water. Constant B appeared to approach 0.333. The full equation becomes then: $P_{ads}=23600.(10^{-0.4pH})(2.77\text{-}1.77;e^{-Ca})\sqrt[3]{o-P}$, with the Ca concentration in mmol l^{-1} and the o-P and P_{ads} concentrations in mg l^{-1}.

For the quantification of the solubility of calcium-bound phosphate the solubility product of apatite being 10^{-50}, as found in the two hard water rivers Rhine and Rhone, was used. With this solubility product the solubility of o-P can be calculated as function of the Ca^{2+} concentration and the pH. The two equations, for adsorption and precipitation, are put together in a so-called solubility diagramme, which describes the o-P concentration as function of the Fe(OOH) concentration in the sediments, and the pH and the Ca^{2+} concentration in the overlying water.

The release of phosphate from the Fe(OOH)≈P complex under anoxic conditions after adding H_2S in inorganic suspensions was shown to be limited. Only when a large excess of H_2S was added there was some release, but if less than 75% of the Fe(OOH) was converted into FeS, there was no release. The possibility of organic phosphate as the source of phosphate release under anoxic conditions is discussed. For a full understanding of this possibility, fractionation of sediment bound phosphate must be carried out in such a way, that these organic phosphates are not hydrolysed.

Introduction

Sediments can accumulate, and under different conditions release, phosphate. Two processes are mainly responsible for the accumulation of inorganic phosphate: adsorption onto ferric hydroxide, Fe(OOH), and precipitation with Ca ions. The first complex formed is written as Fe(OOH)≈P, the second as $CaCO_3$≈P. I use these two abbreviations in order to avoid a discussion on the chemical structure of these complexes. Some remarks on the structure of Fe(OOHO)≈P are made in the discussion. The two processes, the relative importance of which depends on environmental factors, involve different mechanisms and it is not correct to describe the whole as (ad)sorption.

P-adsorption onto Fe(OOH) was proposed by Einsele (1936, 1938), Einsele & Vetter (1938) and Mortimer (1941/42). Mortimer based his hypothesis of a Fe(OOH)≈P complex on the fact that Fe(OOH) and phosphate are released simultaneously into the anoxic hypolimnion from the sediments of a soft water lake and in simulation experiments *in vitro*. He suggested that reduction processes in the sediments cause a reduction of Fe^{3+} to Fe^{2+} with dissolution of phosphate. Einsele (1936, 1938) suggested that the reduction was caused by H_2S; his further reasoning followed Mortimer's. The belief that reduction of Fe(OOH) by H_2S is the cause of phosphate release is widespread. Golterman (1967) reviewed the older hypotheses for the mechanisms involved.

Lijklema (1977) made a first attempt to quantify the adsorption of phosphate onto Fe(OOH); he demonstrated the importance of the pH: at higher pH the adsorption decreases. This article follows Lijklema's approach, but with a different mathematical description, *i.e.* the Freundlich adsorption isotherm. This equation was used by Einsele (1938) qualitatively to describe the adsorption onto Fe(OOH) and by Olsen (1964) who was the first to measure the adsorption of phosphate onto natural sediments quantitatively. Olsen used ^{32}P and pointed out the possibilty that both mechanisms, precipitation and adsorption, concur for the adsorption onto natural sediments and demonstrated the influence of reducing conditions.

The possibility of calcium phosphate precipitation was proposed initially by Hepher (1952, 1958) who experimented with $CaCO_3$ addition to fish ponds. He calculated the solubilty of Ca phosphate with the solubility product of $Ca_3(PO_4)_2$. It was shown later (Golterman, 1967, following Remy, 1956 pages 624-5, 638) that the actual compound involved was apatite, $Ca_{10}(PO_4)_5(OH)_2$, usually written as $Ca_5(PO_4)_3OH$. Because Mortimer's work was done in the English Lake District, where Ca^{2+} does not play a role and where phosphate concentrations were still low, apatite formation was not important. The influence of Ca^{2+} on phosphate storage in sediments was, therefore, only slowly accepted. A firm statement[1] in this respect was made by Golterman, Viner & Lee (1976) during the first symposium on sediment water exchange processes. The evidence for the role of apatite does not come from the isolation or analysis of a pure precipitate, but from the fact that the ionic product $(Ca^{2+})^5\ (PO_4^{3-})^3$ (OH) is often found to approach the solubility product; this is not illogical as apatite is the least soluble calcium phosphate compound in natural waters (Stumm & Morgan, 1981). This compound plays a role mainly in hard waters, as in soft waters the low (Ca^{2+}) and the low pH increase the solubility of calcium phosphate; in soft water its solubility may play a role, but only when phosphate concentrations are extremely high.

The exact quantification of both processes, adsorption and precipitation, is difficult, but is essential for a full comprehension of the importance of exchange processes.

The adsorption system

Adsorption, which is the binding of ions onto the surface of particles, depends on chemical processes, in this case the exchange of a OH^- ion by a phosphate anion. It is clear that factors such as pH and temperature will influence the quantity adsorbed. But Fe(OOH) will also adsorb cations (Stumm & Morgan, 1981) and these will enhance the P adsorption onto the Fe(OOH). Realising the large difference in chemical composition of major elements of rivers and lakes (hard *vs* soft water; high pH *vs* low; shield lakes, hard water lakes *vs*, e.g., estuaries or lagoons), it is necessary to try to quantify these factors.

In the literature two equations for the adsorption process are in use, that of Langmuir and that of Freundlich:

$$X_{\mathrm{ads}} = \frac{(X)}{Ks + (X)} \quad \text{or} \quad X_{\mathrm{ads}} = A.(X)^B$$

(Langmuir) (Freundlich)

in which X_{ads} = quantity adsorbed; (X) = concentration of solute; Ks = saturation constant, related to the binding energy; and A & B are numerical constants.

The kinetics of the phosphate adsorption onto Fe(OOH) is discussed by Froelich (1988), who showed that adsorption is a reversible two-step process. The first step, adsorption onto the surface takes place in a time scale of hours; the second step, the diffusion into the interior of the particles has a time scale of days. In this paper I try to quantify the adsorption equilibrium of phosphate onto Fe(OOH). Because of the time scale of processes in lakes, I did not try to evaluate the kinetics, but studied the equilibria after a week, following Olsen (1964) by using Freundlich's isotherm. The reasons for this choice are given in the discussion.

The precipitation mechanism

In the literature a wide range of values for the solubility product of apatite has been published: values can be found between 10^{-35} and 10^{-60} (Golterman & Meyer,

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[1] One of the most important conclusions from this symposium was that the classical story of Einsele and Mortimer of iron–phosphate interactions was convincingly shown to be of limited importance in governing the overall phosphate exchange processes in several, especially calcium-rich, lakes.

1985). Two approaches are possible: firstly a calculation based on the heat of formation. In this way Kramer (1964) arrived at a value of 10^{-56}. Secondly by measuring the concentrations of Ca^{2+}, phosphate and the pH in experimental systems or in natural waters and calculating the ionic products. Significant experimental problems are: the uncertainty whether equilibrium is reached, the possiblity that $CaCO_3$ is present in a colloidal state and the uncertainty in the measurement of the pK3 of H_3PO_4 (Gosh *et al.*, 1980; Golterman & Meyer, 1985). The formation of $CaCO_3$ (collodial or not) may influence the results, but in the experimental approach $CaCO_3$ cannot be left out in order to simulate natural systems.

The quantitative description of the Fe(OOH)≈P adsorption is then combined with the quantitative description of the solubility of calcium phosphate in a so-called solubility diagramme, which describes the equilibrium of phosphate between the two solid phases, *i.e.* iron and calcium bound phosphates. Such a diagramme must be used when describing or explaining the behaviour of mixed systems. An earlier attempt was made by Golterman (1988), but in that diagramme the influence of Ca^{2+} on the adsorption was not yet taken into account.

The idea that H_2S will release phosphate from Fe(OOH)≈P remains widespread (see discussion), although theoretically unlikely (Golterman, 1973, 1975 & 1984; De Groot (1991) showed in experiments with sediment suspensions that the effect is indeed less than is commonly accepted. Therefore, *in vitro* experiments were carried out to demonstrate the possible effect of H_2S additions to Fe(OOH)≈P suspensions. The release of phosphate from sediments under anoxic conditions should, therefore, be reconsidered. Much more attention should be given to the possible role of org-P, which so far has been often neglected because of too poor isolation techniques.

Materials and methods

Fe(OOH) suspensions were prepared by dissolving $FeCl_3 \cdot 6\,H_2O$ in H_2O and adjusting to pH 8 with NaOH. The precipitate was suspended in H_2O followed by decantation after sedimentation once a day until Cl^- was no longer detectable (usually 4–5 times). The Fe(OOH) (usually 5.4 mmol l^{-1}; 300 mg l^{-1}) was then resuspended in a buffer solution. In the earlier experiments 3 mmol l^{-1} of $NaHCO_3$ was used; Later 3 mmol l^{-1} of borax was used because of the interaction of carbonate with Ca^{2+} at higher pH values. The suspensions were aged at least 2 weeks.

Two series of experiments were carried out. In the first portions of 100 ml of Fe(OOH) suspension were used to which different amounts of o-P were added, at different pH values. $NaHCO_3$ was used as buffer. The equilibrium concentrations were measured after 5–7 days, at ambient temperature. In total 13 different adsorption curves were measured. At least 6 points were measured for each curve; a possible statistical outlier was rejected. Concentrations higher than 1 mg l^{-1} of o-P were avoided.

In the second series pH and Ca^{2+} concentrations were varied between 7 and 8.2 and 0 and 8 mmol l^{-1} respectively. Increasing amounts of o-P were added to 1 l of the Fe(OOH) suspension (again 5.4 mmol l^{-1}) in the borax buffer. Usually the o-P was added in steps of 2.5 mg l^{-1} and the equilibrium concentrations were measured after 5 days. Three series were measured, each at three different pH values and at 4 different Ca^{2+} concentrations; two series were carried out at ambient winter temperatures (≈15 °C) and one at ambient summer temperature (≈25–30 °C). The use of borax buffer was essential in order to prevent apatite precipitation. In the second approach it was easier to maintain a constant pH, in the first approach to maintain a constant temperature. The data were fitted to equation (1a) for further quantification:

$$P_{\mathrm{ads}} = A(\mathrm{o-P})^B \qquad (1a)$$

where P_{ads} = quantity adsorbed per liter or per mg of Fe and o-P is the ortho-phosphate concentration (mg l^{-1}); A and B are constants

In a few experiments the Fe(OOH)≈P suspensions, with 1 or 2 mmol l^{-1} of Ca^{2+} added, were flushed with N_2 and treated with increasing amounts of H_2S, produced in a Kipp apparatus and transferred with an injection piston and needle. The suspensions were kept under N_2 for 2 or 3 days after the H_2S injection.

Soluble phosphate (o-P) was measured with the blue-molybdate method (Method 5.6.2, Golterman *et al.*, 1978); iron with phenanthroline (Method 4.5.1) but using ascorbic acid as reductant. Adsorbed phosphate and Tot-P were measured after extraction (solubilisation) with Ca-NTA (Golterman & Booman, 1988) or with citric acid (0.5 ml 0.1 M per 10 ml suspension) both with dithionite added (50–80 mg per 10 ml). Care must be taken to use only small volumes of these extracts: 5 ml for the Ca-NTA or 2 ml for the citric acid extract. The dithionite should not be deteriorated (check its activity with the original Fe(OOH) suspension). Even as a solid, dithionite deteriorates slowly.

The determination of H_2S, both soluble or as FeS, was carried out as follows:

A solution of Zn acetate (10 or 20 ml of a 1.5% = 0.07 M l^{-1}) was added to the sample and placed in a gas wash bottle. The sample was flushed with N_2 for 20 minutes; the N_2 was passed with a small Pasteur pipette through a beaker with a precisely known excess of NaClO (0.1 M) to which 1 ml Zn acetate was added. 10 ml 4 M H_2SO_4 was added to the sample; flushing continued for 15 minutes. The excess NaClO was directly titrated with 0.05 M As_2O_3 in an automatic titrator with a preset endpoint of 875 mV after addition of 10 ml Na acetate (2 M) and 1 ml of 1 M H_2SO_4. The method was checked with a suspension of ZnS with or without destillation. The ZnS suspension was made by flushing first N_2 and then H_2S through a solution of Zn acetate (0.05 M). Excess H_2S was removed with N_2 and the suspension was kept under N_2. H_2S may be trapped directly in Zn acetate and titrated with I_2. An exactly known excess of I_2 was added and titrated back with As_2O_3. The standard deviation for the I_2 method was 0.25 % and for the NaClO method 1.25 %. The NaClO method is 4 times more sensitive because the oxidation of ZnS with I_2 proceeds to S and with NaClO to H_2SO_4. For very low concentrations the H_2SO_4 can be measured colorimetriccally (Golterman, 1992). This increases the sensitivity 4-fold.

Results

Adsorption experiments

All the results of the first series of experiments to measure the influence of the pH on the adsorption are given in Table 1, a few examples are depicted in Fig. 1 . The values of A and B were found by plotting $\log(P_{\mathrm{ads}})$ against log(o-P). Usually a straight line was found.

I noticed that B was always very near to 0.333; therefore I have fitted the data also with the formula:

$$P_{\mathrm{ads}} = A(\mathrm{o-P})^{0.333} \qquad (1b)$$

By plotting P_{ads} against $(\mathrm{o\text{-}P})^{0.333}$ a straight line was found, which can be forced through (0,0) as log transformations are no longer needed for the curve fitting. It can be seen (Table 1b) that the R^2 values are then somewhat lower, but not significantly. It is now possible to analyse the relation between A and pH. Two curves fitted the data very well (see Table 1b and Fig. 2):

the (2) polynomial $A = a + b\,\mathrm{pH} + c\,\mathrm{pH}^2$ $(R^2 = 0.87)$ and the exponential $A = a10^{-b\mathrm{pH}}$, or $A = a(\mathrm{H}^+)^b$ $(R^2 = 0.96)$.

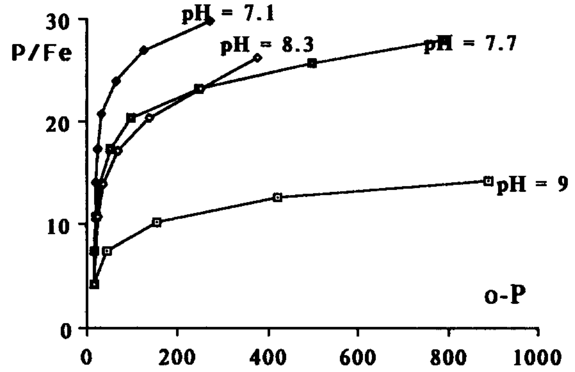


Fig. 1. Adsorption of ortho-phosphate onto Fe(OOH). Y axis: μg P per mg Fe; X axis: ortho-phosphate concentration in μg l^{-1}.

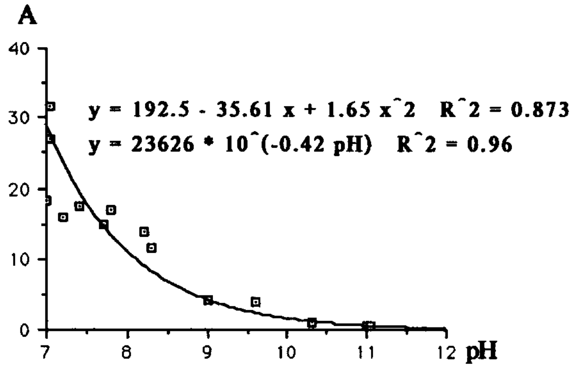


Fig. 2. Influence of pH on the Freundlich adsorption constant A. Line drawn: exponential curve fit.

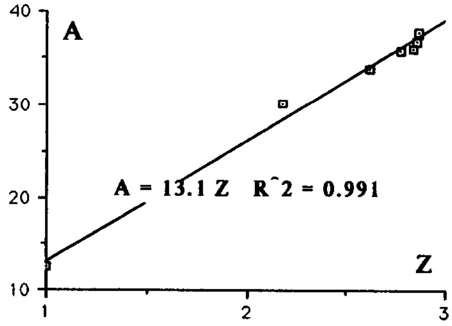


Fig. 3. Freundlich's adsorption constantA as function of Z (={2.86 - 1.86.e^{-Ca}}

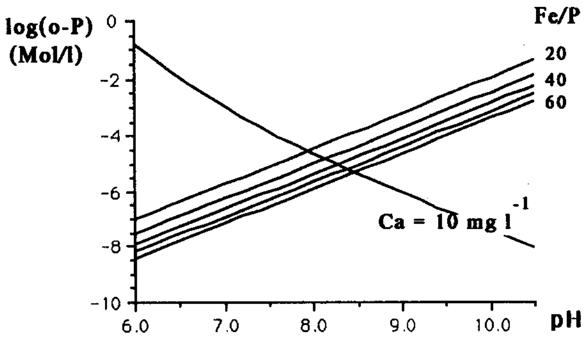


Fig. 4 a. Solubility diagramme of o-P in equilibrium with sediments with Fe/P ratios between 20 and 60 (mg mg^{-1}) and a solute Ca^{2+} concentration of 10 mg l^{-1}.

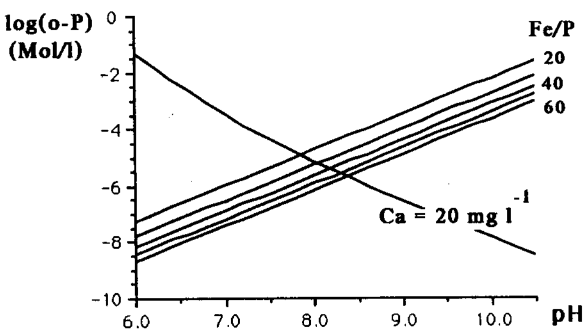


Fig. 4 b. Solubility diagramme of o-P in equilibrium with sediments with Fe/P ratios between 20 and 60 (mg mg^{-1}) and a solute Ca^{2+} concentration of 20 mg l^{-1}.

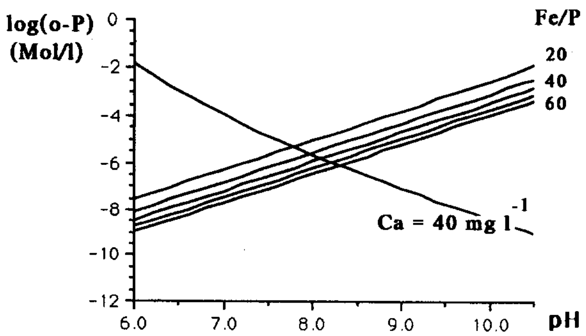


Fig. 4 c. Solubility diagramme of o-P in equilibrium with sediments with Fe/P ratios between 20 and 60 (mg mg^{-1}) and a solute Ca^{2+} concentration of 40 mg l^{-1}.

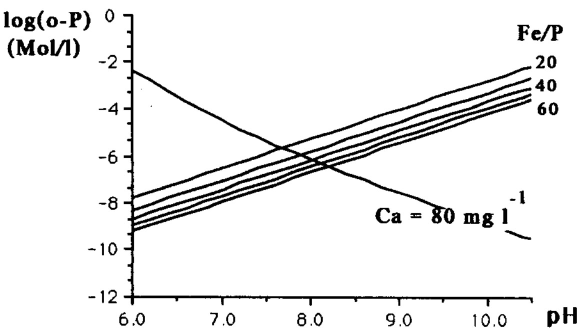


Fig. 4 d. Solubility diagramme of o-P in equilibrium with sediments with Fe/P ratios between 20 and 60 (mg mg^{-1}) and a solute Ca^{2+} concentration of 80 mg l^{-1}.

The polynomial curve gives a good fit till pH = 10, but rises again at higher pH while the exponential gives too high values below pH = 5. Temperature has an effect on the adsorption: at lower temperature, the adsorption becomes stronger. Because, however, the pH of the buffer also changes (lower pH at lower temperature) I could not separate the two effects. The influence between 0 and 20 °C seems smaller in any case than 5%.

Next, in order to explore the corrrect form of the influence of the Ca^{2+} concentration on the adsorption, experiments were carried out with 0–7 mmol l^{-1} of Ca^{2+}. The data are presented in Fig. 3 and are fitted on the curve: $Y = C - (C-1)\,e^{-Ca}$, which equation was chosen as the data suggested an asymptotic influence of the Ca concentration (expressed in mmol l^{-1}) on the adsorption. It can be seen that a satisfactory fit was obtained with $C = 2.86$ at pH 7.6 ($N = 7$; $R^2 = 0.99$) and with $C = 2.68$ at pH = 7 ($N = 7$; $R^2 = 0.99$). The difference between 2.86 and 2.68 is not significant either statistically or in the final numerical outcome; the mean value 2.77 was further used, but a possible pH influence must still be analysed more precisely. Mg^{2+} concentrations have the same effect as those of Ca^{2+}, but for Na^+ the concentration must be higher; a constant influence was found only above 0.1 M l^{-1}. Additional effects have not yet been quantified.

All experiments with varying pH and Ca^{2+} concentrations (in mmol l^{-1}) were fitted with:

$$A = a(10^{-b\mathrm{pH}})(2.77 - 1.77e^{-Ca}) \qquad (2)$$

or, after replacing $(2.77 - 1.77\,e^{-Ca})$ by Z and a log/log transformation:

$$\log A = C_1 + C_2\mathrm{pH} + C_3\log(Z) \qquad (3)$$

The results are:

– For all data of experiments with Ca^{2+} (0–2 mmol l^{-1}) taken together (temperature 15–30 °C):

Log A = 2.04619 – 0.131737 pH + 0.154858 $(2.77 - 1.77\,e^{-Ca})$ $R^2 = 0.74$

– For the data of the two experiments at ≈15 °C:

Log A = 1.98184 – 0.12701 pH + 0.19047 $(2.77 - 1.77\,e^{-Ca})$ $R^2 = 0.91$

Table 1. Freundlich's constants for adsorption equilibra of o-P onto Fe(OOH) (300 mg l^{-1} of Fe^{3+}) at different pH values. Results for best fit curves after log/log transformation and for curves forced through (0,0) with B set at 0.333.{ Ca^{2+} = 1 mmol l^{-1}}

Table 1a. Best fit				Table 1b. Forced through (0,0) and B=0.333	
pH	A	B	R^2	A	R^2
7.04	15.9	0.28	0.92	16.8	0.84
7.1	14.4	0.28	0.92	16	0.85
7.7	10.1	0.25	0.93	10.5	0.84
8.0	9.3	0.27	0.99	9.73	0.99
8.3	11.1	0.30	0.98	11.5	0.96
9.0	4.21	0.21	0.999	3.92	0.84
9.0	4.22	0.27	0.99	4.1	0.96
9.6	4.12	0.22	0.99	3.97	0.92
11.0	0.26	0.57	0.97	0.39	0.82
11.0	0.36	0.70	0.99	0.65	0.90
A=91.1 - 15.5*pH+0.65*pH^2 R^2=0.95 A=22192*10$^{(-0.42)}$ R^2=0.91				A=192.5 - 35.6 pH+1.65pH^2 R^2=0.87 A=23626*10$^{(-0.42*pH)}$ R^2=0.96	

Table 2 a. Release of o-P from a suspension of Fe(OOH)≈P (Tot-Fe; 5.4 mmol l^{-1}) after addition of H_2S (as gas added during the N_2 supply) in the presence of 1 mmol l^{-1} of Ca^{2+}.

Compounds	Concentration				
FeS (mmol l^{-1})	0	1	2	4	5.4[1]
in % of Tot-Fe		≈10	≈20	≈75	100
Fe(OOH)≈P (mg l^{-1})	16.0	19.1	16.1		
o-P (mg l^{-1})	4.0	1.0	4.1		
Fe^{2+} (dissolved)	0.	0	0		
Fe(OOH)≈P (mg l^{-1})	9.9			7.5	5.0[1]
o-P (mg l^{-1}	0.01			2.5	5.0
Fe^{2+} (dissolved)				0	0

[1] An 8-fold excess of H_2S had to be added of which ≈50% is bound onto reduced non-soluble Fe^{2+}.

The equations (1b) and (2) can be combined with the solubility curve of o-P as controlled by the solubility product of apatite (10^{-50}). A first attempt to make such a solubility diagram was made by Golterman (1988); in this diagram the influence of Ca^{2+} on the P-adsorption onto Fe(OOH) was not yet taken into account. In Fig. 4a–d we see the results when the influence of Ca^{2+} on the adsorption of o-P onto Fe(OOH) is also taken into account. For each Ca^{2+} concentration a new solubility diagram should now be calculated. The o-P solubility in the water is thus controlled by the Fe(OOH) concentration in the sediments, the pH and the Ca^{2+} concentration in the water and not by the $CaCO_3$ concentration of the sediments.

Experiments with H_2S.

The experimental data are given in Table 2. Because of the Ca^{2+} influence on the adsorption, in these experiments a Ca^{2+} concentration of 1 or 2 mmol l^{-1} was used, as often found in hard freshwaters. An advantage is that in the presence of Ca^{2+}, the FeS can be centrifuged more easily; without Ca^{2+} often rather stable suspensions were obtained. Table 2 shows that only when nearly all the Fe(OOH) had been converted, phosphate was released but even in this case only up to 50% of the total amount. When less than 75% of the Fe(OOH) was converted into FeS no significant release of phosphate was found. For a total conversion to FeS, an 8-fold excess of H_2S was needed.

A few of the Fe(OOH)/FeS suspensions were extracted with Ca-NTA. If phosphate was bound onto $Fe(OH)_2$, phosphate and Fe should go into solution even without addition of dithionite (which is necessary to dissolve Fe(OOH)). FeS, having a larger stability constant should not go into solution, with or without dithionite. However, as the extractions were not carried out under complete exclusion of O_2, oxidation of FeS took place even in the presence of dithionite. The Fe(OOH) formed went rapidly into solution even without dithionite, unlike the original Fe(OOH) suspension. The difference in particle size of the Fe(OOH) formed by oxidation may cause this behaviour. The separations of FeS and Fe(OOH) and those of $Fe(OH)_2$≈P and Fe(OOH)≈P are, therefore, not possible except under severe exclusion of O_2 (dithionite does not remove dissolved O_2).

In three experiments no measurable quantities of soluble Fe^{2+} could be detected in the FeS/Fe(OOH) suspensions; in one experiment 2 to 4% Fe was found, increasing with the amount of FeS, but in no stoecheiometric relation. In experiment 2b the Ca-NTA/dithionite extraction was carried out in completely filled, closed centrifuge tubes minimalising the FeS oxidation. Of Tot-P 100% was recovered and of the initially present Fe 43%. Together with the measured FeS 101% of the Tot-Fe was recovered.

Table 2 b. Release after 3 days of o-P from a suspension of Fe(OOH)$\approx$P (Tot-Fe; 5.4 mmol l^{-1}) after addition of H_2S (as gas added to the suspension) in the presence of 2 mmol l^{-1} of Ca^{2+}.

Compounds	Concentration					
FeS (mmol l^{-1})	0	0.25	0.9	4.45	4.53	5.4[1]
in % of Tot-Fe		5	16	80	85	100
Fe(OOH)$\approx$P (mg l^{-1})	12.5	12.1	12.2	12.0	12.4	12.1
o-P (mg l^{-1})	0.1	0.32	0.33	.32	0.17	0.32
Fe^{2+} (dissolved)	0.0	n.d.				
FeS (mmol l^{-1})	0	1.2	1.5	2.3	3.15	
in % of Tot-Fe		22	28	42.5	58	
Fe(OOH)$\approx$P (mg l^{-1})	12.5	12.6	12.4	12.6	12.0	
o-P (mg l^{-1})	0.04	0.05	0.050	0.075	0.1	
Fe^{2+} (dissolved)	0.0	0.096	0.102	0.19	0.223	
in % of Tot-Fe		$\approx$2	$\approx$2	$\approx$4	$\approx$4	
Ca-NTA->P					12.5	
Ca-NTA->Fe					2.3 mmol = 43%	

Ca-NTA->P and Ca-NTA->Fe are o-P and Fe extractable with CaNTA + dithionite.

Experiments with clay.

A suspension was made from a marine clay (40 g l^{-1}). The clay consisted for the mayor part of illite, and contained 20% of $CaCO_3$ and some traces of apatite. Phosphate was added in increasing amounts to different subsamples of about 100 ml. After 4–5 days the remaining o-P, and the CaNTA and EDTA extractable P fractions were measured. The results are given in Table 3. Furthermore the Al concentrations in the NTA extracts (with and without dithionite) and in the subsequent EDTA extracts were measured.

It appeared that the Freundlich constant A approached a constant value only if the total amount of P_{ads} was taken into account and if B was set at 0.6. However, if the CaNTA extractable P_{ads} was taken, the constant B became again 0.333.

The Al concentrations found were 25 μg g^{-1} of clay in the Ca-NTA extract with and 27.5 μg g^{-1} in the Ca-NTA extract without dithionite and in the subsequent EDTA extracts 60 and 50 μg g^{-1} respectively after the addition of 12 mg l^{-1} of P, of which 50 μg g^{-1} were adsorbed on the clay as NTA extractable. The NTA extractable Fe(OOH) was 400 μg g^{-1}. This results in a Fe/P ratio of 8 and a Al/P ratio of 0.5.

Table 3. Phosphate adsorption onto a clay suspension. Suspension d.w. = 50 gr l^{-1}; pH = 8.3 extractable P= 0.071 mg g^{-1}. Two adsorption coefficients have been calculated: A (Tot) for the total amount adsorbed and A (FeOOH) for the NTA extractable amount.

P-added (mg l^{-1})	o-P (mg l^{-1})	CaNTA-P (mg l^{-1})	A (Tot) (B=0.6)	A (FeOOH) (B=0.333)
0	0.07	0.70	−0.34	1.73
2	0.88	1.44	1.21	1.50
4	1.52	1.88	1.93	1.64
6	2.75	2.14	1.77	1.53
9	5.20	2.71	1.41	1.57
12	7.42	3.50	1.38	1.81
				Mean: 1.63
				St.dev.: 0.12

Discussion

The two processes of P accumulation on sediments, adsorption and precipitation, must be well distinguished, although they are both reversible. However, precipitation leads to a constant, maximal, solute concentration, controlled by the solubility product, and all extra input into the system will precipitate. The solubility can easily be calculated when all components of the solid phase are known. For phosphate this means the Ca^{2+} concentration, the pH and the temperature, although the latter plays a minimal role. On the contrary, adsorption does not lead to a constant concentration and additional input will be distributed over the liquid and solid phases.

For the description of phosphate adsorption onto Fe(OOH) two equations are available, that of Freundlich and that of Langmuir. In the Langmuir equation, the energy of formation plays a role and it is assumed that there is a maximum number of sites, all energetically equal. It is, however, possible, and even likely, that the amount of energy involved in the formation of Fe(OOH)≈P is not constant. Spheric hindrance and/or shifts in the electric charges of the bondings involved may increase with increasing o-P adsorption. In a theoretical study I have shown (Golterman, 1994a), that if two molecules (sites) of Fe(OOH) are rendered inactive for every P adsorbed by one of these processes, the chemical equilibrium will mathematically lead to the Freundlich equation with $B=0.333$, or the cube root of o-P. If the factor two changes as the phosphate concentration increases, e.g. from 1.8 to 2.2 then the problem becomes insoluble, but the results will still cause the constant B to approach 0.33. The Langmuir isotherm permits a gradual change neither of the P adsorption capacity, nor of the bonding energy.

Curve fitting fails to distinguish between the Langmuir and the Freundlich equations because the two equations approach a straight line at low o-P concentrations and because of the relatively high imprecision in the data: If data are calculated with one equation and random errors of 5% are added, the two equations yield the same R^2 (Golterman, 1991).

The Freundlich equation was used by Einsele (1938) qualitatively to describe the adsorption onto Fe(OOH) and by Olsen (1964) quantitatively for the adsoprtion onto natural sediments. Fox (1992) mentioned the occurrence of iron bound phosphate in some soft water rivers and mentioned that the equilibrium concentrations follow the Freundlich isotherm. He gave, however, neither the calculated constants, nor the influence of pH or the Ca^{2+} concentration on the adsorption.

Twinch & Breen (1982), Gunatilaka (1982) and Brinkrnan (1993), among many others, used the Langmuir equation. Twinch & Green present data on the Langmuir constants b and K (in $1\ mg^{-1}$ and $1\ \mu g^{-1}$ resp.) as functions of sediment depth; the variability shown might be explained by assuming that the concentration of extractable Fe(OOH) varied with sediment depth. Neither of these authors addressed the question whether the bonding energy is constant or not.

Lijklema (1977) quantified the adsorption of o-P as Fe(OOH)≈P using the numerical fit:

$$P_{\mathrm{ads}}\,\mathrm{Fe} = 0.298 - 0.031\mathrm{pH} + 0.201(\mathrm{o} - \mathrm{P})^{0.5}. \quad (4)$$

This formula predicts that positive quantities will be adsorbed when o-P = 0, which obviously cannot be true.

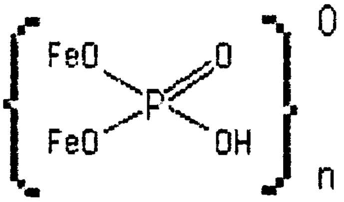
In trying to measure the two Freundlich constants, I noticed that the uncertainty in our experiments is larger than expected for chemical experiments. This is caused by different factors: variable temperature, the difficulty to keep the pH constant with low buffer concentrations (especially with the bicarbonate buffer and with the borax buffer at pH near 7). Furthermore, because of the frequent shaking or stirring colloidal particles may have been measured as dissolved phosphate. These different factors combined cause the R^2 values to be somewhat lower than expected. The values for B varied around 0.3. By setting B at 0.333, a somewhat lower R^2 was found; the use of the cube root can be explained theoretically (Golterman, 1994).

The influence of the Ca concentration on the adsorption can be described by:

$$A/A_{\max} = C - (C-1)e^{-\mathrm{Ca}}. \quad (5)$$

I choose this equation because the data suggested that the Ca influence can be described by an asymptote. If Ca = 0, the original equation (2) is reproduced and for Ca approaching 3 mmol l^{-1} its maximal influence is obtained. In two experiments the maximal influence was a factor 2.77 (2.68 and 2.86) times the adsorption constant without Ca^{2+}. Influence of the electrical double layer has been mentioned as the cause of this effect (Stumm & Morgan, 1981) and the fact that the influence approaches an asymptote strengthens this idea. There is, as yet, no chemical model explaining the Ca influence, but the R^2 is sufficiently high to justify the choice of equation (6).

Even the chemical structure of the Fe(OOH)≈P complex is not well known. Syers & Curtin (1989), proposed a binuclear complex of the following structure:



which they based on the studies with infrared absorption spectra of Parfitt *et al.* (1976), but it should be noted that the infrared spectra were made with dried samples. Drying, however, changes the structure of the Fe(OOH)$\approx$P complex. It seems not unlikely that hexahydrates $Fe(H_2O)_6(OOH)$ are involved.

$Al(OH)_3$ is often supposed to adsorb o-P as well (Lijklema, 1980; Danen-Louwerse *et al.*, 1993). Lijklema showed phosphate adsorption onto $Al(OH)_3$ in experiments *in vitro*, where high concentrations $Al(OH)_3$ were used in limited volumes. Danen-Louwerse *et al.* working in lakes did, however, not measure the Al, nor did they give any evidence of the existence of an Al-P complex. Their extraction methods (using NaOH and HCl and ammonium oxalate-oxalic acid; pH = 3) do not distinguish between Fe or Al bound P, while interference with org-P will occur (De Groot & Golterman, 1991). Thermodynamically it seems rather unlikely as $Al(OH)_3$ is not extremely insoluble ($pKs = 10^{-8}$, but depends strongly on the pH; complex formation with other compounds will increase this minimal solubility considerably, Ringbom, 1966[2]) and will not accumulate in sediments. It is even more unlikely that Al still bound into a silicate structure would be able to adsorb o-P. If there were an Al(OOH)$\approx$P complex it should be extractable with Ca-NTA, as the complex constant of Al-NTA is sufficiently small, while furthermore the presence of dithionite should not be necessary. When o-P was extracted with Ca-NTA I found only traces of Al in these extracts (in the order of magnitude of one tenth of the P adsorbed), and indeed the presence of dithionite made no difference. In the subsequent EDTA extracts also only traces of Al were found, negligible compared with the quantities of Fe (0.7 and 0.87 mg g^{-1} of clay). There are, therefore, till the present, no indications that $Al(OH)_3$ plays a role in the phosphate cycle in lake sediments. The situation is of course different from soils, were the solubility does not play such an important role and where Al-P complexes can be found (see, e.g., Beek *et al.* (1977) and Van Riemsdijk *et al.* (1977)).

P release under anoxic conditions

It is widely believed (Bostrøm *et al.*; 1982, Gächter & Meyer, 1993; De Jonge *et al.*, 1993 for marine sediments) that reduction of Fe(OOH), either by organic matter or by H_2S, with concomitant release of o-P, is the cause of o-P release under anoxic conditions in sediments following lake stratification (for a review of the old concept, see Golterman (1967)). When oxic conditions return after overturn, Fe(OOH), freshly precipitated or already present, would re-adsorb the o-P in solution. Although very few experiments have addressed the problem and no experimental data have been published, the assumption is nevertheless carried far. For example, Caraco *et al.* (1993), use an extremely vague correlation between sulphate and iron and phosphate release, not realising that, in the first place, the reducing capacity should be taken into account. Some doubt about this, now called classical picture, was expressed by Golterman (1973a, 1973b) who argued that Thomas (1965) showed that iron bound phosphate does not go into solution even in activated sludge digestion. Lee (1977) showed that this classical picture is not true in anoxic sediments from Lake Mendota. Golterman (1984) argued that the Fe(OOH)$\approx$P complex protects the Fe(OOH) against reduction (it is a more stable complex than Fe(OOH) itself) as long as the reducing capacity is not in excess — which is usually the case. I calculated that the reducing capacity due to sinking dead organic matter in a hypolimnion is usually only sufficient for the reduction of 1% of the Fe(OOH) present.

In our experiments there was only P release from Fe(OOH)$\approx$P if at least 75% or more of the Fe(OOH) was reduced. Large quantities of H_2S are, therefore, needed and with lower quantities o-P was not released at all. The fact that a sediment is black is, however, no indication that large amounts of FeS are indeed present. A suspension of 20% FeS + 80% Fe(OOH) is as black as a suspension of pure FeS.

In theory FeS and Fe(OOH) can not coexist in a suspension. Thermodynamically the following reaction must take place:

$$FeS + 2Fe(OOH) + 2H_2O \rightarrow S + 3Fe^{2+} + 6OH^- \quad (6)$$

---

[2] I measured a concentration of 55 $\mu g\ l^{-1}$ of Al^{3+} in an experimental tank with equilibrated hard water to which 1 g m^{-3} was added.

In natural sediments the two components may, however, exist together. The reaction rate is slow: when in our experiments 20% FeS was present, it took generally several days before the suspension became red again, with S becoming visible. There is, furthermore, a constant new formation of FeS in sediments following the reduction of SO_4^{2-} to H_2S, if sufficient sulphate is present. In a few lakes, the sulphate concentration may be limting factors, but normally it is the reducing capacity. In estuaries and lagoons the supply of sulphate is nearly unlimited. Furthermore, in our experiments and in those of De Groot (1991) indications for the formation of vivianite were found, if much FeS was formed, which will again not lead to the release of o-P as it is a rather unsoluble compound. De Groot (1991) did show that the release was small indeed when Na_2S solutions were added to Camargue and Garonne sediments containing Fe(OOH)≈P. The quantitative interpretation of his experiments is difficult, as the high pH of Na_2S may have induced shifts towards Ca-bound P.

If the reduction of Fe(OOH) is caused by organic matter in the hypolimnion, the reasoning does not change, as the energy released will be even less than with H_2S. The idea that under anoxic conditions P release originates from org-P and not from Fe(OOH)≈P is gradually beginning to be mentioned. De Montigny & Prairie (1993) showed that neither the Mortimer model, nor a bacteria-catalysed P release could explain Fe and P release from a highly organic sediment. They suggested that bacterial lysis was the source of P release in their experiments.

Gächter *et al.* (1988) challenged the Mortimer hypothesis again and tried to demonstrate the active role of bacteria. Unfortunately, the most likely source of P release in their flux chamber experiment is Ca-bound P. They argue that the Mortimer model is not true as Fe and P are not released at the same rate. They did not take Ca-bound P release into account, because the release rates were not the same, and even changed during their experiments. Both arguments are, however, not valid. If P were released from Fe(OOH)≈P with obviously a large excess of Fe(OOH) still present as well, the two release rates need not be identical. The same is true for Ca-bound P release. $CaCO_3$ and apatite are dissolved simultaneously, but the ratio of the two dissolution rates will depend, among other factors, on the degree of undersaturation following the drop of pH. Gächter *et al.* (1993) again stressed the importance of direct bacterial release. Their C and P cell contents of biovolume are, however, extremely high (Do bacteria not contain water?), while their overall result based on multiplying three reaction rates (from different lakes) with their inbuilt uncertainties, may cause errors of 100%. The only way to demonstrate from which source P is released is by using a functional fractionation scheme. I suggest that bacterial P could be measured as o-P in the hot NaOH extract after extraction with chelators and HCl, as suggested in De Groot & Golterman. In Camargue sediments this fraction is, however, never more than 5% of Tot-P.

It seems likely that the source of the release of org-P is one of the pools of organic phosphates (De Groot & Golterman, 1993; Golterman, 1994b; De Groot & Fabre, 1993). These pools are much larger if sequential extractions with chelators are used than with NaOH and HCl as extractants (De Groot & Golterman, 1991) and it seems likely that mineralisation of org-P is the source of anoxic P release. De Groot (1993) showed that one of these pools (Acid Soluble Organic P) was mineralised during desiccation of Camargue sediments. Moutin *et al.* (1993) and Mesnage & Picot (1994) showed seasonal variations in the pools of ASOP and ROP, and although the reaons for these variations are not yet understood, these fractions seemed to be relatively active. The phytate, measured in the ROP pool could well be the organic phosphate accumulation which Gächter suggests to be an important compound, not yet taken into account. After sedimentation, part of the recently deposited org-P escapes, following mineralisation, as o-P towards the hypolimnion, before it is entrapped as Fe(OOH)≈P, since the diffusion into the sediment is a slower process than dissolution into the overlying water.

The cause of the concurrent release of Fe^{2+} and o-P is the decreased exchange with the because of stratification, no longer mixed water column. As soon as stratification sets in and vertical mixing stops or is reduced, the o-P will accumulate just above the sediments, like the Fe^{2+}. When a hypolimnion becomes anoxic, the pH will automatically decrease because of the CO_2 produced. This will even enforce the adsorption of o-P onto Fe(OOH), but may solubilise apatite. It has to be studied whether this process leads to solubilisation of o-P in an anoxic hard water hypolimnion in addition the release from the org-P pool. Comparing soft with hard water lakes may suggest an answer to this question.

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