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Seasonal variations of P compounds and their concentrations in two coastal lagoons (Herault, France)

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Abstract

This article concerns seasonal variations in the phosphate concentrations in two coastal lagoons near Montpellier (Mediterranean coast, France). The o-P concentration in the overlying water is highest during summer. The role of the sediment, particularly that of the different P fractions in the sediment, is discussed. Significant variations, especially in the FeOOH$\approx$P fraction, occur. For both Tot-P_{sed} and the FeOOH$\approx$P fraction a gradient from surface to bottom is observed, as well as a distinct decrease in the FeOOH$\approx$P fraction in the surface sediments during summer and autumn. Variations in the FeOOH$\approx$P fraction appear to be compensated by variations in the $CaCO_3\approx$P fraction. These variations appear to be determined by the ferric hydroxide concentration. This compound represents only a small part (maximally 15%) of the total iron in the sediments and is related to the dissolved oxygen content of the immediately overlying water. Besides the fractions o-P, Fe(OOH)$\approx$P, a large part of the $CaCO_3\approx$P fraction is potentially bioavailable. A large proportion of the Tot-P_{sed} is therefore bioavailable.

Abbreviations: In principle the general abbreviations are used (see page vi). Furthermore:
Fe(OOH)$\approx$P = Ferric hydroxide bound phosphate
$CaCO_3\approx$P = Calcium carbonate bound phosphate
ASOP = Acid soluble phosphate
ROP = Residual organic phosphate
Tot-N = Kjeldhahl N (including NH_3)

Introduction

The coastal lagoons, which cover 13% of the world's coastal areas, are among the most productive ecosystems of the biosphere (Nixon, 1982). Their main characteristics are brackish water, shallowness and high productivity. As a result of the increase in input and the progressive accumulation of nutrients, the Mediterranean lagoons of Palavas (Languedoc, France) are subject to considerable eutrophication: algal followed by anoxic conditions and massive fish-kills occur frequently (Lieutaud *et al.*, 1992). The nutrients accumulate in the sediments, where they become more concentrated than in the water. Part of them can, under certain conditions and by different processes, return into solution (Lerman, 1978; Böstrom *et al.*, 1988; Enel & Löfgren, 1988).

Studies on phosphate dynamics must include the sediments (Golterman, 1982; Forsberg, 1989). This is even more important in the case of lagoons because here, as Nowicki & Nixon (1985) remarked, for a given sediment surface the water volume is small. The influence of benthic processes on water chemistry will therefore be strong.

Phosphate occurs in sediments in organic and inorganic form. The release of phosphate from sediments into the overlying water is related to the mineralisation of recently deposited organic matter and to fast mixing with the water column (Postma, 1981; Nowicki & Nixon, 1985; Sfriso *et al.*, 1988). The decomposition of the biodegradable organic matter in the sediments is enhanced by high summer temperatures. At that time the O_2 demand usually surpasses the input, which is restricted by the lower solubility of O_2 at higher temperatures. This decrease in oxygen content of the deepest water may influence the inorg-P in the sediments.

This paper concerns the mechanisms that may explain the seasonal variations in P measured in the overlying water and in the sediments.

Materials and methods

In 1990 two coastal lagoons (site A: étang du Prévost, surface 2.9 10^6 m^2 and volume 2.4 10^6 m^3, sites B and C: étang de l'Or, surface 32 10^6 m^2 and volume 25 10^6 m^3) were studied. Sampling was carried out during four seasons. Variables were measured simultaneously in the overlying water, the interstitial water and the sediments.

Three sampling sites were chosen because of their difference in salinity: A: high salinity, B: intermediate salinity, C: low salinity. The sites and the corresponding catchment area are represented in Fig. 1.

Chemical analyses

pH, temperature, O_2 and salinity were measured in the field, directly after sampling. The pH meter (Ponselle) was calibrated each time just before the measurements. The chemical analyses were carried out according to the French norms for water analysis (AFNOR): o-P using molybdate-antimony, ammonia using indophenol, Ca^{2+} with atomic absorbtion, org-C was measured as CO_2 (I.R. photometry) after digestion, Tot-N using Kjeldahl method. Iron was measured after Golterman *et al.* (1978), I.B.P. no. 8, 4.5.1.

Overlying water

Three samples, at three depths (surface, middle, bottom), were taken at each site in each season in the middle of the afternoon. The samples, kept at 4 °C, were filtered (GF/F filter) the same day and analysed the next day. The chlorophyll content was determined in a sample taken the same month, but not always on the same day.

Sediments

5 cm sediment samples, down to 25 cm depth, were obtained by means of a corer at each site and in each season. pH was measured at once by putting the electrode in the sediment each five centimeter (Table 2). Each sample, kept at 4 °C, was brought to the laboratory for immediate sieving, first a 2 and then a 0.2 mm sieve. The homogeneous suspension (<200 μm) was divided into two parts; one for determination of the P fraction, the other to be lyophilised. The parameters, granulometry, water content (H = water weight/total weight) and porosity ($\varnothing = Vol_{water}/Vol_{tot}$), were determined in the 2 mm sieve preparation, and the variables (Tot-Ca, Tot-Fe, org-C and Tot-N) were determined in the lyophilised sediment fraction, in the spring samples.

Sequential phosphate extraction was carried out according to Golterman & Booman (1988) and de Groot & Golterman (1990) (see Fig. 2). This method uses chelating agents for the extraction of the inorganic part, *i.e.* the $FeOOH \approx P$ and $CaCO_3 \approx P$. Two organic fractions were separated: ASOP and ROP. On the sampling day a suspension of about 0.1 g ml^{-1} of sediments was

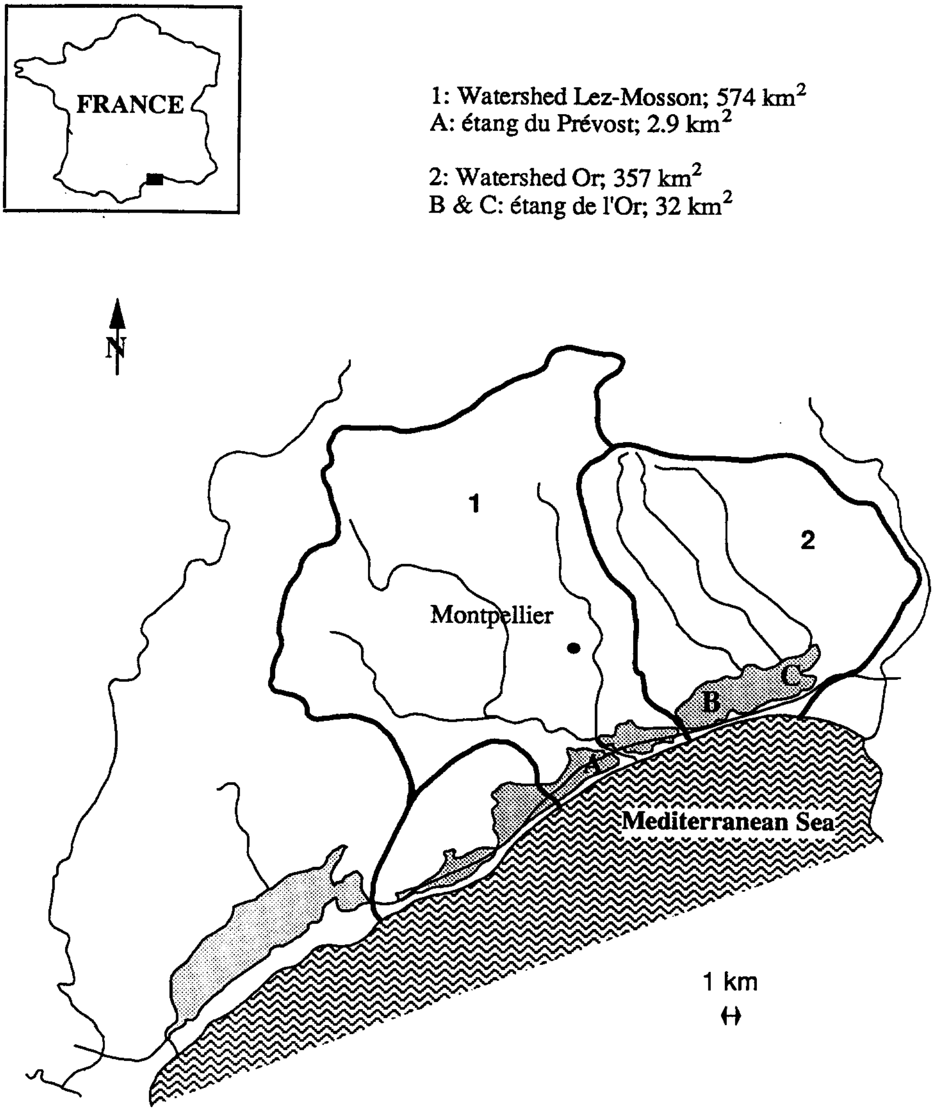

Fig. 1. Map of the study area and localisation of the three sites A, B & C.

passed through a 0.2 mm sieve and stored at 4 °C. The analysis was started the next day.

Calculation of the extrapolated solubility product of apatite

The solubility product of apatite, $Ks = (Ca^{2+})^5 (PO_4^{3-})^3(OH)$, was calculated considering the following equilibria:

$$Ca_5(PO_4)_3OH \Leftrightarrow 5Ca^{2+} + 3PO_4^{3-} + OH^-$$

$$H_3PO_4 + H_2O \Leftrightarrow H_2PO_4^- + H_3O^+$$

$$H_2PO_4^- + H_2O \Leftrightarrow HPO_4^{2-} + H_3O^+$$

$$HPO_4^{2-} + H_2O \Leftrightarrow PO_4^{3-} + H_3O^+$$

Ionic strength is calculated according to Talbot *et al.* (1990) from the relation:

Table 1. Characteristics of the overlying water (mean and std dev. of three measurements for each season in the water column).

Site		A					B					C				
Season		Spring	Summer	Autumn	Winter	Mean	Spring	Summer	Autumn	Winter	Mean	Spring	Summer	Autumn	Winter	Mean
Temperature (°C)		9.1 ± 0.1	24.6 ± 0.4	20.9 ± 0.4	10.3 ± 0.2	16 ± 8	13.1 ± 0.1	27.7 ± 0.6	14.0 ± 0.2	7.2 ± 0.3	16 ± 9	14.0	26.6 ± 0.4	20.5 ± 0.5	8.0 ± 0.2	17 ± 8
Salinity (g l^{-1})		20.6 ± 0.2	33.7 ± 0.4	28.9 ± 0.7	32.3 ± 0.5	29 ± 6	21.2 ± 0.1	21.1 ± 1.1	15.2 ± 0.3	16.1 ± 1.9	18 ± 3	13.8	15.2 ± 0	18.7 ± 0.5	14.8 ± 0.5	16 ± 2
O_2	Surf.	10.5	5.1	8.6	9.7	8.5 ± 2.4	10.4	6.6	9.5	> 15	> 10.4 ± 3.5	11.4	4.5	13.2	> 15	11.0 ± 4.6
(mg l^{-1})	Mid.	10.5	5.2	6.9	9.5	8.0 ± 2.4	10.3	6.6	9.5	> 15	> 10.4 ± 3.5	11.8	4.1	12.5	> 15	10.9 ± 4.7
	Bot.	8.6	4.1	5.2	9.5	6.9 ± 2.6	10.4	6.2	0.6	7.2	6.1 ± 4.1	11.8	3.2	3.8	13.8	8.2 ± 5.4
pH		8.94 ± 0.01	8.36 ± 0.03	8.15 ± 0.03	8.02 ± 0.01	8.4 ± 0.4	8.55 ± 0.01	7.87 ± 0.01	7.90 ± 0.01	8.54 ± 0.23	8.2 ± 0.4	9.18 ± 0.05	7.67 ± 0.02	8.08 ± 0.15	8.47 ± 0.06	8.4 ± 0.6
Calcium (mg l^{-1})		378 ± 4	339 ± 7	306 ± 2	300 ± 7	331 ± 36	287 ± 6	233 ± 5	221 ± 5	194 ± 8	234 ± 39	258 ± 5	181 ± 7	225 ± 2	191 ± 4	214 ± 35
o-P (μg l^{-1})		5 ± 2	22 ± 3	4 ± 1	8 ± 3	10 ± 8	44 ± 2	491 ± 42	5 ± 2	4 ± 0	136 ± 237	15 ± 2	193 ± 9	168 ± 23	2 ± 1	95 ± 100
Total P (μg l^{-1})		99 ± 20	143 ± 9	148 ± 41	87 ± 27	119 ± 31	147 ± 67	817 ± 33	344 ± 10	276 ± 24	396 ± 292	126 ± 39	528 ± 7	937 ± 46	290 ± 52	470 ± 352
Ammonia (μgN l^{-1})		1.0	16 ± 11	9 ± 6	25 ± 9	13 ± 10	16 ± 3	13 ± 2	11 ± 2	15 ± 6	14 ± 2	6 ± 2	25 ± 5	17 ± 12	10 ± 5	15 ± 8
Chlorophyll *a* (μg l^{-1})		3.6	12.2	162		59 ± 89	2.5	14.8	176.2	41.1	59 ± 80	2.7	40.9	248.8	34.4	82 ± 113
Pheophytin (μg l^{-1})		18.8	6.2	33		19 ± 13	1.5	12.0	58.6	25.1	24 ± 25	1.0	32.7	113.6	11.2	40 ± 51

Table 2. Characteristics of the sediment (* value for Spring period, ** mean value of 8 measurements).

Site	A					B					C				
Depth (cm)	0–5	5–10	10–15	15–20	20–25	0–5	5–10	10–15	15–20	20–25	0–5	5–10	10–15	15–20	20–25
Clay (%)	27.4				35.0	35.2				41.8	30.2				48.2
Fine silt (%)	27.1				37.5	21.5				44.0	24.8				43.2
Coarse silt (%)	11.2				8.2	11.1				5.3	7.4				3.0
Fine sand (%)	11.7				6.4	5.9				5.8	18.4				3.2
Coarse sand (%)	22.5				12.9	26.0				3.1	19.2				2.3
Water content (%)	52.2	49.4	52.0	53.9	54.2	64.6	64.5	62.1	58.1	55.9	66.1	61.0	61.1	59.3	65.4
Porosity (%)	72.5	69.1	72	73.3	73.1	79.4	80.3	80.8	77.7	72.7	79.8	78.9	77.7	76.7	80
Total phosphorus** (μ g^{-1})	617	556	514	500	477	561	398	354	338	345	575	374	327	291	290
Std deviation	34	36	26	24	22	40	17	19	15	17	82	38	28	12	22
pH Spring*	7.68	7.55	7.39	7.38	7.39	8.30	7.49	7.48	7.24	7.22	8.13	7.34	7.31	7.22	7.00
pH Summer	6.99	6.88	7.01	6.87	6.86	7.55	7.44	7.15	7.10	7.05	7.31	7.15	7.09	7.06	7.00
pH Autumn	7.40	7.55	7.30	7.26	7.12	7.01	6.86	6.88	6.87	6.92	7.04	6.96	6.99	6.91	6.86
pH Winter	7.51	6.90	6.89	6.81	6.77	7.63	7.52	7.14	7.12	7.09	7.36	7.28	6.96	6.88	6.86
Total calcium (mg g^{-1})*	119	118	113	116	121	126	95	83	79	84	138	134	134		135
Total iron (mg g^{-1})*	17.4	18.0	21.2	20.0	20.4	17.1	22.0	24.3	23.7	22.9	15.7	17.3	17.4		17.3
Total organic P (μg g^{-1})*	194	176	169	156	149	243	189	165	166	178	246	125	110	139	153
Organic carbon (mg g^{-1})*	19.8	21.9	20.5	20.0	20.6	39.4	36.8	27.8	21.4	17.1	41.0	27.5	26.7	21.5	22.8
Total nitrogen (mg g^{-1}*	2.32	2.91	2.44	2.38	2.63	4.94	4.38	3.11	2.34	1.87	5.08	3.31	3.08		2.36

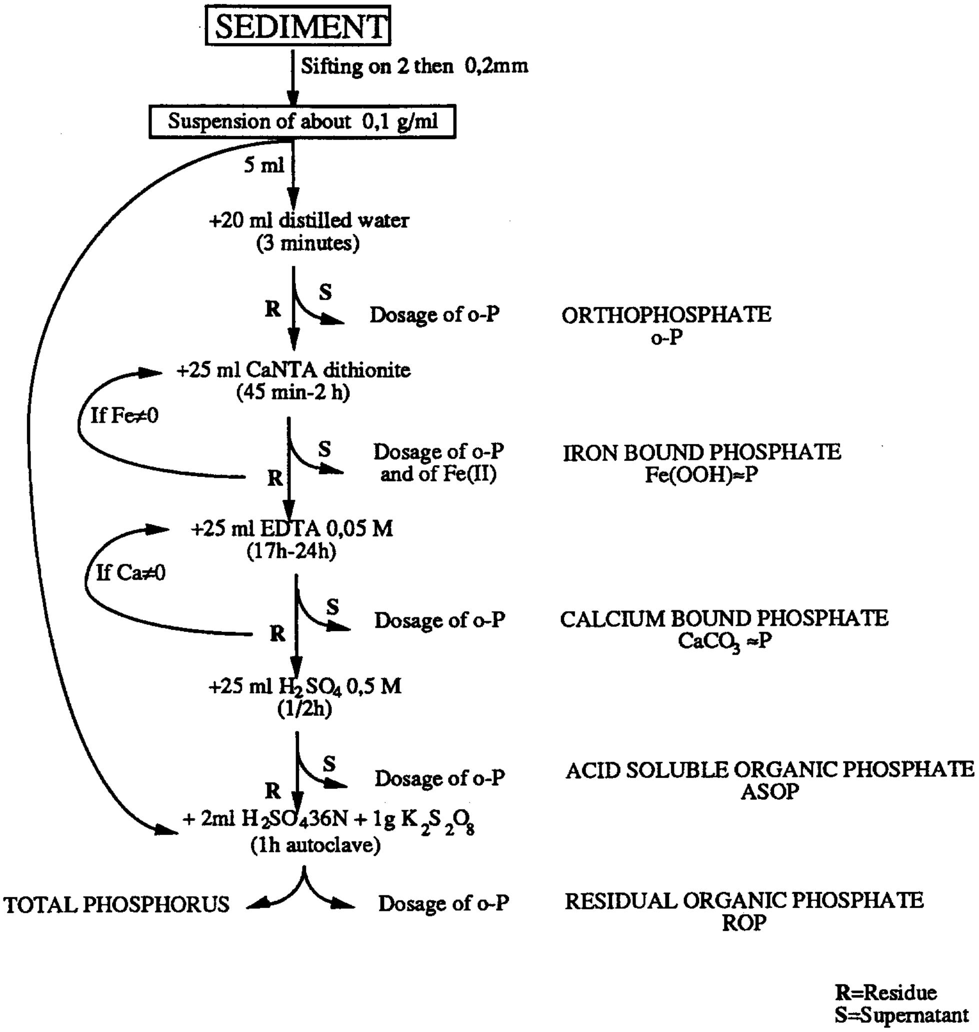

Fig. 2. Sequential extraction of sediment P according to Golterman & Booman (1988) and De Groot & Golterman (1990).

$$I = 0.0021 + 0.0148\,x_{25}$$

where

x_{25} = conductivity at 25 °C in μS cm^{-1}

I = ionic strenght (mM)

Activity coefficients of the z-valent ions, γ_z, were calculated from the modified Debye-Hückel equation (Davies, 1964):

$$\mathrm{Log}\,\gamma_i = -A * z_i^2 * f(I)$$

$$\text{with } f(I) = \left(\frac{I^{0,5}}{1 + I^{0,5}} - 0,3 * I\right)$$

where

I = molar ionic strenght

A = the Debye-Hückel constant;

we use A = 0.5.

From the dissociation constant of H_3PO_4 ($pK_{a3} = 12,3$, $pK_{a2} = 7,2$, $pK_{a1} = 2,2$), we calculate:

$$[\text{o-P}] = \alpha_{PO_4(H,I)}[PO_4^{3-}]$$

with

$$\alpha_{PO_4(H,I)} = 1 + \frac{(H_3O^+)}{K'_{a3}} + \frac{(H_3O^+)^2}{K'_{a3}K'_{a2}} + \frac{(H_3O^+)^3}{K'_{a3}K'_{a2}K'_{a1}}$$

and

$$pK'_{a3} = pK_{a3} - 2{,}5 * f(I),$$
$$pK'_{a2} = pK_{a2} - 1{,}5 * f(I),$$
$$pK_{a1} = pK_{a1} - 0{,}5 * f(I)$$

Thus:

$$Ks^* = \frac{\gamma_2^5[Ca^{2+}]^5\gamma_3^3[\text{o-P}]^3(OH)}{\alpha^3_{PO_4(H,I)}}$$

$$\text{with } (OH) = \frac{10^{-14}}{(H_3O^+)}$$

All the calculations are carried out for T = 25 °C because the effect of the temperature is less than the effect of the ionic strength.

Calculation of the quantity of P adsorbed onto FeOOH

Golterman (1988) proposed to calculate the quantity of P adsorbed onto FeOOH using the following equation:

$$P/Fe = A[\text{o-P}]^B$$

where

$A = 0.1847 - 0.017pH$
$B = 0.2$
$[\text{o-P}]$ = o-P concentration in $mg \cdot l^{-1}$
P/Fe = mg of P adsorbed per mg of Fe (FeOOH).

The o-P concentration used is the value obtained in the first step of the fractionation scheme (Fig. 2).

Results

Overlying water

The values shown in Table 1 represent the mean and the standard deviation of three analysis. For O_2 the three results are given.

In the course of the year temperatures varied between 7.2 and 27.7 °C. Salinity was higher at site A (28.9 ± 5.9 g l^{-1}) than at site B (18.4 ± 3.2 g l^{-1}) and at site C (15.6 ± 2.1 g l^{-1}). The O_2 concentrations decreased at the three sites from spring till summer. In summer they were distinctly below saturation. A clear difference between the O_2 concentrations of the surface and bottom waters appeared, particularly in autumn. pH also decreased from spring till summer. The lowest value was 7.67 (site C, summer); the highest value was 9.18 (site C, spring). The largest variations occurred at site C.

Calcium concentrations were high (Site A: 331 ± 36, site B: 234 ± 39, Site C: 214 ± 35 mg l^{-1}). These concentrations also decreased at the three sites in summer. The o-P concentrations varied between 2 and 491 μg l^{-1}. The maximum was always observed in summer. The variations in concentrations were larger at site B and site C (Etang l'Or) than at site A (Etang du Prévost). The Tot-P_{diss} concentrations were considerably higher than the o-P concentrations. The minimum (87 ± 27 μg l^{-1}) was observed at site A in December and the maximum (937 ± 46 μg l^{-1}) at site C in September. The maximal concentration at site A was 148 ± 41 μg l^{-1}. The mean NH_3 concentrations were low (site A: 13 ± 10, site B: 14 ± 2, site C: 15 ± 8 μg l^{-1}). The minimum was found at site A in spring.

Sediments

The main characteristics of the sediments are represented in Table 2. Granulometry of the sediments of the three sites showed a composition of about one third clay (< 2 μm), one third silt 2–50 μm) and one third sand (> 50 μm). The clay and fine silt content (< 20 μm) increased with depth, while the coarse silt and fine and coarse sand concentrations decreased. The water content of the surface sediments was lower at site A, where it was 52% of total sediment weight, while it was 64.6% and 66.1% at sites B and C respectively. Porosity was 72.4, 79.4 and 79.8% of the total volume for site A, B and C respectively. Interstitial water was on the average 61% of the weight and 77% of the volume of the surface sediments.

The Tot-P concentration in the surface sediment was higher at site A ($617 \pm 34\ \mu g\ g^{-1}$) than at sites B and C (561 and 575 $\mu g\ g^{-1}$). The concentration decreased with depth at all sites. At site A the concentration decreased gradually with depth, while at site B and C a sudden decrease in concentrations occurred between the first and second 5 cm layers (163 and 201 $\mu g\ g^{-1}$ resp.).

In all cases the sediment pH decreased with depth. The maximum was observed at the surface in spring (Site A: 7.68, site B: 8.30, site C: 8.13). A considerable decrease in pH was observed between spring and summer. The minimum at site A was observed in summer (6.99); at sites B and C in autumn (7.01 and 7.04 resp.). The largest variations in pH were therefore observed at the latter two sites.

The calcium concentration in the sediments was very high. Supposing Ca to be mainly present at $CaCO_3$, this represented between 20 and 35% (d.w.) of the sediment. The Ca phosphate concentration was negligible. (e.g. at site A, where the $CaCO_3 \approx P$ concentration is a maximum at the surface, the concentration of Ca bound as $CaCO_3 \approx P$ was only 0.56%, assuming that the Ca phosphate occurred only as apatite). Calcium concentrations at site A (120 mg g^{-1}) and site C (135 mg g^{-1}) hardly changed with depth. At site B the maximum observed at the surface (126 mg g^{-1}) and the concentrations decreased with depth to about 80 mg g^{-1} between 10 and 25 cm.

Tot-Fe in the sediment was between 15.7 and 24.3 mg g^{-1} (d.w.). The minimum concentrations occurred at the surface at all three sites. The lowest concentrations were measured at site C.

The org-P (ASOP + ROP) decreased with depth at all sites. The org-C and Tot-N concentrations varied in the same way.

$$\text{org-C} = 0.27 + 7.54 * \text{Tot-N},\ R^2 = 0.97,\ n = 15.$$

Maximum concentrations occurred at the surface at sites B and C ($C \approx 4$ mg g^{-1} and $N \approx 0.5$ mg g^{-1}) and decreased with depth (2 and 0.2 resp.). At site A the values ($C \approx 2$ mg g^{-1} and $N \approx 0.25$ mg g^{-1}) hardly varied with depth.

Figure 3 gives the results of the fractionation of P_{sed}; the X-axis presents depth and season, while the Y-axis presents the P concentration.

A decrease in Tot-P^{sed} with depth was observed at all sites in all seasons. The annual mean for each depth is given in Table 1. The sum of the fractions (Fig. 3) for a given depth varied little in the course of the year except at site C, where a minimum was observed for the surface sediments in September. The o-P fraction was $1.1 \approx 0.5\%$ of the Tot-P^{extr}; the minimum was 0.4% and the maximum 2.4%.

$Fe(OOH) \approx P$ was $9.4 \pm 5.1\%$ of Tot-P_{extr}. The values were always maximal in the top 5 cm layer ($15.1 \pm 5.6\%$) and decreased with depth. This gradient was observed at all sites and in all seasons. For each site the values for the surface sediments are highest in spring (Site A: 80, site B: 110 and site C: 172 $\mu g\ g^{-1}$) and lowest in autumn (48, 50 and 56 $\mu g\ g^{-1}$). The difference was larger at site C (116 $\mu g\ g^{-1}$) than site B (60 $\mu g\ g^{-1}$) and site A (32 $\mu g\ g^{-1}$). In all cases the $Fe(OOH) \approx P$ was highest in spring, decreased from spring till summer and from summer till autumn, and increased from autumn till winter. Iron was measured with the same extraction and was supposed to be FeOOH which can absorb o-P. It was maximally 15% of the Tot-Fe_{sed}.

The $CaCO_3 \approx P$ fraction was the largest ($47.9 \pm 8.8\%$). The maximum was found at the surface at all three sites (312 ± 34, 202 ± 45 and $229 \pm 45\ \mu g\ g^{-1}$ respectively). The concentrations are highest at site A were the calcium concentrations in the water were also highest. The concentrations decreased slightly with depth, but much less than the $Fe(OOH) \approx P$ fraction: the following values correspond with the 20–25 cm

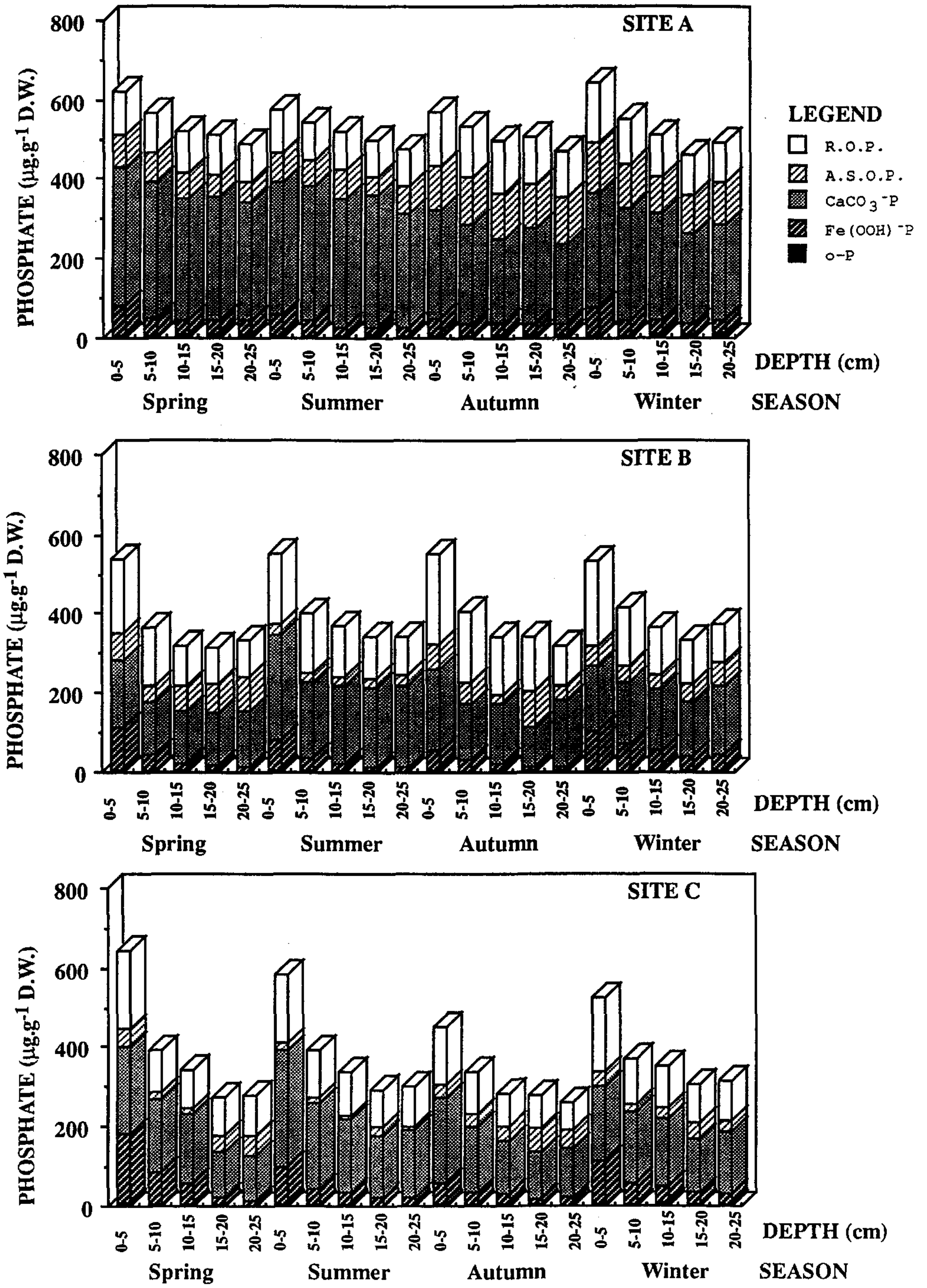

Fig. 3. Seasonal variations of P-fractionation in the sediments.

layer (Site A: 258 ± 45, site B: 172 ± 29, site C: 140 ± 28 $\mu g\ l^{-1}$). As to the seasonal variations, a maximum was noted for sites B and C in summer (Site B: 262, site C: 294 $\mu g\ g^{-1}$) and a minimum in winter (Site B: 164 $\mu g\ g^{-1}$, site C: 188 $\mu g\ g^{-1}$). At site A the maximum was noted in spring

(346 $\mu g\ g^{-1}$) and the minimum in autumn (276 $\mu g\ g^{-1}$). The ASOP fraction (12.8 ± 6.4%) was higher at site A (87 ± 28 $\mu g\ g^{-1}$) than at sites B (49 ± 21 $\mu g\ g^{-1}$) and C (31 ± 13 $\mu g\ g^{-1}$). No significant variations with depth were observed.

The ROP fraction (28.8 ± 6.9%) was highest at the surface at all three sites and lower at site A (Site A: 128 ± 18, site B: 203 ± 24, site C: 177 ± 21 $\mu g\ g^{-1}$). The concentrations decreased with depth; for the sediments of the 20–25 cm layer they were: (Site A: 102 ± 11, site B: 95 ± 5, site C: 93 ± 15 $\mu g\ g^{-1}$). The analytical error, calculated as $(2 * |\Sigma Fr\text{-}Tot\text{-}P|)/(\Sigma Fr + Tot\text{-}P)$ was 5.7% ($n = 60$).

Discussion

Phosphate cycles in many coastal lagoons show remarkable analogies, especially the summer maximum of the o-P in the overlying water which is generally related to the mineralisation of organic matter at the bottom when temperature are high (Nixon, 1982; Postma, 1981; Sfriso, 1988). The calcium concentrations in the lagoons are high and the pH measured in the overlying water is always higher than the pH at which calcium phosphate precipitate. To explain the concentrations in the overlying water an equilibrium with an inorganic calcium phosphate compound may be assumed. The decrease in pH observed during summer might partly explain the increase in o-P concentrations during this period. Another similarity between many lagoons is the limit of the maximum concentrations measured (generally below 150 $\mu g\ l^{-1}$). Nixon (1982) questioned why the differences in external input did not entail more differences in the concentrations. Although the input from the catchment area is much higher at site A than at sites B and C (Lieutaud *et al.*, 1992), the maximum o-P concentration in the overlying water is lower at site A where calcium concentrations are very high. The extrapolated solubility product (Table 3) pKs* = 51.6 ± 2.4 may be compared with the extrapolated solubility product calculated from data published by Golterman (1982) for 2 natural hard water rivers: pKs* = 51.1 ± 0.9. The larger standard deviation observed in coastal lagoons may partly be explained by the influence of algae caused rapid changes in the pH and o-P values.

The difference between the concentrations of o-P and Tot-P_{diss} cannot be explained entirely by the presence of phytoplankton, except in autumn. Analysis of the white precipitate recovered on the filter when a sample, taken in a period without algal bloom, was filtered, showed that it contained phosphates and carbonates: part of Tot-P_{diss} is suspended in the form of calcium phosphate. Tot-P_{diss} does not represent all the P in the water column; a considerable part is stored by macrophytes. The appearance and spread of *Ulva* sp. in

Table 3. Data for the calculation of the extrapolated solubility product of apatite Ks*.

[calcium] M	[o-P] M	pH	Conductivity mS cm^{-1}	Ionic strength (I) M	f(I)	Ks*
9.4E-3	1.6E-7	8.94	33.3	0.5	0.3	49.9
8.5E-3	7.1E-7	8.36	50.2	0.7	0.2	50.1
7.6E-3	1.3E-7	8.15	43.7	0.6	0.3	53.6
7.5E-3	2.6E-7	8.02	48.3	0.7	0.2	53.2
7.2E-3	1.4E-6	8.55	34.3	0.5	0.3	49.2
5.8E-3	1.6E-5	7.87	34.1	0.5	0.3	49.3
5.5E-3	1.6E-7	7.90	24.6	0.4	0.3	55.3
4.8E-3	1.3E-7	8.54	26.1	0.4	0.3	53.3
6.4E-3	4.8E-7	9.18	22.4	0.3	0.3	48.3
4.5E-3	6.2E-6	7.67	24.6	0.4	0.3	52.0
5.6E-3	5.4E-6	8.08	30.3	0.4	0.3	50.0
4.8E-3	6.5E-8	8.47	24.0	0.4	0.3	54.5

spring is an immediate result of the eutrophication of these lagoons. In the water compartment they can contain up to 35 times more P (g m^{-2}) than the surrounding water at site A during part of the year (Lieutaud *et al.*, 1992). Rapid decomposition of these *Ulva* sp. has needs a direct effect on the o-P concentration in the water column, but this is limited because of calcium phosphate precipitation: the equivalent of the maximal P concentration in the *Ulva* sp. is never observed in the water. Calcium appeared to play the role of a regulator of o-P concentration in the overlying water.

The sediments influence obviously the relation between P input and concentration observed. The change in Tot-P_{sed} concentration with depth appears to be a clear indication that the input from the catchment area is increasing with time. A decrease in Tot-P_{sed} concentrations (Σfractions) with depth was in fact observed in all cases (Fig. 3). The sudden change between the layers 0–5 cm and 5–10 cm at sites B and C can be related to the increase in population of the catchment area, which is distinctly greater than that of the population of the catchment area of site A (Crivelli & Ximenes, 1992).

In the sediments, the o-P fraction represents in the order of 1% of the Tot-P_{sed}, the Fe(OOH)$\approx$P 9%, the $CaCO_3 \approx$P 48%, the ASOP 13% and the ROP 29%. The results shown in Fig. 3 indicate a similarity of Tot-P_{sed} and of the fractions for sites B and C which lie, however, at a distance of several km. This suggests on the one hand a relative homogeneity of the storage mechanisms for P from the water column to the sediments for the whole lagoon, and, on the other hand, a relatively poor sediment mixing.

The largest fraction is that of the calcium-bound phosphate. Precipitation of calcium phosphate must be considered as an essential storage mechanism for P in sediments.

Among the other fractions of the Tot-P_{sed}, the Fe(OOH)$\approx$P fraction is considered to be the most reactive one in the lake environment, as release from the sediments to the overlying water is usually associated with reduction of Fe(OOH) and therefore with release of P adsorbed onto their surface (Mortimer, 1942). Golterman (1984) indicates that phosphate seems to protect iron from reduction and therefore that the P release generally associated with the reduction of iron may partly be of organic origin. The amount of Fe(OOH)$\approx$P is always highest at the surface and decreases rapidly with depth in close relation with the iron hydroxide concentration (Fig. 4). For all analyses together we found the following correlation between Fe(OOH)$\approx$P and Fe(OOH):

$$\mathrm{Fe(OOH)} = 12.5 + 0.052 * \mathrm{Fe(OOH)} \approx \mathrm{P}, \quad R^2 = 0.82,\ n = 45 \text{ with P in } \mu\mathrm{g\,g^{-1}}$$

The correlation improves when we look at each site separately, as is shown in Fig. 4. The amount of FeOOH practically determines the quantity of P adsorbed onto these hydroxides. This compound represents maximally 15% of the Tot-Fe concentration. Thus, the 'active' iron represents only a small proportion of the total iron in the sediments.

The Fe(OOH) concentration depends on the redox conditions, which in turn depend on the bacterial activity of an environment with a given chemical composition. The variations in pH in the sediments reflect the variations in redox conditions and it is possible to relate the FeOOH concentration to the pH of the surface sediments (Fig. 5.1). The O_2 content of the water overlying the water-sediment interface can be related to the pH of the surface sediment (Fig. 5.2: the value for site C in December has been discarded from the regression calculation). The lower the O_2 content, the lower the pH. It is therefore possible to relate for a given ecosystem the O_2 concentration of the water near the interface to the amount of P adsorbed onto the Fe(OOH) in the surface sediments (Fig. 5.4): nitrate, which act as an intermediate electron acceptor is supposed to play an unimportant role in this ecosystem because of its low concentration in water and sediment. To test the validity of the correlations (Fig. 5), we used the critical value for the correlation coefficient. All relations are significant ($p < 0.01$).

In Fig. 4, relation of iron bound phosphate with iron hydroxide in the sediments is shown; for the surface sediments the season are represented. The

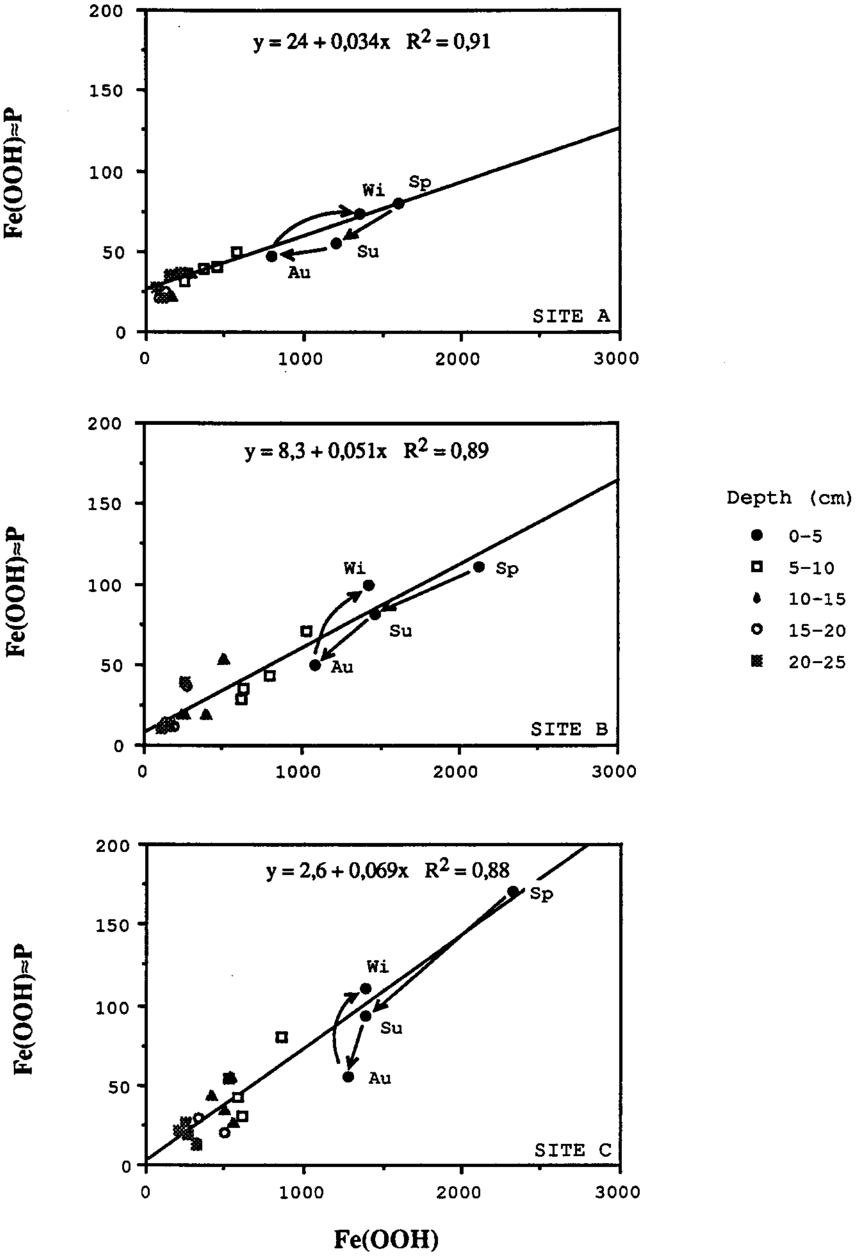

Fig. 4. Iron bound phosphate versus iron hydroxide in the sediment (both in $\mu g\ g^{-1}$ of DW).

reduction of Fe^{3+} between spring and summer and the oxidation between autumn and winter appear distinctly. Part of the Fe(OOH) is reduced when the O_2 content of the bottom water, and therefore the redox conditions of the sediment, are low: part of the Fe(OOH) probably becomes FeS. The quantity of Fe(OOH)≈P depends very much on the state of the hydroxide (Lijklema, 1977): This is clearly shown at sites B and C where between autumn and winter, a small quantity of recently oxidized Fe(OOH) adsorbed much P. On the contrary, the quantity of P released into the interstitial water between spring and summer is proportional to the quantity of reduced iron. In

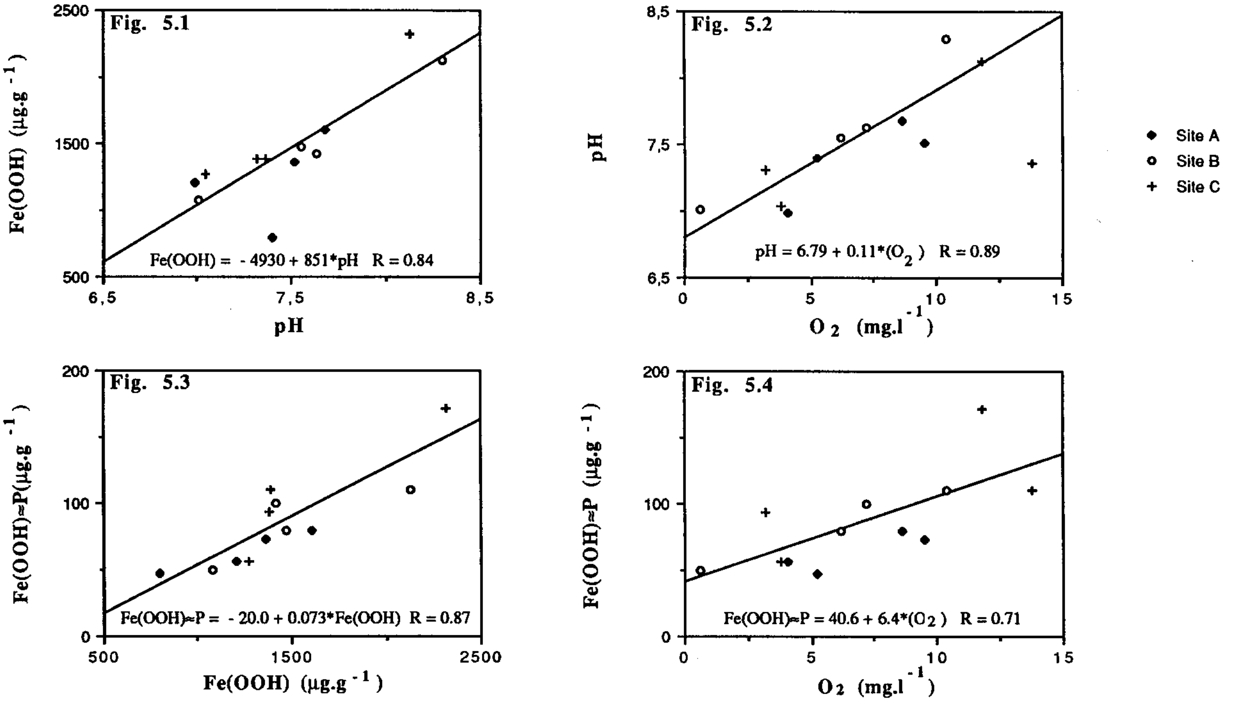

Fig. 5. 1,2,3,4. Simple regression between Fe(OOH), Fe(OOH)≈P and pH measured in surface sediment, and O_2 measured in bottom water.

Table 4, the measured quantity of P adsorbed onto FeOOH in surface sediments, and the value calculated according to the equation of Golterman (1988), are indicated. The values show good agreement, the change in FeOOH may explain the change in FeOOH≈P. The variations of

Table 4. Comparison betwen FeOOH≈P measured and calculated according to the equation of Golterman (1988).

Site	Season	pH sediment	[o-P] measured 1 extraction		P/Fe calculated mgPads/mgFe	FeOOH measured $\mu g\, g^{-1}$	FeOOH≈P calculated $\mu g\, g^{-1}$	FeOOH≈P measured $\mu g\, g^{-1}$
			($\mu g\, g^{-1}$)	($mg\, l^{-1}$)				
A	Spring	7.68	4.4	2.9	0.067	1610	108	80
	Summer	6.99	2.7	1.8	0.074	120	89	56
	Autumn	7.40	3.7	2.4	0.070	800	56	48
	Winter	7.51	3.6	2.4	0.068	1360	92	73
B	Spring	8.30	2.7	1.3	0.046	2130	98	111
	Summer	7.55	2.5	1.2	0.059	1470	86	81
	Autumn	7.01	3.2	1.6	0.072	1080	77	50
	Winter	7.63	3.1	1.5	0.060	1420	85	100
C	Spring	8.13	10.2	5.0	0.064	2320	149	172
	Summer	7.31	4.8	2.3	0.072	1380	99	94
	Autumn	7.04	2.6	1.3	0.068	1270	87	56
	Winter	7.36	4.7	2.3	0.070	1390	98	111

FeOOH may probably be explained by a mineralisation process: the organic material is essentially composed by Ulva and we measured a net decrease of the biomass in the end of the Spring period, and a complete desperation between the end of summer and autumn at site A (Lieutaud, 1992).

The amount of $Fe(OOH)_{sed}$ which can be reduced, can be calculated as done by Golterman (1984), who found in a hypothetical lake that only 2 to 3% of the primary productivity was available for this process causing a reduction of less than 1% of the iron. With our data (primary productivity = 200 g m^{-2} y^{-1} of C (Vaulot & Frisoni, 1982) and $Tot\text{-}Fe_{sed} \approx 20$ mg $g^{-1} \approx 0.5$ kg m^{-2} (0–5 cm)), and assuming 2.5% of the primary productivity again available and that 1 equivalent of reducing power equals 4 g of C, we arrive at the following calculation:

$[(2.5/4) * 56]/500 = 7\%$ of the $Tot\text{-}Iron_{sed}$ may be reduced considering the precedent hypothesis. This correspond to 1400 μg g^{-1} of Fe, which is approximately the quantity observed (Fig. 4).

The great variations observed in the $Fe(OOH) \approx P$ fraction ought to lead to a very high concentration of o-P in the interstitial water in summer and in autumn; it should be found in the first extraction of the sequential analysis carried out with distilled water. This, however, is not the case; it seems that the variations in the $Fe(OOH) \approx P$ fraction are compensated by variations in the $CaCO_3 \approx P$ fraction. The interstitial water is a calcium-rich environment and the release of o-P from the $Fe(OOH) \approx P$ fraction can lead to the formation of inorganic calcium phosphate. Figure 6 shows the variations in the $CaCO_3 \approx P$ fraction in relation to the variations in the $Fe(OOH) \approx P$ fraction for the surface sediments. The line indicates that the same quantity of $Fe(OOH) \approx P$ is converted into $CaCO_3 \approx P$ or vice versa. A solubility equilibrium with calcium phosphate can explain the variations in these fractions, if iron is assumed to be the driving force. From spring till summer, part of the Fe(OOH) is reduced and is followed by a $FeOOH \approx P$ desorption: large amount of o-P is released into the interstitial water. This leads to supersaturation and therefore to precipitation of calcium phosphate: the $Fe(OOH) \approx P$ fraction decreases and the $CaCO_3 \approx P$ fraction increases. From autumn till winter part of the iron is oxidized and adsorbs o-P. There is a subsaturation which leads to $CaCO_3 \approx P$ being dissolved: the $Fe(OOH) \approx P$ fraction increases and the $CaCO_3 \approx P$ fraction decreases. This supposes that the assumed inorganic calcium phosphate is reversible.

De Groot (1992) suggests that the formation of $Fe_3(PO_4)_2$ and/or $FePO_4$ may limit the release of $Fe(OOH) \approx P$ on the reduction of Fe(OOH): this phenomenon may be simultaneous with calcium

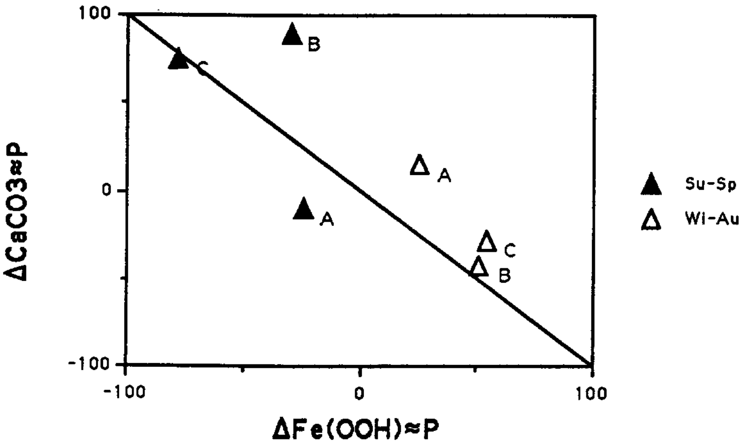

Fig. 6. Difference in $CaCO_3 \approx P$ against difference in $FeOOH \approx P$ between summer and spring and between winter and autumn ($\Delta \mu g$ g^{-1} DW).

phosphate formation but apatite precipitation should be favorize in this range of pH (Stumm & Mogan, 1981).

De Graaf & Golterman (1989) have shown that in recently formed sediments, the sum of Fe and Ca bound P was available for algal growth in 10 dutch lakes. As the input of P in the two mediterranean lagoons comes mainly from domestic sources and not from erosion, most of the $CaCO_3 \approx P$ in these lagoons is recently formed and will therefore be potentially available for algal growth.

For the org-P, we distinguished 2 fractions, and acid soluble (ASOP) and the residual fraction (ROP). Both of them represent 41.6% of the Tot-P_{sed}. The ROP fraction accounted for 70% of the org-P_{sed}. The nature of these compounds has not yet been elucidated except that the ROP fraction seems to contain considerable amounts of phytate (De Groot & Golterman, 1993). From our figures (Fig. 3), we have the impression that the concentration of these compounds do not change very much, except that the ROP decreases with depth. De Groot & Fabre (1993) have shown considerable change in the ASOP fraction in marshes during dessication. As these conditions are not likely to occur in such lagoons, we think that the P in these two pools is at least temporarily withdrawn from the P cycle.

Conclusion

The high calcium concentrations in the water of the lagoons and the pH which is constantly higher than that at which calcium phosphate precipitates allow the assumption that precipitation of calcium phosphate constitutes an essential mechanism for P storage in the sediment of the two studied mediterranean lagoons. The $CaCO_3 \approx P$ fraction is indeed the largest in the sediments. $Fe(OOH) \approx P$ is generally considered to be the most easily movable fraction in the sediment. It is closely related to the Fe(OOH) concentration which constitutes only a part (maximum: 15%) of the total iron in the sediments. The seasonal variations in this fraction can be related to the decomposition of organic material which entails a decrease in the O_2 content of the water at the water-sediment interface. In this way, the decomposition of organic matter has a double effect in the cycle of phosphate in the lagoons: on the one hand it returns to circulation part of the P from the organic matter and on the other hand it can affect the inorg-P fraction in the sediments significantly. It appears that the mayor part of the P released at the time of the reduction of the Fe(OOH) reprecipitates in the form of calcium phosphate in the interstitial water. The state of the iron in the sediments, which depends on the redox conditions, seems to be the driving force for these changes. The variations in the $CaCO_3 \approx P$ fraction allow the assumption that it is, largely, bioavailable.

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