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DECREASE OF PHOSPHATE CONCENTRATION IN A HIGH RATE POND BY PRECIPITATION OF CALCIUM PHOSPHATE: THEORETICAL AND EXPERIMENTAL RESULTS

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Abstract—The mechanism involved in the decrease of phosphate in a high rate pond (HRP) is investigated. The calcium concentration in the water (1.25–3.75 mM) and the high pH obtained in the reactors (8–10), result in the precipitation of calcium phosphate minerals. Although calcium hydroxyapatite [$Ca_5(PO_4)_3OH$, $pK_s = 57$] is the thermodynamical stable state, the phosphate concentration is determined by the solubility of the amorphous tricalcium phosphate [$Ca_3(PO_4)_2$, $pK_s = 25.2$]. This is confirmed by the calculation of the theoretical predicted solubility as well as various experiments. The relationship between pH and phosphate concentration may be used to optimize the efficiency of this type of reactor to produce a minimum concentration of phosphate in the effluent.

Key words—phosphorus removal, wastewater treatment, high rate pond, calcium, phosphate, chemical precipitation, hydroxyapatite, pH

INTRODUCTION

The reduction of inorganic phosphate concentration in wastewater is an inevitable preoccupation for modern society. The study of phosphate behaviour with respect to calcium may be an interesting tool to achieve this aim. The concentration of orthophosphate (o-P) may depend on the content of calcium in calcium rich waters (Hepher, 1958; Golterman, 1973; Golterman and Meyer, 1985) including lime-treated wastewaters (Jenkins and Menar, 1972; Jenkins, 1980) and from hard water biological treatment plants (Arvin, 1979; Nurdogan, 1988); it therefore appears that the equilibrium between the o-P and the solid phase determines the concentration of o-P in solution. Although the relationship between phosphate and calcium is unquestionable, different authors (Arvin, 1979; Golterman and Meyer, 1985; Menar and Jenkins, 1972; Snoeyink and Jenkins, 1980) disagree on the composition of the solid phase; it seems that apatite, $Ca_5(PO_4)_3OH$, amorphous tricalcium phosphate, $Ca_3(PO_4)_2$, brushite, $CaHPO_4 \cdot 2H_2O$, as well as octacalcium phosphate, $Ca_4H(PO_4)_3$, may determine the equilibrium phosphate concentration. The precipitation is known to be controlled by the pH and by the concentration of calcium and phosphate (Larsen and Jensen, 1986; Abbona *et al.*, 1986).

The principle of the high rate pond (HRP) is to use an algal culture to reduce the concentration of pollutants in the effluent; it differs from a waste stabilization pond in many respects (e.g. small depth, short residence time and permanent agitation). The HRP process, developed by Oswald in 1963, permits a considerable decrease of o-P to be obtained at Mèze (Hérault, France) (Picot *et al.*, 1991). The calcium concentration (1.25–3.75 mM) and the high pH obtained in the reactors (8–10) induce the precipitation of calcium phosphate with the assimilation by algae as a secondary phenomenon.

This paper investigates the chemical mechanisms involved in the reduction of phosphate concentration in the HRP of Mèze. The results obtained by weekly sampling of the HRP during 1988 are discussed together with the results of experiments designed to test the hypothesis of a calcium phosphate precipitation and the analysis of deposits found in the HRP. Furthermore, theoretical solubility of the four abovementioned calcium phosphate solids was studied in detail to aid the identification of the mineral formed in the HRP.

MATERIALS AND METHODS

In situ experiments

The pilot plant at Mèze (Hérault, France) consists of two ponds with a primary basin. The small depth (35 cm), short residence time (4–8 days), permanent agitation and flow rate of 15–20 cm s^{-1} are parameters chosen to improve algal growth. These two ponds (A and B) have similar characteristics and differ only in the residence time (Fig. 1).

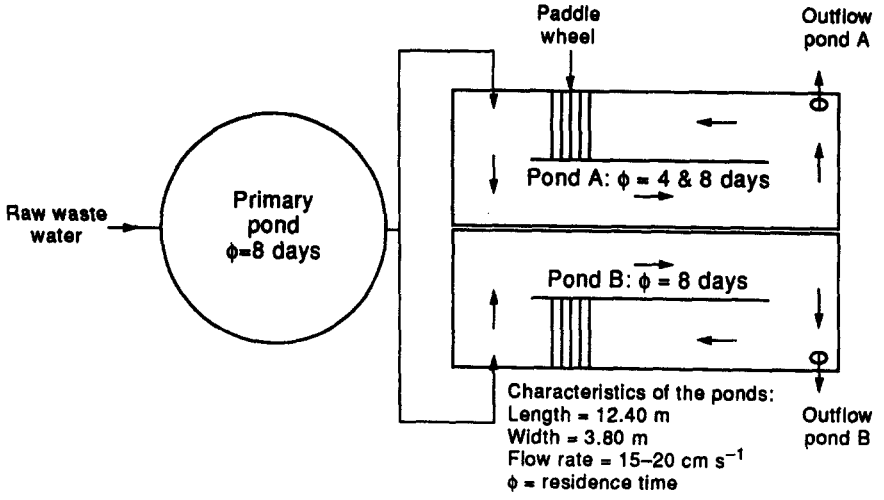

Fig. 1. Plan view of the high rate pond pilot system.

They behave as continuous-flow–stirred-tank-reactors as the composition of the water in the reactors and in the outflow are similar. The main characteristics of the influent of the HRP, which is the outflow of a primary pond with a residence time of about 8 days, are presented in Table 1. Weekly sampling was always carried out at the inflow and the outflow of each reactor at 15.00 h. The water samples were filtered through Whatman GF/C microglass filters and analysed the same day in the laboratory.

In the HRP basins, a deposit was found in some places; the fractional analysis of the phosphates from two samples of the deposit was done according to the method of Golterman and Booman (1988) and De Groot and Golterman (1990). This method separates organic, calcium-bound and iron-bound phosphates.

Laboratory experiments

Precipitation of calcium phosphate was investigated using solutions having the same concentration of calcium and phosphate as those found in the HRP. The initial solutions, composed of $CaCl_2$ and KH_2PO_4, were put in BOD bottles to protect them from atmospheric CO_2 and the pH was adjusted with NaOH. The samples were slightly agitated for 2 h, filtered through a GF/C filter and the o-P concentration in the filtrate was measured.

Chemical analysis

Chemical analysis was done according to French standards for water analysis (AFNOR). The o-P was analysed according to the method of Murphy and Riley (1962) which has been adopted in the AFNOR Norme Française (AFNOR NFT 90023). The method gives the concentration of total o-P:

$$[PO_4]_t = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] + [CaPO_4^-] + [CaHPO_4] + CaH_2PO_4^+].$$

The calcium analysis (AFNOR NFT 90016) gives the concentration of total calcium:

$$[Ca]_t = [Ca^{2+}] + \Sigma(\text{calcium complexes}).$$

Theoretical calculations

The theoretical solubility was determined using the conditional calculation scheme introduced by Schwarzenbach (1957), and further developed by Ringböm (1963). This method is based on the calculation of a new constant, the conditional one, which equals the product of the measured values (e.g. $K_s^* = [Ca]_t[PO_4]_t$). It permits parallel reactions in solution to be taken into account, like, for example, the formation of calcium phosphate ion-pairs, in the case of the precipitation of a sparingly soluble salt. Activity coefficients of the z-valent ions, γ_z, were calculated from the modified Debye–Hückel equation proposed by Davies (1964): $\log \gamma_z = -Az^2[I^{(1/2)}/(1 + I^{(1/2)}) - 0.3I]$ were I is the molar ionic strength and A is the Debye–Hückel constant. The ionic strength was determined by conductivity measurement of both inflow and outflow of the HRP during the period (17.05.88–23.08.88). The relation $I(\text{mM}) = 0.0021 + 0.0148x_{25}$, where x_{25} is the conductivity at 25°C in μS cm^{-1}, is given by Talbot *et al.* (1990). Constants described with a "′" correspond to values which take into account the effect of ionic strength.

Table 1. Average composition of the inflow and outflows A and B of the HRP (weekly sampling 1988)

	Inflow		Outflow (A)		Outflow (B)	
Variables	Mean	SD	Mean	SD	Mean	SD
Water temperature (°C)	16.6	10.3	17.0	7.2	17.0	7.2
Suspended matter (mg l^{-1})	149	44	188	103	151	112
Chlorophyll *a* (mg l^{-1})	0.61	0.47	1.10	0.78	1.22	1.26
Chemical oxygen demand (mg l^{-1})	378	161	323	159	273	184
Dissolved COD (mg l^{-1})	190	136	102	51	83	44
pH	7.8	0.4	8.7	0.6	8.6	0.5
Dissolved oxygen (mg l^{-1})	0.22	0.11	11.6	9.2	12.7	8.4
Calcium (mg l^{-1})	129	14	119	19	118	21
Kjeldhal nitrogen (mgN l^{-1})	38.8	4.1	30.4	11.0	23.3	11.7
Ammonium (mgN l^{-1})	21.6	5.7	9.1	9.8	7.4	8.8
o-P (mgP l^{-1})	6.8	1.2	4.2	2.2	4.2	2.1
Total phosphorus (mgP l^{-1})	11.3	1.3	8.8	3.2	8.1	2.3

Reactions and equilibrium constants at 25°C applied are as follows:

$$H_3PO_4 + H_2O \leftrightharpoons H_2PO_4^- + H_3O^+$$
($K_{a_3} = 10^{-2.2}$; Stumm and Morgan, 1981)

$$H_2PO_4^- + H_2O \leftrightharpoons HPO_4^{2-} + H_3O^+$$
($K_{a_2} = 10^{-7.2}$; Stumm and Morgan, 1981)

$$HPO_4^{2-} + H_2O \leftrightharpoons PO_4^{3-} + H_3O^+$$
($K_{a_1} = 10^{-12.3}$; Stumm and Morgan, 1981)

$$Ca^{2+} + PO_4^{3-} \leftrightharpoons CaPO_4^-$$
($\beta_1 = 10^{6.5}$; Sillen and Martell, 1971)

$$Ca^{2+} + HPO_4^{2-} \leftrightharpoons CaHPO_4$$
($\beta_2 = 10^{2.5}$; Sillen and Martell, 1971)

$$Ca^{2+} + H_2PO_4^- \leftrightharpoons CaH_2PO_4^+$$
($\beta_3 = 10^{1.4}$; Sillen and Martell, 1971)

$$Ca_5(PO_4)_3OH \leftrightharpoons 5Ca^{2+} + 3PO_4^{3-} + OH^-$$
($K_s = 10^{-57}$; Stumm and Morgan, 1981)

$$Ca_3(PO_4)_2 \leftrightharpoons 3Ca^{2+} + 2PO_4^{3-}$$
($K_s = 10^{-25.2}$; Meyer and Eanes, 1978)

$$CaHPO_4 \cdot 2H_2O \leftrightharpoons Ca^{2+} + HPO_4^- + 2H_2O$$
($K_s = 10^{-6.6}$; Stumm and Morgan, 1981)

$$Ca_4H(PO_4)_3 \leftrightharpoons 4Ca^{2+} + H^+ + 3PO_4^{3-}$$
($K_s = 10^{-46.9}$; Stumm and Morgan, 1981).

The calculation procedure may be explained with amorphous tricalcium phosphate as an example:

$$K_s = (Ca^{2+})^3(PO_4^{3-})^2 = 10^{-25.2}$$

$$K_s^* = [Ca]_t^3[PO_4]_t^2 \approx [Ca^{2+}]^3[PO_4]_t^2$$

Thus

$$[PO_4]_t = (K_s^*/[Ca^{2+}]^3)^{1/2}.$$

Considering the above-mentioned equilibrium, we have:

$$[PO_4]_t = [PO_4^{3-}]\alpha_{PO_4(H,Ca)}$$

With

$$\alpha_{PO_4(H,Ca)} = 1 + (H_3O^+)/K'_{a_1} + (H_3O^+)^2/K'_{a_1}K'_{a_2} + (H_3O^+)^3/K'_{a_1}K'_{a_2}K'_{a_3} + [Ca^{2+}](\beta'_1 + (\beta'_2(H_3O^+))/K'_{a_1} + (\beta'_3(H_3O^+)^2/K'_{a_1}K'_{a_2}))$$

$$K_s^* = [Ca^{2+}]^3[PO_4]_t^2 = ([Ca^{2+}]^3/\gamma_2^3)([PO_4^{3-}]^2/\gamma_3^2)\alpha^2_{PO_4(H,Ca)} = K_s\alpha^2_{PO_4(H,Ca)}.$$

And thus:

$$[PO_4]_t = (K_s^*\alpha^2_{PO_4(H,Ca)}/(\gamma_2^3[Ca^{2+}]^3\gamma_3^2))^{(1/2)}.$$

For this calculation, $\alpha_{Ca} = [Ca^{2+}]/[Ca]_t$ was set to 1. The formation of the molecular species $Ca_3(PO_4)_2$ was neglected. The free calcium concentration, $[Ca^{2+}]$, was calculated on a microcomputer by successive approximation of the α_{Ca} value using $[CO_3]_t$ and $[SO_4]_t$ measured in the HRP during a short period.

$$[CO_3]_t = [CO_3^{2-}] + [HCO_3^-] + [CO_{2aq}] + [CaCO_3^0] + [CaHCO_3^+]$$
$$= [CO_3^{2-}](1 + (H_3O^+)/K'_{a_4} + (H_3O^+)^2/(K'_{a_4}K'_{a_5}) + [Ca^{2+}](\beta'_4 + (\beta'_5(H_3O^+))/K'_{a_4}))$$

$$[SO_4]_t = [SO_4^{2-}] + [CaSO_4^0] = SO_4^{2-}](1 + \beta'_6[Ca^{2+}])$$

with $pK_{a_4} = 10.3$, $pK_{a_5} = 6.35$, $\log\beta_4 = 3.15$, $\log\beta_5 = 1.0$, $\log\beta_4 = 2.31$ (Sillen and Martell, 1971). Thus

$$[Ca]_t = [Ca^{2+}] + [CaPO_4^-] + [CaHPO_4] + [CaH_2PO_4^+] + [CaCO_3^0] + [CaHCO_3^+] + [CaSO_4^0] = [Ca^{2+}]\alpha_{Ca}$$

with

$$\alpha_{Ca} = 1 + [PO_4^{3-}](\beta'_2 + (\beta'_2(H_3O^+))/K'_{a_1} + (\beta'_3(H_3O^+)/(K'_{a_1}K'_{a_2})) + [CO_3^{2-}](\beta'_4 + (\beta'_5(H_3O^+))/K'_{a_4}) + [SO_4^{2-}]\beta'_6.$$

RESULTS AND DISCUSSION

Laboratory experiments showed that calcium phosphate precipitated immediately when the initial pH $\geqslant$ 8.0. The experiments were stopped after 2 h; results are represented in Table 2. The X-ray analysis of a precipitate, from a solution which had an initial pH of 9, showed that the precipitate was amorphous.

The concentrations of o-P in the HRP in 1988 are plotted against pH in Fig. 2. The assumption that an equilibrium between dissolved phosphate and a solid phase of calcium phosphate is rapidly reached, permits the superposition of the values obtained from reactors A and B. As the calcium concentrations in the common inflow of the two reactors are always above 100 mg l^{-1}, the inflow phosphate concentrations were included with the other results shown in Fig. 2. When pH > 7.5, the phosphate concentration is related to the pH in the inflow as well as in the outflow water. The regression analysis to an exponential function ($[PO_4]_t = 2035 \times 10^{-0.495pH}$, $r^2 = 0.69$) showed that 69% of the $[PO_4]_t$ variation over the year is explained by the variation of pH (Fig. 2).

The phosphate concentration in the deposit found in the HRP was about 60 mg Pg^{-1} dry wt of which 92% was recovered as a calcium bound fraction (Table 3). This result substantiates the assumption of a calcium phosphate precipitation. The quantity found in the HRP was 200 times higher than observed in the sediment of surrounding coastal lagoons.

When pH > 7.5, an amorphous calcium phosphate is expected to control the concentration of o-P. As the error in the estimation of the calcium concentration

Table 2. pH, calcium and o-P concentrations (mM) in the precipitation experiment

	pH initial	pH final	$[Ca]_t$	$[PO_4]_{t\ initial}$	$[PO_4]_{t\ final}$
Sample 1	8.0	7.5	2.7	0.280	0.214
Sample 2	9.0	8.7	2.7	0.280	0.066
Sample 3	9.0	8.7	2.7	0.280	0.063
Sample 4	10.0	9.9	2.7	0.280	0.017
Sample 5	10.0	9.9	2.7	0.280	0.018

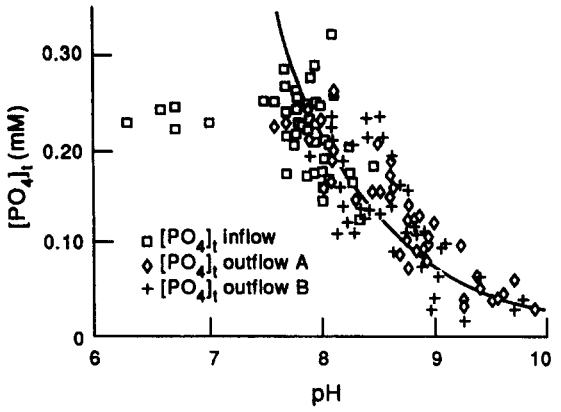

Fig. 2. pH (x-axis) and o-P concentration (y-axis) in the two HRPs (1988).

is approximately the same as the change caused by the loss of phosphate by mineralization, it was not possible to interpret the ΔCa/P molar ratios to identify the calcium phosphate phase forming; this is even more uncertain if a calcium carbonate precipitation is occurring when pH > 8.5 (Table 4). Thus, we calculated the theoretical solubility of the four minerals that could control the phosphate concentration in the reactors for the minimum and maximum pH, 7.5 and 10.0, respectively, and for an ionic strength of $I = 0.032$ M. The ionic strength, calculated from the conductivity measurement, was 0.032 ± 0.004 M; no significative differences were observed between the inflow and the outflows of the reactors. The experimental results for the HRP reactors are also shown in Fig. 3 (a–d).

For the amorphous tricalcium phosphate $Ca_3(PO_4)_2$ [Fig. 3(a)]:

$$[PO_4]_t = (K_s \alpha^2_{PO_4(H,Ca)}/(\gamma_2^3[Ca^{2+}]^3\gamma_3^2))^{(1/2)}$$

($pK_s = 25.2$; Meyer and Eanes, 1978).

For the apatite $Ca_5(PO_4)_3OH$ [Fig. 3(b)]:

$$[PO_4]_t = ((K_s \alpha^3_{PO_4(H,Ca)})/(\gamma_2^5[Ca^{2+}]^5\gamma_3^3 \times (10^{-14}/(H_3O^+))))^{(1/3)}$$

($pK_s = 57$; Stumm and Morgan, 1981).

For the brushite $CaHPO_4$ [Fig. 3(c)]:

$$[PO_4]_t = (K_s \alpha_{HPO_4(H,Ca)}/[Ca^{2+}])$$
$$= (K_s \alpha_{PO_4(H,Ca)} K'_{a_1})/\gamma_2[Ca^{2+}]\,(H_3O^+)$$

($pK_s = 6.6$; Stumm and Morgan, 1981).

Table 3. Percentage of total phosphorus fractions in the deposit found in the HRP according to Golterman and Booman (1988). ($P_{tot} \approx 60$ mgP/g dry wt)

Water soluble phosphates	0.3
Iron-bound phosphates	3.9
Calcium-bound phosphates	92.7
Organic phosphates	3.1

For the octacalcium phosphate $Ca_4H(PO_4)_3$ [Fig. 3(d)]:

$$[PO_4]_t = (K_s \alpha^3_{PO_4(H,Ca)}/(\gamma_2^4[Ca^{2+}]^4\gamma_3^3(H_3O^+)))^{(1/3)}$$

($pK_s = 46.9$; Stumm and Morgan, 1981).

With

$$\alpha_{PO_4(H,Ca)} = 1 + (H_3O^+)/K'_{a_1} + (H_3O^+)^2/K'_{a_1}K'_{a_2} + (H_3O^+)^3/K'_{a_1}K'_{a_2}K'_{a_3} + [Ca^{2+}](\beta'_1 + \beta'_2(H_3O^+)/K'_{a_1} + \beta'_3(H_3O^+)^2/K'_{a_1}K'_{a_2}).$$

The result in Fig. 3 suggests that the amorphous tricalcium phosphate is the solid phase involved in the reaction. Phosphate concentrations are one thousand times greater than the value expected for apatite solubility. This result, which goes against thermodynamic considerations may be explained by the presence of magnesium ions which do not interfere with the formation of the amorphous phase while the conversion to a crystalline phase is delayed or even completely inhibited (Abbona *et al.*, 1986). The inhibition of calcium hydroxyapatite precipitation in the presence of fulvic, humic and tannic acids has also been reported (Inskeep and Silvertooth, 1988). For the brushite [Fig. 3(c)], the predicted solubility at high pH is different from the measured values. The same observation was made for the octocalcium phosphate at low pH [Fig. 3(d)]. In the case of the laboratory experiment, we did not obtain the apatite form because of the short duration of the experiments. The kinetics of the amorphous to crystalline calcium phosphate transformation are critically dependent upon the solution composition (Meyer and Eanes, 1978) which are generally very different from those used in biological studies. Precipitation of magnesium-phosphate, and specially struvite $MgNH_4PO_4$, was not investigated in this study because the ratio Mg/Ca is about 0.3 in the HRP which is expected to favour calcium phosphate phase precipitation (Abbona *et al.*, 1986).

This pseudo-equilibrium between tricalcium phosphate and calcium hydroxyapatite, has been described by Menar and Jenkins (1972) and Snoeyink

Table 4. Total calcium concentration in the different ranges of pH (weekly sampling 1988)

pH $[Ca]_t$	7.25–7.75	7.75–8.25	8.25–8.75	8.75–9.25	9.25–9.75	9.75–10.0
Mean (mM)	3.074	3.213	3.241	2.743	2.264	1.897
SD	0.176	0.357	0.341	0.528	0.413	0.247
n	10	63	35	24	12	2

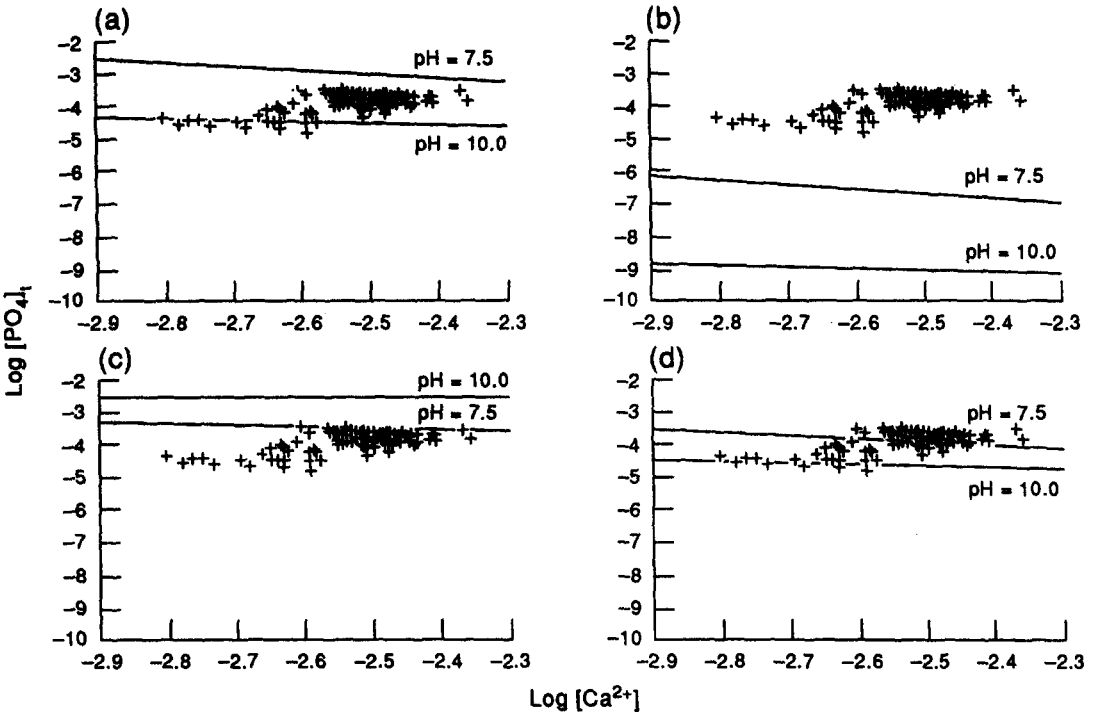

Fig. 3(a–d). Logarithm of phosphate concentration (M) vs logarithm of calcium concentration (M). Theoretical curves of each calcium phosphate species for pH = 7.5 and 10.0 ($I = 0.032$ M), and experimental measurements in the HRP (1988). (a) Amorphous tricalcium phosphate, (b) apatite, (c) brushite and (d) octacalcium phosphate.

and Jenkins (1980). The assumption that the competitive formation of the two above-mentioned salts rather than the post-formation of apatite takes place in certain situations, was published by Larsen and Jensen (1986).

Remark: there is a large uncertainty in the determination of apatite solubility due to the great differences related to the theoretical solubility product ($pK_s = 57$ reported in Stumm and Morgan 1981, $pK_s = 56$ reported in Charlot 1983, $pK_s = 54.6$ calculated by Moreno et al., 1968, $pI = 50$ calculated by Golterman and Meyer 1985 for two hard water rivers). But in any case, it could explain the high pH dependent phosphate concentration observed in the HRP.

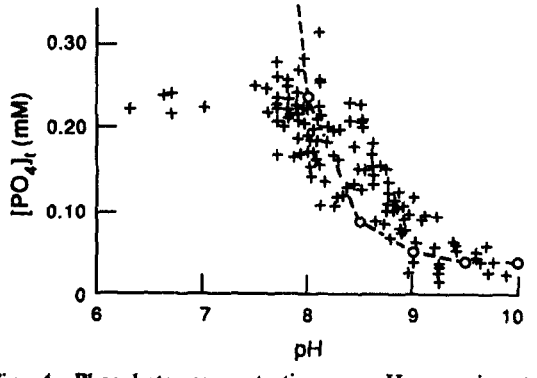

Fig. 4. Phosphate concentration vs pH; experimental measurements in the HRP (1988) and theoretical predictions generated using data in Table 4 from the expected solubility of tricalcium phosphate.

Figure 4 presents the theoretical o-P concentration versus pH when the amorphous tricalcium phosphate is considered as the solid phase in controlling the solution composition. The results were determined for the calcium concentrations measured in the HRP (Table 4), $I = 0.032$ M and $T = 25°C$. The data points of $[PO_4]_t$ and pH from the HRP are also shown on the graph. Experimental and theoretical results suggest the precipitation of the amorphous tricalcium phosphate $Ca_3(PO_4)_2$ phase.

Table 5 shows the comparative results obtained by taking into account the ionic strength and α_{Ca} on the predicted solubility of $Ca_3(PO_4)_2$ at a pH = 8. At this pH, total calcium concentration was 3.2 mM (Table 4) and for the α_{Ca} calculation, the concentrations of $[CO_3]_t$ and $[SO_4]_t$ were taken as 0.01 and 0.00025 M, respectively. The inclusion of ionic strength is more important than taking into account the calcium speciation, i.e. α_{Ca}. Thus, replacing $[Ca^{2+}]$ by $[Ca]_t$ in the solubility calculation is a useful first approximation.

Table 5. Theoretical solubility of $Ca_3(PO_4)_2$ at pH = 8.0: effect of taking into account ionic strength (I) and $\alpha_{Ca} = I <=> [Ca^{2+}] = [Ca]_t$. For α_{Ca} determination: $[CO_3]_t = 0.01$ M and $[SO_4]_t = 0.00025$ M

I (M)	$[Ca]_t$ (mM)	$[Ca^{2+}]_t$ (mM)	$[PO_4]_t$ (mM)
0	3.20	2.63	0.108
0	3.20	3.20	0.091
0.032	3.20	2.85	0.281
0.032	3.20	3.20	0.241

The o-P concentration in the HRP may be predicted from the measurement of the total calcium concentration, pH and conductivity, if the solid phase $Ca_3(PO_4)_2$ is assumed to be the controlling phase. For the prediction of the o-P concentration, the solid phase which has to be considered is a crucial factor and to a lesser extent the pH and the ionic strength. The use of the free calcium concentration instead of total calcium concentration is not so important for the prediction. The effect of temperature on the solubility of the calcium phosphates, which is in the same order of magnitude as taking into account free calcium concentration, is not discussed here.

CONCLUSION

The concentration of o-P in the water of HRP at Mèze is determined by the solubility of a calcium phosphate mineral. Theoretical calculations indicate that it is probably an amorphous phase in pseudo-equilibrium [$Ca_3(PO_4)_2$, $pK_s = 25.2$; Meyer and Eanes, 1978]: phosphate concentrations are much higher than the values expected for calcium hydroxyapatite in equilibrium [$Ca_5(PO_4)_3OH$, $pK_s = 57$; Stumm and Morgan, 1981]. As the dissolved calcium concentrations are high in the calcareous region near Mèze, the pH of the water in the HRP determines the concentration of phosphate (Fig. 2). The pH is clearly correlated to the photosynthetic activity (Abeliovich, 1986) and so the algae indirectly play a central role in the reactors of the HRP. Their function is thus not limited to oxygen delivery. If the difference between inflow pH and outflow pH is maximal, i.e. when photosynthetic activity is high, the decrease in the dissolved phosphate concentration is maximum. As a result, the management of this kind of reactor may be possible by adapting the residence time to the season conditions. A decrease in dissolved phosphate concentration may be achieved by increasing the residence time in the HRP when the photosynthetic activity is low.

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