

Kinetic model of the fixation of phosphates on particles of sediments

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Abstract

The adsorption of phosphates on sediments was studied by distinguishing between the mineral and bacterial biomass compartments. Enrichment with Ca^{2+} , Fe^{3+} and Al^{3+} validates a multilinear model.

Introduction

Understanding the process of the fixation of phosphorus on sediments is important for water-quality control (Overman and Chu, 1977; Boström et al., 1982). For this reason, a number of studies have been carried out on the variation of phosphorus fixed by or released from sediments with time. The kinetic equation obtained can be said to be of the first order (Fried et al., 1957; Larsen et al., 1965; Probert and Larsen, 1972) or of the second order (Kuo and Loste, 1974).

The study of the fixation of phosphates by sediments is made difficult because of the complex and diversified structure of a sediment (a mixture of living and inert matter). As a first approximation, we can consider that the sediments can be divided into two groups: one group made up of a biomass (X) and the other, a non-living group (Mi). According to this subdivision, a model can be proposed (Fig. 1):

- The biomass fixed to the sediment transfers an electrostatic potential that can, before bacterial assimilation, induce biosorption of phosphates. After biosorption, assimilation will reach a state of equilibrium, accompanied most probably by a redistribution of phosphates among the various groups.
- Other than the biomass, the abiotic groups (Fe^{3+} , Ca^{2+} , Al^{3+}) can also constitute sites of phosphate fixation. Nevertheless, metals are generally held as precipitated salts (carbonates...) or in fairly stable organic complexes. If the cation forms soluble salts or compounds which are not very stable, the phosphates will be able to interact strongly, probably through precipitation.

The goal of our tests was to verify the frequency with which sediments contain metals and to explain the role played by the biomass present in the kinetics of phosphate fixation and release.

Material and methods

This study of the kinetics of incorporation was carried out on sediments of freshwater lakes (Gouet, Côtes d'Armor, France). Various cations in the sediments were determined by atomic absorption. The methods used to collect and prepare the samples and conduct the analyses have been described previously (Bonzongo et al., 1989). The sediments studied present the physico-chemical characteristics as summed up in Table 1.

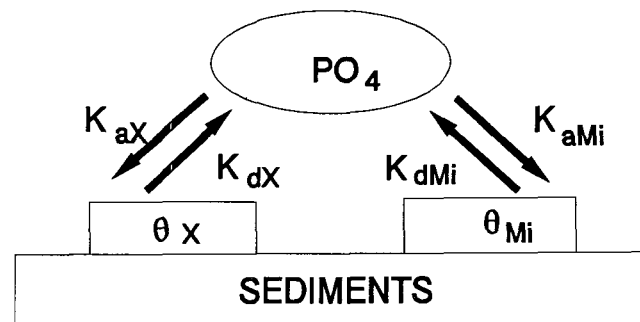


Figure 1

Model of the incorporation of phosphates in sediments

Enrichment of sediments

Multiplication of the biomass

To study the role of the microbial biomass of sediments in the fixation of phosphates, various glucose masses (0, 10, 20, 100 and 500 mg) were added to the equivalent of 5 g of dry sediments. The mixture was left to incubate at room temperature ($20 \pm 2^\circ\text{C}$). After bacterial growth had taken place, the following measurements were carried out: adenosine triphosphate (ATP), (Jones and Simon, 1977); the residual glucose (Dubois et al., 1965); and the phosphorus content in the different fractions according to the AFNOR T-90-023 standard, after fractionation as performed by Bonzongo et al. (1989). The equivalent of 5 g of dry sediments was then used for the kinetic incorporation.

Addition of calcium, iron and aluminium salts

Calcium, iron and aluminium were added to the sediments in the form of: CaCO_3 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ respectively. As in the case of glucose, the addition was accomplished by enriching the sediments separately with 0, 10, 20 and 30 mg of Ca^{2+} , Fe^{3+} and Al^{3+} for 5 g of dry sediment. The sediment thus treated was used for incorporating phosphates.

Kinetic incorporation of phosphates

Sediments and the phosphate solution, prepared from KH_2PO_4 , were placed in a 100 ml flask (Fig. 2) in a ratio of 1 g of dry sediment per 100 ml of solution. The mixture was brought up to $\text{pH}=7$ using a Tris buffer and regulated by the addition of either

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| TABLE 1 PHYSICO-CHEMICAL CHARACTERISTICS OF SEDIMENTS STUDIED | | | |
|--|-----------------|--|-----------------------------------|
| Water content (% dry weight) | 75.59% | Various fractions of phosphorus in sediment | P $\mu\text{g/g}$ of dry sediment |
| Ca ⁺⁺ $\mu\text{g/g}$ of dry sediment | 17400 | Total Organic P | 670 |
| Mn ²⁺ $\mu\text{g/g}$ of dry sediment | 16920 | Bacterial-P | 179 |
| Al ³⁺ $\mu\text{g/g}$ of dry sediment | 28000 | NH ₄ Cl-P | 22 |
| MPN bacteria/g of dry sediment | 10 ⁹ | NaOH (N/10) -P | 1500 |
| Total P $\mu\text{g/g}$ of dry sediment | 2990 | HCl-P | 291 |
| | | NaOH SN 85 °C | n.d. |

HCl or NaOH. The mixtures were shaken to ensure aeration and brought up to room temperature. Sediments enriched with glucose were also aerated with an air pump. Initially the phosphorus concentration was 20 mg P/l of solution. Samples were taken with an automatic pipet to ensure homogeneity. Dissolved phosphorus was added to the samples after filtering with an 0,2 μm sartorius filter. The experiment was performed three times and the results given correspond to the average of the three values attained.

The incorporation of the "inert group" was judged by inhibiting the biomass activity by adding 20 g of chloroform per litre of mixture.

After incorporation, the phosphates in the sediments were analysed to emphasise the sites involved in the fixation of phosphate (Bonzongo et al., 1989).

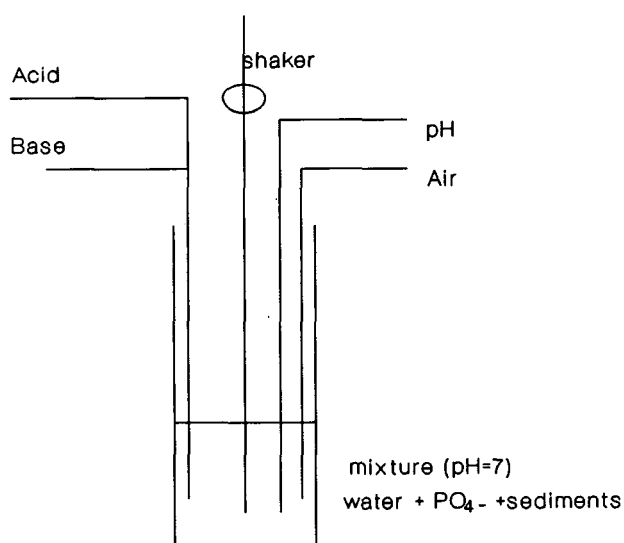


Figure 2
Experimental apparatus

Results and discussion

Nomenclature

- K_{ax} and K_{aMi} = Constants for P-fixation
 O_x = Mass of fixed PO_4 per mass of biomass
 O_{Mi} = Mass of fixed PO_4 per mass of elements of the abiotic group
 X = Biomass
 Mi = Abiotic group
 t = time
 P_w = mg of P/l of solution
 P_s = mg of P/g of dry sediment
 P_{sM} = Maximum concentration of P which can be fixed by the sediments (mg of P/g of dry sediments)
 P_{se} = mg of P fixed at equilibrium per unit of mass of dry sediments

Role of the biomass

Fractionation of the phosphorus in the sediments which was performed after this treatment showed that the multiplication of the bacterial biomass of the sediments was accompanied by a transfer of the phosphorus fixed on the inert particles towards live organic groups (Fig. 3).

Residual glucose after bacterial growth had stopped was around zero for the sediments having received 10, 20 and 100 mg of glucose. However, when the added dose of glucose was 500 mg, bacterial growth stopped when approximately 50 μg of glucose per gram of dry sediment remained. The sediments probably had a nutrient deficiency which exhausted them before all of the glucose could be consumed.

From these results, we can conclude that bacteria lacking sufficient energy and carbon for growth do use the phosphorus of the mineral group. These results confirm those of Harrison et al. (1972) which showed that isolated bacteria from Lake Klamath

could solubilise phosphates precipitated on metallic cation when a carbohydrate source of energy was present.

The kinetics of phosphate biosorption on sediment activated by glucose are represented in Fig. 4. Rapid biosorption followed by an equilibrium condition reached after 50 min can be observed. Initially it was assumed that the salts did not contain enough available metals to accomplish precipitation of the phosphate and that two sorption phenomena exist. We can then write a model of initial sorption rate (disregarding desorption):

$$\frac{dP_s}{dt} = K_{ax}P_w(\theta_x)S + \sum K_{aMi}P_w\theta_{Mi}S \quad (1)$$

If a "doping agent" is added, it provokes an increased density of the sites of biosorption and if we assume that the desorption constants are weak, O_x increased while O_{Mi} decreases:

$$+ \frac{dP_s}{dt} = \frac{dP_{so}}{dt} + K_{ax}P_w(\theta_x - \theta_{xo}) + \sum K_{aMi}P_w(\theta_{Mi} - \theta_{Mio}) \quad (2)$$

If, following this activation, the inorganic contribution to fixation is "masked"; then comparing the sediment with biomass to a sterilised sediment, we obtain Fig. 5 which validates this model with:

$$\frac{1}{P_w} \left(\frac{dP_{so}}{dt} \right)_i = K_{ax}X + K_0 \quad (3)$$

It was observed that this speed corresponds with the initial biosorption. After 2 h equilibrium with assimilation was reached. The fixed phosphate will now be compared to the ATP measurement. Figure 7 shows that:

$$K_{ax} = [0,45 (ATP) + 8,3] \cdot 10^{-3} \quad (\Delta P_{se} = 0,45 (ATP)) \quad (4)$$

We observed that during assimilation, a biomass was produced; the scale of this equilibrium can be verified thus: 1 mg of P = 0,5 g of biomass or 0,6 mg of ATP.

Role of inorganic groups

We indicated in Table 1 that the sediment which is the object of our tests contained 17 mg Fe^{3+} /g dry sediment, 28 mg Al^{3+} /g dry sediment, 1,7 mg Ca^{2+} /g dry sediment and 2 mg Mn^{2+} /g dry sediment. In our experiments, we incorporated 1 g of dry sediment /100 ml of solution, to which we added 20 mg P/l. In one litre of mixture, we initially had 20 mg P for a large amount of metal (170 mg Fe^{3+} , 280 mg Al^{3+} , 17 mg Ca^{2+} and 20 mg Mn^{2+}).

To the sediments were added $Al_2SO_4 \cdot 7H_2O$ and $CaCO_3$. The first hydrolysed towards pH 7, the second was hardly soluble. Figures 7, 8 and 9 show the kinetics of the fixation of P by sediment enriched with Fe^{3+} , Al^{3+} and Ca^{2+} . They also show the importance of a weak dose of Fe^{3+} in relation to the initial iron content, thus demonstrating the very low availability of Fe^{3+} and Al^{3+} in the sediment. The added Fe^{3+} and Al^{3+} induced a precipitation of phosphate in salt form.

Calcium carbonate, which is not very soluble, was added in the form already present in the sediment. This led to an equation similar in form to the Langmuir equation. However, a model analogous to the one present for the biomass will suffice.

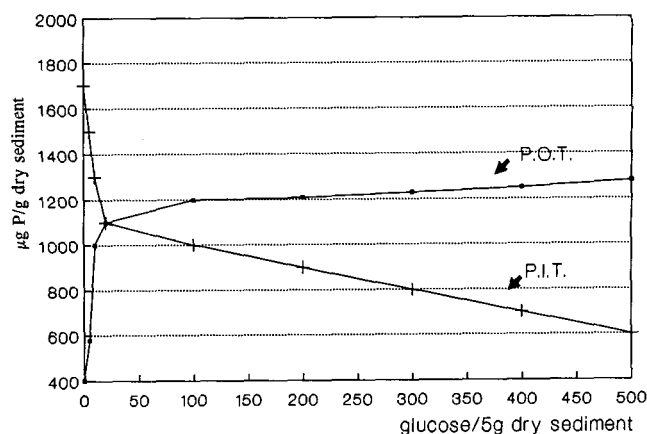


Figure 3
Evolution of the various fractions of phosphorus (TOP, TIP total and inorganic phosphorus)

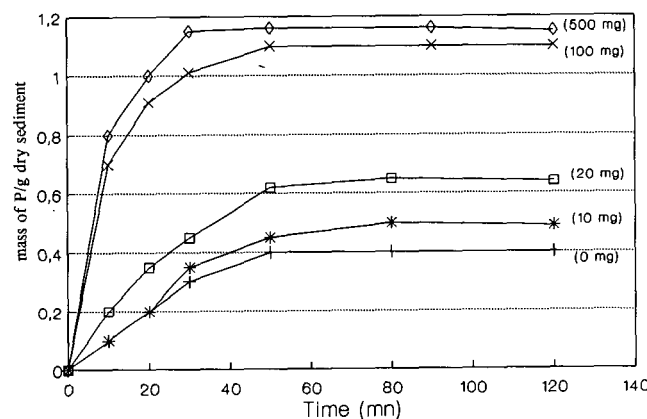


Figure 4
Kinetics of P-fixation by sediments with various biomasses
(Glucose: 0, 10, 20, 100, 500 mg)

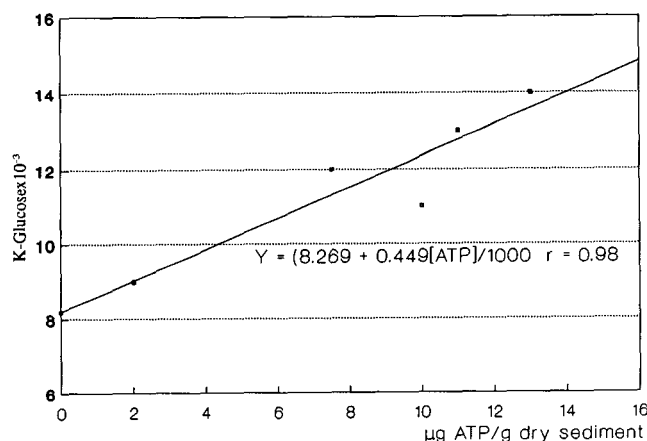


Figure 5
Fixation constants for the biomass

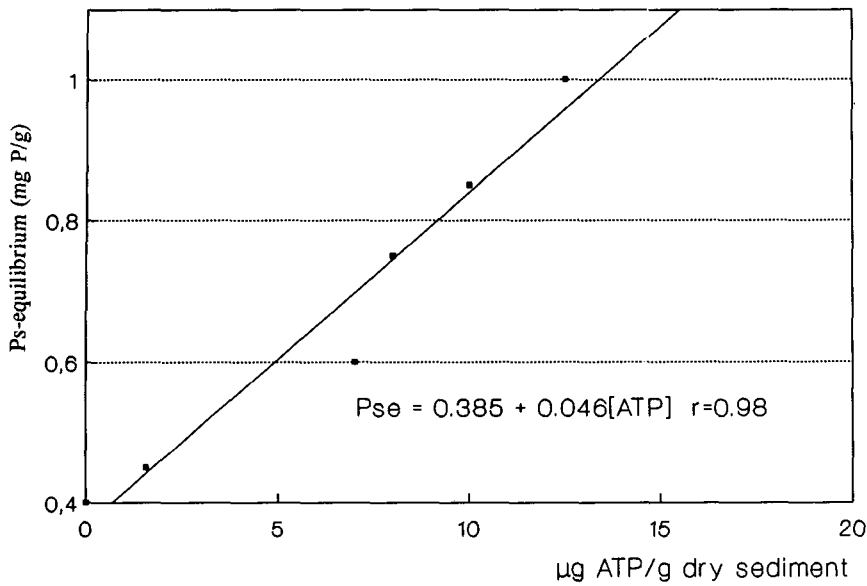


Figure 6
Relationship between phosphorus and biomass at equilibrium

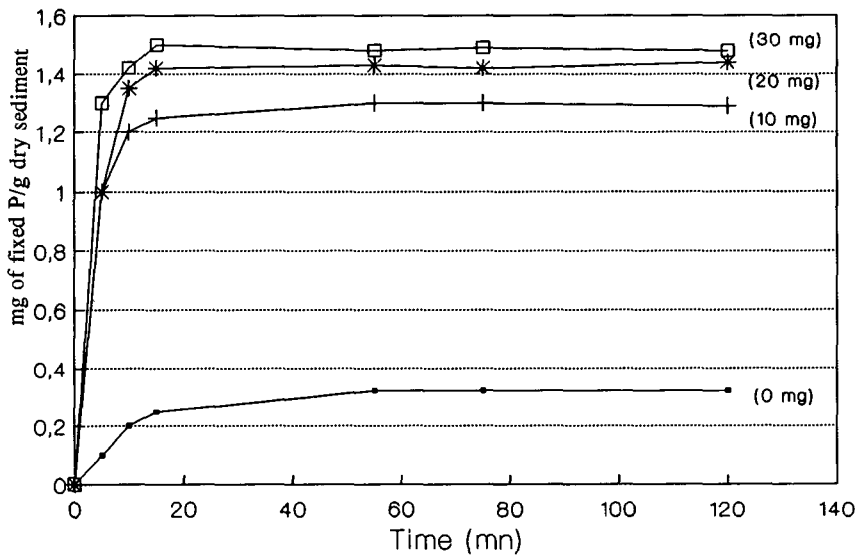


Figure 7
Kinetics of P-fixation by sediment enriched with iron (0, 10, 20, 30 mg Fe⁺⁺⁺/5g dry sediment)

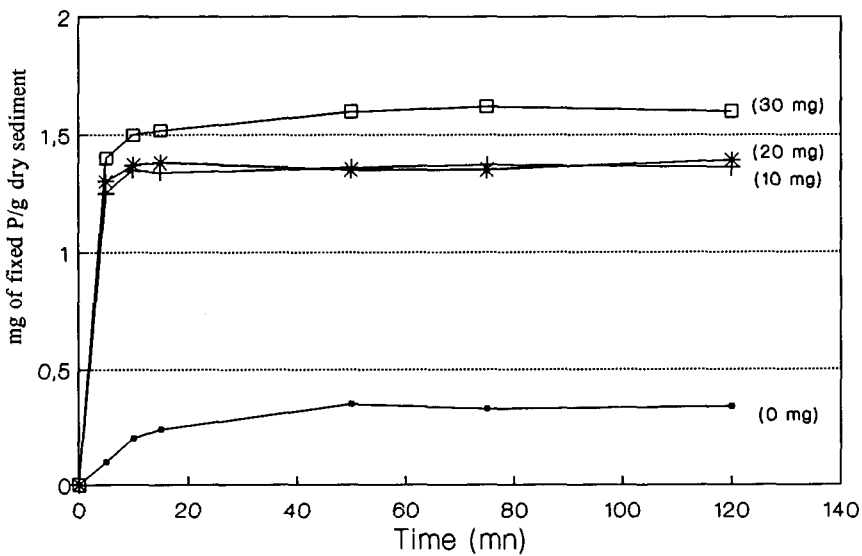


Figure 8
Kinetics of P-fixation by sediment enriched with Aluminium (0, 10, 20, 30 mg Al⁺⁺⁺/5g dry sediment)

Figure 9
Kinetics of P-fixation by sediment enriched with calcium (0, 10, 20, 30 mg Ca⁺⁺/5g dry sediment)

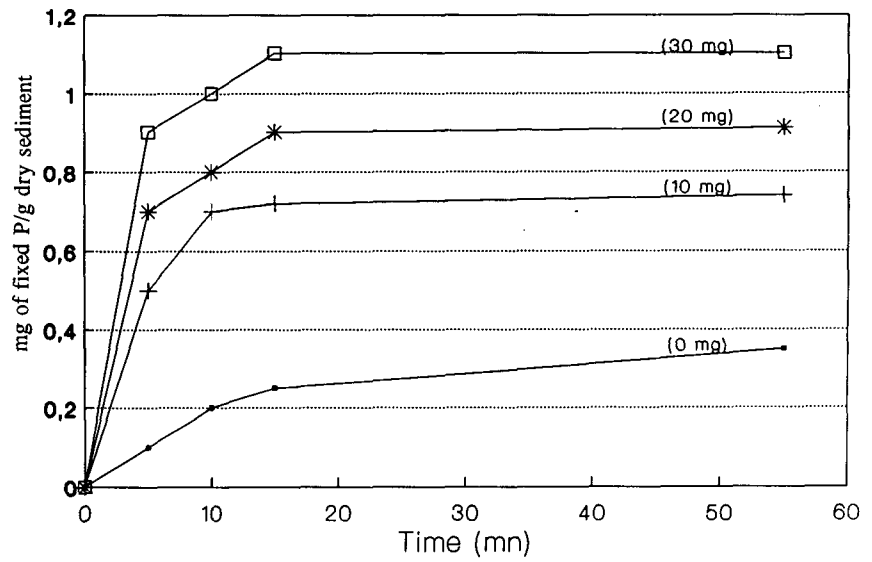


Figure 10
Constants for P-fixation by sediments with various calcium concentrations

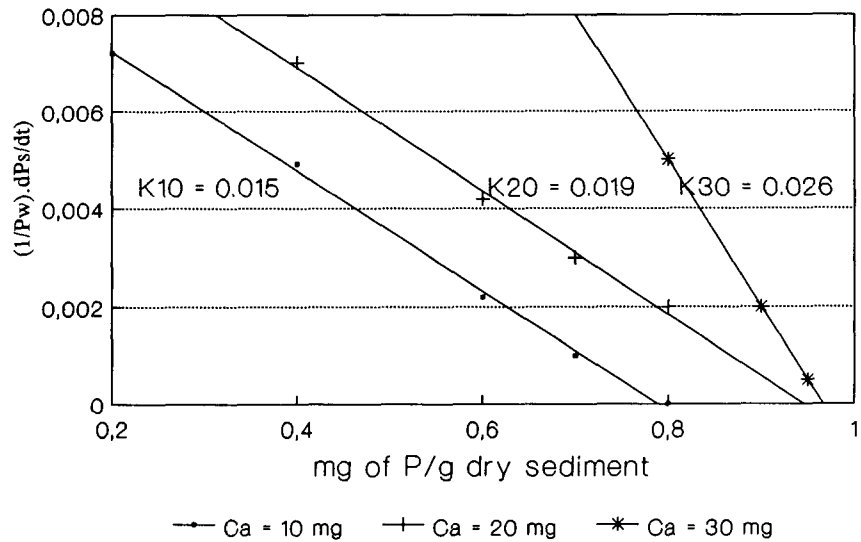
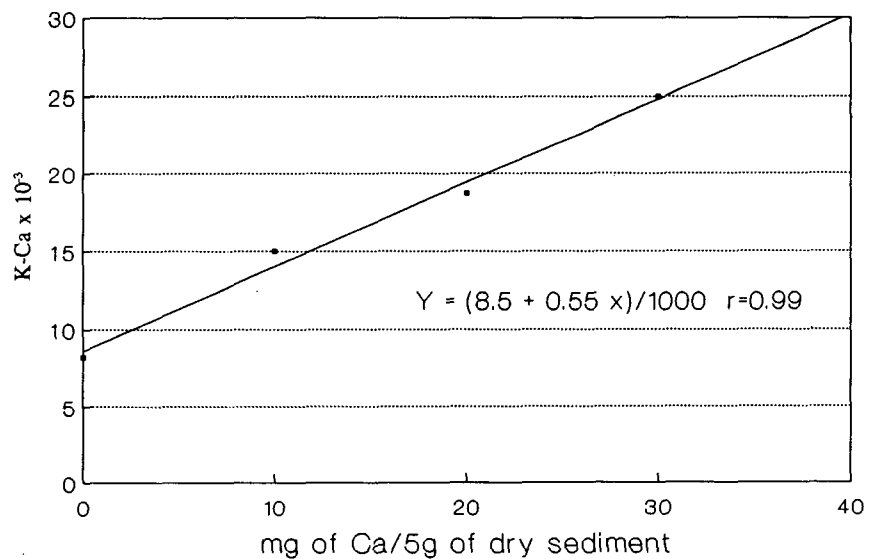


Figure 11
Relationship between the fixation constants and the mass of calcium added



$$\frac{I}{P_w} \left(\frac{dP_s}{dt} \right) = K_{aMi} (O_M) \cdot S = K_{ca} (P_{sM} - P_s) \quad (5)$$

We found that the curve is positive with respect to the mass added (Fig. 11). $K_{CaCO_3} = (8,5 + 0,552 \cdot Ca)10^{-3}$ with Ca^{2+} corresponding to the mass of calcium per mass of dry sediment.

K_{CaCO_3} increases linearly with the mass of $CaCO_3$ corresponding to the increase of the surface transfer of phosphates to carbonate. Therefore P_{sM} also seems to increase with the level of incorporation of soluble salt.

To summarise:

- The Fe^{3+} and the Al^{3+} in the sediments studied are not readily available for the fixation of phosphate and the incorporation of a relatively low amount of available Fe^{3+} or Al^{3+} induces a large elimination of phosphate by chemical "dephosphorisation".
- Incorporation of Ca^{2+} in the sediments with amounts identical to those of Fe^{3+} and Al^{3+} favors only a weak elimination of phosphate.

Conclusion

Incorporation of phosphates in sediments is dependent upon the composition of the materials. In our experiments, we have shown that a model of biosorption could be applicable if the sediments containing the bacteria and the phosphatic liquor are well mixed. After a fairly short time, the phosphates that assimilated well correlated with the biomass of the materials.

As for the fixation of phosphates in abiotic groups, it seems that the metals Fe^{3+} , Al^{3+} and Ca^{2+} play an important role, but that the availability of metals for the incorporation of phosphates in

sediments is very low, so a very small dose of soluble salts induces a large elimination, which is not observed in non-treated material. Precipitated salts which are not very soluble, or form stable compounds, create sites of physio-sorption with weak affinity.

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