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COMPARISON OF PHOSPHORUS AND NITROGEN RELEASE FROM AEROBIC AND ANAEROBIC SEDIMENTS: AN EXPERIMENTAL STUDY

P.R.S. Cavalcante[1], V. Gandais-Ruban[2], D. Demare[2]

[1]Departamento de Oceanografia e Limnologia - UFMA, Praça Gonçalves Dias, 21, CEP 65020-240, São Luís, MA
[2]Laboratoire Central des Ponts et Chaussées - BP 19 - 44340, Bouguenais, France

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ABSTRACT

The release of orthophosphates, ammonium, nitrites, nitrates and iron of the Erdre river's sediments (France) was studied to investigate the risks of eutrophication increase, due to internal loading.

An one-month long laboratory experiment was carried out using a simulation canal in which the temperature, water flow velocity and light were controlled. The use of two benthic chambers (one cylindrical, in contact with the air, the other, rectangular, tight sealed) allowed the study of aerobic and anaerobic conditions in the canal.

Dissolved oxygen and redox potential appeared to play a major role in the release of nutrients. Under high concentration of dissolved oxygen, nitrogen is oxidized and phosphorus is not released. Non Apatite Inorganic Phosphorus (NAIP) and Organic Phosphorus (OP) do not vary in the sediment. In anoxia, there is a solution of iron together with a release of orthophosphates. At the same time, NAIP and OP concentrations decrease in the sediment. These results showed that internal loading can be responsible for an increase in eutrophication of Erdre River, in the case of oxygen depletion.

RESUMO

A liberação de ortofosfato, amônia, nitrito, nitrato e ferro de sedimentos eutróficos do rio Erdre (França, foi estudada a fim de avaliar os riscos de incremento da eutrofização, devido a carga interna.

Um experimento, com duração de um mês, foi efetuado com um canal de simulação, no qual a temperatura, a velocidade de fluxo e a intensidade de luz foram controladas. Duas câmaras (uma cilíndrica, em contato com o ar, e outra, retangular, fechada) permitiram o estudo sob condições oxidantes e redutoras.

O oxigênio dissolvido e o potencial redox parecem desempenhar um papel importante na liberação dos nutrientes. Quando a concentração de oxigênio é elevada, o nitrogênio é oxidado e o fósforo não é liberado. O Fósforo Inorgânico Não-Apatítico (PINA) e o Fósforo Orgânico (PO), não variam nos sedimentos. Em anoxia, ocorre a solubilização do ferro e a liberação dos ortofosfatos. Simultaneamente, as concentrações de PINA e PO decrescem nos sedimentos. Os resultados indicaram que, no caso de empobrecimento em oxigênio, a liberação de nutrientes, a partir dos sedimentos, pode contribuir para o incremento da eutrofização do rio Erdre.

INTRODUCTION

For the last 30 years, eutrophication of lakes and rivers has become an increasing problem in most industrialized countries (Vollenweider, 1968, 1981; Wetzel, 1975; Baley-Watts, 1990).

Although N, C, Si control the primary production of algal biomass, P is regarded as a key factor, first responsible for the development of eutrophication and, therefore, likely to cause a degradation of water quality (Gillion, 1984; Esteves, 1988).

Several methods have already been proposed for the restoration of lakes and rivers (Barroin, 1991; Van Der Does *et al.*, 1992). The reduction of the external phosphorus loading should be the best solution (Boers, 1991; Ambühl & Bührer, 1993), but it has to be drastic in order to be efficient (Cullen & Forsberg, 1988) and is, therefore, not easy to implement. Furthermore, the success of these measures is often limited (Van Liere *et al.*, 1990; Rossi & Premazzi, 1991), partly because there might be a resistance of the foodweb to changes (Van Dunk & Gulati, 1989) and mainly because of the phosphorus release from the sediments.

There are many forms of phosphorus in the aquatic environment, present either as dissolved or particulate phases, that can be organic or inorganic. Insoluble organic phosphate is bound to such as phospholipids, inositol, phosphoproteins, so forth, while insoluble inorganic phosphates are generally bound to clay minerals, iron hydroxides or minerals such as apatite, hydroxyapatite, strengite, vivianite or variscite.

Soluble inorganic phosphates, that is orthophosphates ($H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}), are considered as bioavailable (Williams *et al.*, 1980; Peters, 1981), their occurrence, being dependent on the water pH (Oluyedun *et al.*, 1991), as well as exchanges and equilibrium between interstitial water, sediment, and water.

It is now admitted (Malati & Fox, 1985; Boers, 1991) that the development of certain conditions at the sediment-water interface favors the phosphorus release; this is the case for low oxygen contents, high values of pH and temperature, low redox potential. Bacterial and other biological activities probably also play a role in the release of phosphate to the water column, particularly in aerobic exchanges (Kamp-Nielsen, 1974).

Many studies have already been carried out on the behavior of phosphorus at the sediment-water interface (Kamp-Nielsen, 1974; Boers & Van Hese, 1988; Fox *et al.*, 1989; Levine & Schindler, 1989).

Nutrient fluxes have been quantified both in laboratory (Jacoby *et al.*, 1982; Drake & Heaney, 1987; Boers & Van Hese, 1988; Schroeder *et al.*, 1992) and field experiments (Devol, 1987; Jansen & Andersen, 1992).

In the case of laboratory experiments, especial attention has to be paid to a proper simulation of environmental conditions, such as temperature, pH and redox potential (Holdren & Armstrong, 1980; Boström & Petterson, 1982; Boers, 1991).

The objective of the present work is to evaluate the potential release of phosphate from the sediments of an eutrophic river located in the western part of France. Besides phosphate release, NH_4^+, NO_2^-, NO_3^- and Fe were also investigated.

MATERIAL AND METHODS

This study was carried out using a simulation canal in which the temperature, water flow velocity and light could be controlled. Redox potential (Eh), pH, dissolved oxygen were also measured.

The sediment used was from the Erdre River, an eutrophic river in western France and we tried to compare the fluxes from aerobic and anaerobic sediments for a water temperature of 24°C, simulating summer conditions.

The sediment was collected by means of a box core sampler, conditioned in plastic boxes and immediately transported to the laboratory. After homogenization, it was put on the simulation canal before water addition. Previous analysis demonstrated that the sediment had oxidizing characteristics at surface (< 10 mm) and reducing ones in the deep layers.

The Canal

The experimental canal (Fig. 1) was composed of 2 water tanks (upstream and downstream) and a sediment tank (Marchandise & Robbe, 1978; Roger, 1988), with a total water volume of 7.5 m³.

The water temperature was set at 24°C and flow were regulated with a velocity of 10 $cm.s^{-1}$. Fluorescent tubes (100 W) above the canal simulate day/night alternancy.

Two plexiglas benthic chambers, one cylindrical with a surface of 0.045 m² and a

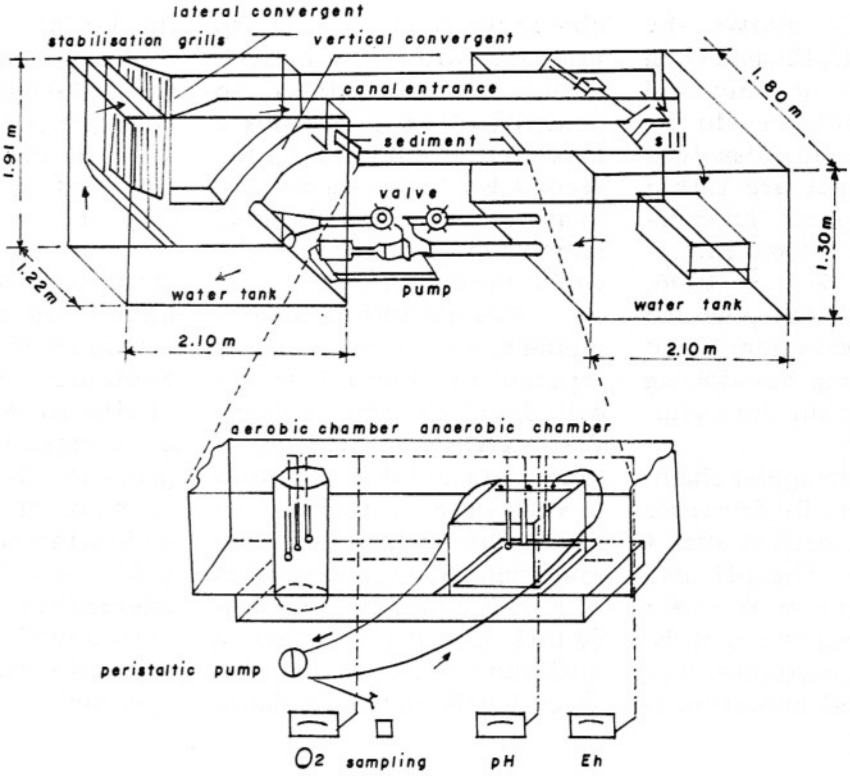

Figure 1 - The simulation canal.

volume of 17 l, the other rectangular with a surface 0.0718 m^2 and a volume 21.4 l, set in the sediment tank enabled the study of aerobic and anaerobic environments, respectively.

The fluxes in mg.m^{-2}.d^{-1} were calculated taking into account the water nutrient concentration, the volume of the benthic chambers and the sediment surface area enclosed in the chamber, according to the following equation:

$$F = \frac{NV_{bc}/t}{A}$$

Where :
F = flux (mg.m^{-2}.d^{-1})
N = water nutrient concentration (mg.l^{-1})
V_{bc} = benthic chamber volume (l)
t = time (days)
A = benthic chamber area (m^2)

Constant aeration was maintained in the cylindrical chamber throughout the experiment whereas anoxia characterized the rectangular chamber in which water was regularly sampled by a peristaltic pump. No water was added in the benthic chambers, after every sampling intervals, in order to maintain the water volume constant.

The pH, Eh and dissolved oxygen were measured in both chambers, in the water column (Fig. 1). Samples were taken daily for 28 days (the duration of the experiment).

The analysis

The sediment was characterized at the beginning and at the end of the experiment by speciation phosphorus using William's method (Williams *et al.*, 1976). Water samples for chemical analysis were filtered (Millipore 0,45 µm). Filtration under a nitrogen flux was performed, in order to prevent the oxidation of the samples from the anaerobic chamber. Ammonia, nitrite, nitrate and orthophosphate were measured by spectrophotometry (Perking Elmer Lambda 5), following AFNOR standards (AFNOR, 1990). Analysis of iron were carried out by means of flame atomic absorption spectroscopy (Varian Spectra 300). Ponselle and Tacussel electrodes were used for the determination of pH, Eh (Ag/AgCl reference electrode), and O$_2$.

RESULTS

The Erdre river sediment is sandy silt, rich in organic matter (28 - 34%) with a mean water content of 87% (Cavalcante, 1995).

Figure 2 shows the variations of pH, Eh, and O_2 in the water for aerobic and anaerobic conditions. In the oxic environment, dissolved oxygen and pH are rather constant throughout the experiment with values of 6.3 mg l^{-1} ± 0.36 and 8.3 ± 0.06, respectively. Redox potential regularly increases from 106 to 234 mV, revealing the oxidizing conditions within the cylindrical chamber.

In the rectangular chamber, oxygen rapidly decreases and anoxia is reached after 4 days (Fig. 2). The pH also shows a diminution from 8.5 at the beginning to 6.8 at the end of the experiment. The redox potential evolution is cha-racterized by a sharp increase (after few hours), which can be related to denitrification. It reaches a maximum of 500 mV on the second day, before decreasing to about -500 mV. This value remains then stable until the end of the experiment.

The evolution of ammonium, nitrite and nitrate is reported in Figure 3. In the cylindrical chamber, N-NH_4^+ first increases to 1.32 mg l^{-1} (third day) and then decreases to value near 0.1 mg l^{-1} on the fourth day, due, probably, to nitrification. The concentration of N-NO_2^-, initially very low (0.001 mg l^{-1}), reaches a maximum (0.32 mg l^{-1}) after seven days before decreasing to the initial value. Regarding nitrate, the concentration increases to 4.0 mg l^{-1}; a fall happens after sixteenth day (2.2 mg l^{-1}). There is then a stabilization followed by a new increase (Fig. 3).

In the rectangular chamber, N-NH_4^+ increases all through the experiment, to a maximum of 4.2 mg l^{-1}. This is explained by the lack of nitrification in this anoxic environment. The reduction process characterizes the evolution of nitrite and nitrate with an increase in nitrite (from 0.001 to 0.05 mg l^{-1}) and a diminution in nitrate (from 0.71 to 0.03 mg l^{-1}). After the ninth day, both concentrations remain very low.

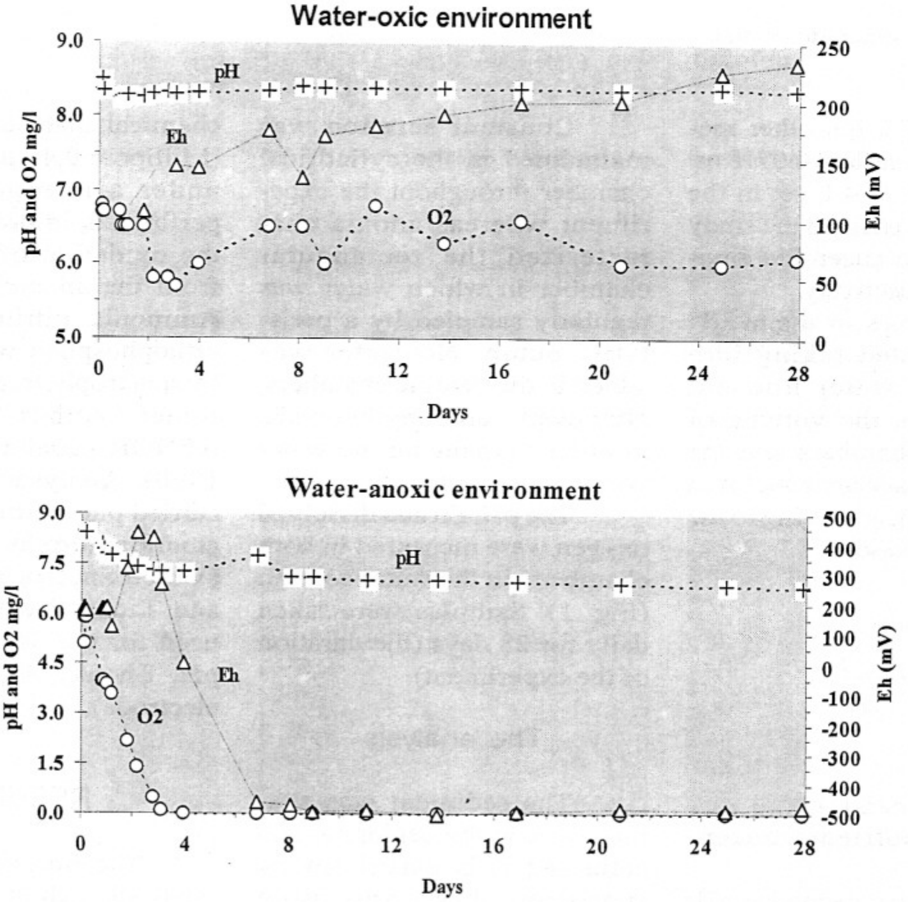

Figure 2 - Evolution of pH, O_2 and redox potential in the water-oxic and anoxic environments (Erdre river sediment).

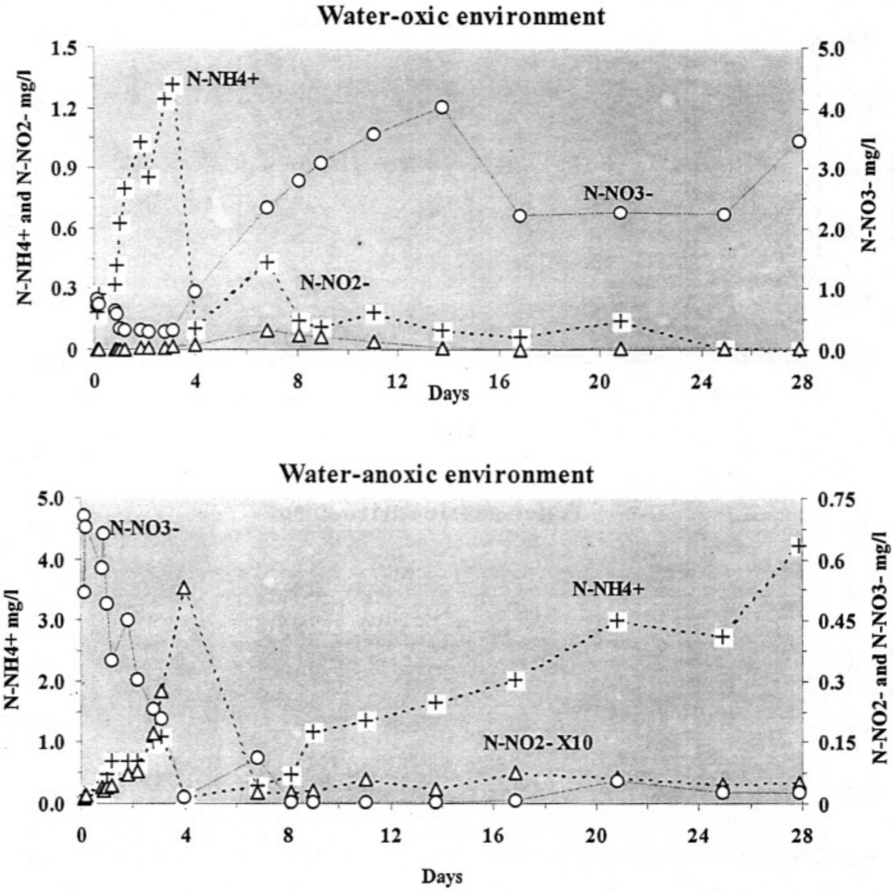

Figure 3 - Evolution of ammonia, nitrite and nitrate in the water-oxic and anoxic environments (Erdre river sediment).

Figure 4 shows the variations of orthophosphates in the two chambers. Orthophosphates remain below the detection limit (0.02 mg l^{-1}) in the oxic environment. The small increase on first day is due to resuspension of the sediment because of a movement of the aeration system at the bottom. The evolution is quite different in anoxia, where a sharp increase (to 1.57 mg l^{-1}) is observed. This behavior is in agreement with that of iron. In the cylindrical chamber, iron concentration remains very low throughout the experiment, but increase slightly at the beginning to 0.074 mg l^{-1}. From day 12 to the end, the concentration is rather stable at 0.02 mg l^{-1}. The concentration is 30 times higher in anoxic conditions and rapidly increases from 0.011 to 3.4 mg l^{-1}.

Nutrient fluxes

In the oxidizing environment, 19.8 mg of N-NH$_4^+$ are released in three days. The flux of ammonia is, therefore, 142.0 mg.m^{-2}.d^{-1}. The fluxes of N-NO$_2^-$ and N-NO$_3^-$ are 18.0 and 89.0 mg.m^{-2}.d^{-1}, respectively. Phosphate and iron do not show any release.

The situation is quite different in anoxia. In this case, N-NH$_4^+$ N-NO$_2^-$ fluxes are smaller than those calculated in the cylindrical chamber, being 44.0 and 4.0 mg.m^{-2}.d^{-1}, respectively. On the contrary, P-PO$_4^{3-}$ release is very important with a flux of 19.0 mg.m^{-2}.d^{-1}. The flux of iron, due to the reduction of Fe^{3+} to Fe^{2+}, is also higher in anoxic conditions (32.0 mg.m^{-2}.d^{-1}).

DISCUSSION

In the cylindrical chamber, where oxygen was almost at the saturation level, the ammonium reoxidation was the most important process. In these aerobic conditions, the mineralization of organic matter produces ammoniac nitrogen which is oxidized to nitrite and nitrate. Because of the high oxygen content, phosphorus

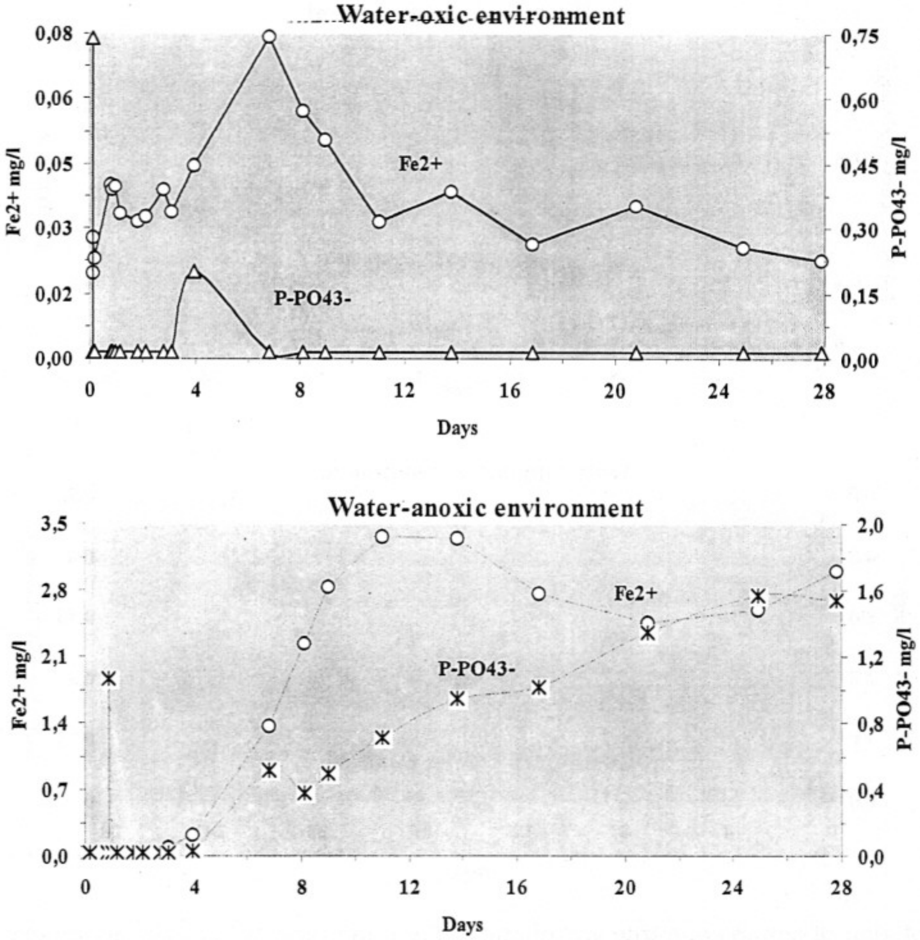

Figure 4 - Evolution of orthophosphates and iron in the water-oxic and anoxic environments (Erdre river sediment).

remains bound to the sediments. High redox potential favors the formation, at the sediment surface, of a thin layer of ferric hydroxide, on which orthophosphate ions from the reduced zone of the sediment are absorbed. The diffusion of these ions towards the overlaying water is, therefore, inhibited (Boström & Petterson, 1982), but this process seems to be dependent both on the amount of iron hydroxide and on pH value (Malati & Fox, 1985; Fox *et al.*, 1989).

The phosphorus speciation performed on the sediment confirms the absence of diffusion; fractionation before and after the experiment shows no difference in Non Apatite Inorganic Phosphorus (NAIP) and Organic Phosphorus (OP), the forms of phosphorus likely to be released in the water column (Fig. 5). These results enhanced the aptitude of the sediments to fix phosphorus under specific conditions.

In the rectangular chamber, once oxygen is depleted, the ammonium production showed a gradual growth along the investigation period. The nitrate was reduced to nitrite and later to elementary nitrogen.

According to Balzer (1982), after Golterman (1975), redox potential of about 400 - 450 mV is necessary for the reduction of nitrate into nitrite. As anoxia goes on and Eh reaches 260 mV (with O_2 < 0.1 mg l^{-1}), Fe^{+3} is reduced into Fe^{+2}, inducing the solubilization of ferric hydroxides. Fe reduction is also due to a decrease in pH, which drops from 8.5 to 6.8 at the beginning of the survey. Figure 4 shows that orthophosphate release happens together with iron solubilization. This coincidence was first noticed by Mortimer (1941). The diminution of NAIP and OP in the sediment at the end of the experiment confirms the orthophosphate release (Fig. 5). The slight decrease of Fe (day 16) could not be associated to the reaction of Fe^{+2} with sulfur, since the pyrite or vivianite were not detected by x-ray diffractometry.

The results show that internal loading from the sediment can be responsible for an increase in eutrophication in the Erdre river. A reduction of external inputs is, therefore, not always synonymous of immediate restoration of the water body. Phosphates release at the water-sediment interface can be responsible for a delay in the river restoration.

It is worth to emphasize that on tropical regions, where the high incidence of light and elevated temperatures favor intense metabolic activities of organisms and rapid organic matter and nutrient cycling, the sediments not always play a significant role in the trophic state of these environments.

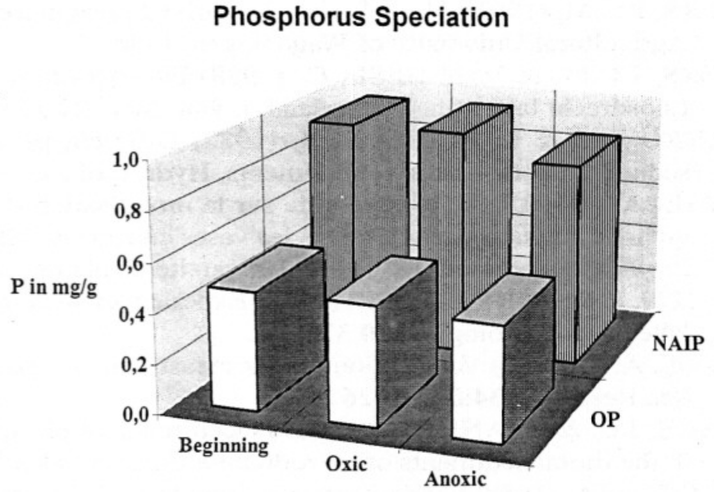

Figure 5 - Phosphorus speciation in the Erdre river sediments in the beginning of the experiment and after 28 days in the oxic and anoxic chambers. NAIP = Non Apatite Inorganic Phosphorus. OP = Organic Phosphorus.

CONCLUSION

The results of this lab experiment show that specific conditions of the environment such as temperature, dissolved oxygen and redox potential play a major role in phosphorus exchanges and nitrogen evolution at the water-sediment interface.

The simultaneous study of oxic and anoxic conditions shows that nutrients behave quite differently in the two environments. When oxygen is abundant, nitrogen transformation prevails and orthophosphates tightly bound to the sediment do not diffuse into the water column; the concentration of NAIP and OP in the sediment do not vary. On the contrary, during anoxia, orthophosphates are released, which is attested by a diminution of NAIP and OP in the sediment. At the same time, there is a solubilization of iron. Therefore, because of this internal source of phosphorus, P concentration in the water is likely to increase, in spite of a reduction of external inputs. In order to estimate the potentiality of P release and the period of release, it is necessary to investigate dissolved oxygen at the water-sediment interface and to perform analysis of different forms of phosphorus in the sediment on a year-time basis.

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