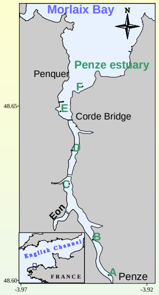
A preliminary study on the role of sedimentary phosphorus in the development dynamics of *Alexandrium minutum* in the Penzé Estuary (NW France).

Françoise Andrieux-Loyer*, Xavier Philippon*, Roger Kérouel*, Agnès Youenou*, Claire Labry*, Gallioz, C.
* IFREMER, B.P. 70, 29280 Plouzané, France ; Francoise.Andrieux@ifremer.fr

Introduction

The Morlaix Bay (NW France) and particularly the Penzé estuary flowing into it, have been subjected to recurrent annual toxic blooms of the dinoflagellate *Alexandrium minutum* since 1988. The conditions leading to the development of *A. minutum* (hydrology and nutrient concentrations) have been fairly well studied (Maguer *et al*., 2004). However, the role of sediments in the dynamics of nutrients controlling the primary production is still inadequately known. Laboratory experiments on *A. minutum* growth control and one of its competitors -*Heterocapsa triquetra*- have shown that *A. minutum* was only predominant in mixed culture deprived of phosphate for 5 days and then subjected to a phosphate supply. **It is essential to specify the role of phosphorus in *A. minutum* growth and in particular to verify if the sediment can generate such phosphorus supplies in the water column.**

Diffusive fluxes and forms of phosphorus during bloom development were studied during the early summer 2003 in the intermediate area (station D) and in summer 2004 along the salinity gradient (stations A to F). This study was carried out during low hydrodynamic conditions (low river flow, neap tide and low tide). With these data we intend to answer two questions : to what extend can benthic fluxes contribute to the phosphate enrichment of the water column and to what extend can the phosphorus sedimentary stock counterbalance a reduction in phosphate external loadings to prevent the bloom from fully developing.



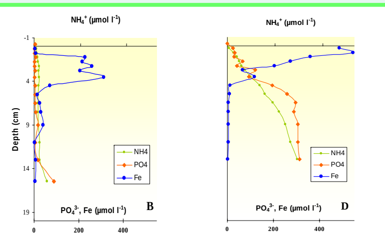
Materials and Methods

Sediment cores were taken using a conventional Barnett multi-tube corer (Barnett and others, 1984). The sediment was sectionned in 0.5 cm slices in the upper 3 centimeters of the sediment, 1 cm slices from 3 to 8 cm, 2 cm slices from 8 to 14 cm and 3 cm slices from 14 to 20 cm.

Slices from corresponding depth intervals were centrifuged to separate the pore water from the solid phase. The pore water was analysed using segmented flow analysis for phosphate, nitrate, nitrite (Tréguer and Le Corre, 1975) and ammonium (Kérouel and Aminot, 1997). The major reservoirs of sedimentary phosphorus (phosphate bound to ferric oxides (Fe-P) and organic phosphorus (Orga-P)) were determined using the sequential method of Psenner *et al*. (1988). In addition, authigenic and detrital forms of calcium bound phosphate (Ca-P) were measured following Ruttenberg (1992). Iron that was extracted in the dithionite solution (called BD-Fe) is considered to represent oxidized iron species able to bind phosphate.

Results

1- Benthic versus river fluxes



Decomposition products (NH_4^+, PO_4^{3-}) of organic matter in sediments showed higher concentrations in the intermediate estuary (D) than in the inner and outer estuary. Mineralization which occurs in Penzé sediments consumes O_2 (0 mg L^{-1} at 0-0.5 cm), then nitrate (<6 µmol L^{-1} at 0-0.5 cm) and iron.

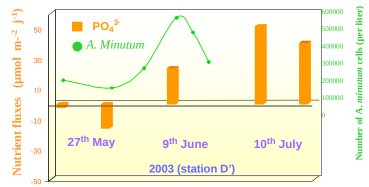
Diffusive fluxes were calculated from interstitial vertical profiles, using Fick's first law (Krom and Berner, 1980) :

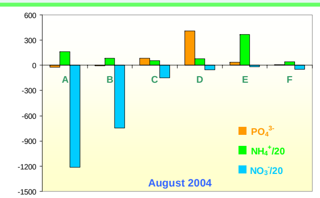
$$Fd = -\phi \times Ds \times (\frac{dC}{dz})$$

Ds : diffusion coefficient in sediment (m^{2} h^{-1})

Φ : sediment porosity

dC:dz : concentration gradient at sediment-water interface (µmol m^{-3} m^{-1})



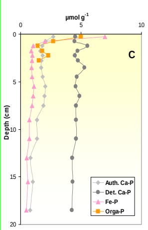


A sediment phosphate uptake was observed in 2003 before the maximum of *A. minutum* bloom. A release occurred during and after the maxima of cells (600 000 cells L^{-1}). This could be the response of the sediment to the decrease in concentrations in the water column due to phosphate uptake by the phytoplanktonic community. At the end of the bloom, water column concentrations were very low (0.1 µmol l^{-1} in July) which explained the highest fluxes. In August 2004, results highlighted the ***heterogeneity*** of ***fluxes*** along the estuary. The highest phosphate fluxes (from 85 to 407 µmol m^{-2} j^{-1}) were observed in the intermediate estuary. The nitrate fluxes were predominantly negative, *i.e.* into the sediment, indicating that denitrification occurs.

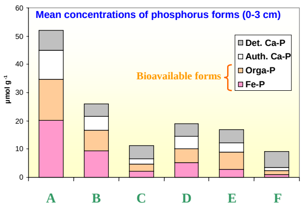
These data can be used to give a rough estimate of the role played by sediments in the nutrient budget of the estuary. Taking into account the studied area (about 2 km²), inputs of phosphate from sediments ranged from 1 to 5 kg j^{-1} in 2003, which represented about 2-25 % of the external discharges in May-June (20 to 40 kg j^{-1}). In August 2004, in the intermediate estuary (from Eon Bridge to Corde Bridge: about 0.5 km²), inputs from sediments represented about 20 to 30 % of the external loadings.

2- Sedimentary phosphorus versus external loadings

This study aims to improve our understanding of *A.* minutum events, so the notion of bioavailability must be taken into account. Potentially bioavailable phosphorus in sediments corresponds to the amount that can be released as soluble phosphate, therefore becoming available for algal growth. Bioavailability can be assessed by bioassays. However, when phosphorus form concentrations are known it is possible to determine the upper limit of the potentially bioavailable phosphorus. In the anoxic sediments of the Penzé estuary, PO_4^{3-} can be released both from the reduction of Fe oxides-bound phosphate (Fe-P) and from the mineralization of organic matter (Orga-P).



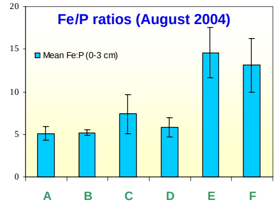
Maximum values of Fe-P and Orga-P occurred at surface layers and declined with depth to stable values. **Fe-P maxima** were attributed to **Fe oxides** present in the oxic layer which can act as a trap for upward diffusing phosphate. **Orga-P** profiles reflected the fate of organic matter which is mineralized after its accumulation in the uppermost layers, following the productive period.



Higher Fe-P concentrations in the inner part of the estuary, seemed to be correlated to freshwater influence. Freshwater transport of phosphorus was shown mainly adsorbed to Fe oxides (Lebo, 1991).

➢ We have calculated the **bioavailable phosphorus** on a **sedimentary layer of 3 cm** likely to be subject to bioturbation or resuspension. In the **inner** part of the estuary (~0.5 km²), and taking into account the average bioavailable phosphorus concentrations (15 µmol g^{-1}), there is a potentially bioavailable phosphorus **pool of about 35 tons P**. In the **intermediate** and **outer** parts of the estuary (~1,5 km²), the mean concentration of bioavailable phosphorus is 3 µmol g^{-1}, which corresponds to a stock of **23 tons P**. This total load of potentially bioavailable phosphorus which corresponds to **six years of external loadings**, could be released from sediments in the event of favourable environmental conditions (notably if oxygen conditions in the near bottom waters deteriorated).

The Fe:P ratio is considered to be an **indicator** of **free sorption sites** for phosphate ions on iron hydroxide surfaces. **Fe:P ratios in sediments** showed that the inner and intermediate areas were the most important in terms of P liberation. Low Fe:P ratios suggest less capacity to adsorb phosphate or even saturation of sorption sites. This area should therefore contribute in **maintaining eutrophic conditions**, despite management efforts to reduce nutrient loadings from freshwaters.



Conclusions

✓This preliminary study highlighted the **spatio-temporal heterogeneity** of nutrient supplies from sediments in the Penzé estuary. This could partly be attributed to the fact that the Penzé estuary like many other estuaries are highly dynamic environments (Sanders *et al*., 1997), where sediments are subject to important resuspension.

✓The release of phosphate from sediments in the early summer 2003, after the maxima of bloom represented about 25 % of the external loadings. In August 2004, the supplies from sediments reached 30 % of the external supplies. However calculated benthic fluxes could be underestimated in comparison with fluxes measured by benthic chambers. Large discrepancies have already been reported and attributed either to the bioturbation provoked by certain species of the benthic macrofauna (Callender, 1982) or the release of gas bubbles which enhances transport during the summer (Martens and Klump, 1980).

✓Pools of bioavailable phosphorus in the surface sediment were about 6 times higher than the annual net-export of P (10 ton year^{-1}) from the estuary. **When measures are taken to reduce nutrient inputs into estuarine systems, it is therefore essential to consider that phosphorus availability may persist as a result of sediment supply, even after reducing the external point sources.**

References: Callender and Hammond, *Est. Coast. Shelf Sci*., 1982, 15, 395-413 ; Kérouel and Aminot, *Mar. Chem*., 1997, 57, 265-275 ; Lebo, *Mar. Chem*., 1991, 34, 225-246 ; Maguer *et al*., *Limnol. Oceanogr*., 2004, 49(4), 1108-1114 ; Martens and Klump, 1980, *Geochim. Acta*, 44, 471-490 ; Ruttenberg *et al*., *Limnol. Oceanogr*., 1992, 37 (7), 1460-1482 ; Sanders *et al*., *Jour. Sea Res*., 1997, 37(12), 3-23 ; Tréguer and Le Corre, 1975, UBO, France ;

Ifremer ICREW