Phosphorus dynamics and bioavailability in sediments of the Penzé Estuary (NW FRANCE). Relation to annual P-fluxes and occurrences of *Alexandrium minutum*.

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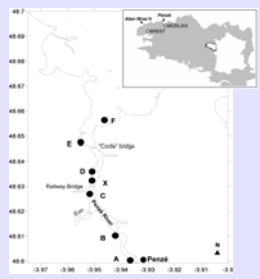
Introduction

The Morlaix Bay (NW France) has 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). Maximum of cells densities were found in early summer (temperature over 16 °C), during low river flow and neap tide and with salinities close to 26. 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 (Labry *et al*., 2004). *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.*

Sediment P-pools and diffusive fluxes were studied during the early summer 2003 in the intermediate area (station X) and in December, March, June, August 2004-2005 along the salinity gradient (stations A to F). Samplings were carried out under similar hydrodynamic conditions (low river flow, neap tide). This study aims to specify the phosphorus dynamics and bioavailability in sediments for a better understanding of *Alexandrium minutum* occurrences. With these data we intend to answer two questions: to what extend can the phosphorus sedimentary stock counterbalance a reduction in phosphate external loadings to prevent the bloom from fully developing and to what extend can benthic fluxes contribute to the phosphate enrichment of the water column.



The Penzé river, with a modest average flow of 2.5 $m^3\ s^{-1}$ discharges into the Morlaix Bay, along the North Brittany coast. Due to the large tidal range (9 m on springs in Morlaix Bay), the sea penetrates deeply into the flooded valley which constitutes the upper part of the estuary. The overall length of which is approximately 6 km. The Penzé drains an area of 141 km^2 consisting largely of intensively cultivated hinterland.

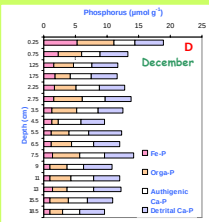
Materials and Methods

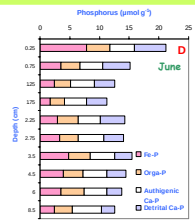
Sediment cores were collected using a hand corer. The pore water was analysed using segmented flow analysis (Aminot and Kérouel, 2006). The major reservoirs of sedimentary phosphorus (phosphate bound to ferric oxides (Fe-P) and organic phosphorus (Orga-P)) were determined using the sequential method of Psenner *et al*. (1988). Authigenic and detrital forms of calcium bound phosphate (Ca-P) were measured following Ruttenberg (1992). Iron, extracted in the dithionite solution (so called BD-Fe), is considered to represent oxidized iron species able to bind phosphate.

Results

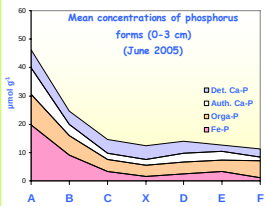
1- Phosphorus speciation and availability : sedimentary P versus external loadings

This study aims to improve our understanding of *A. minutum* events, so the notion of bioavailability must be taken into account. The knowledge of phosphorus forms gives us the upper limit of the potentially bioavailable phosphorus. In the anoxic sediments of the Penzé estuary, phosphate can be released both from the reduction of Fe oxides-bound phosphate (Fe-P) and from the mineralization of organic matter (Orga-P).

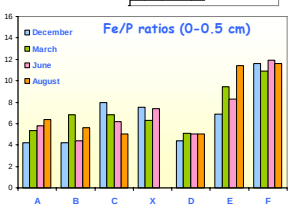




The highest Fe-P and Orga-P concentrations occurred always at surface layers and declined with depth to constant values. Fe-P maxima were attributed to Fe oxides present in the oxic layer which can act as a trap for upward diffusing phosphate. Orga-P profiles reflected the fate of organic matter which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



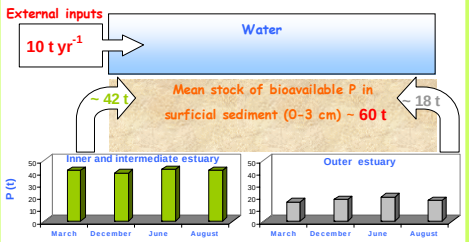
The inner part of the estuary, with the highest freshwater influence, always represented the largest sinks of potentially bioavailable P (Fe-P + Orga-P). This area is characterized by low current velocities and long residence times which allow the sedimentation of fine particles rich in organic matter and in Fe oxides. Moreover, the increase in pH with salinity increase may produce release of P adsorbed on the iron complexes because of competition with OH^- ions. In addition, the Fe/P ratios suggest that the inner and intermediate areas are the most important in terms of P liberation. Fe/P ratio is considered to be a measure of free sorption sites for phosphate ions on iron-oxyhydroxides. Low Fe/P ratios (<8) suggest less capacity to adsorb phosphate or even saturation of sorption sites (Paludan and Jensen, 1995).



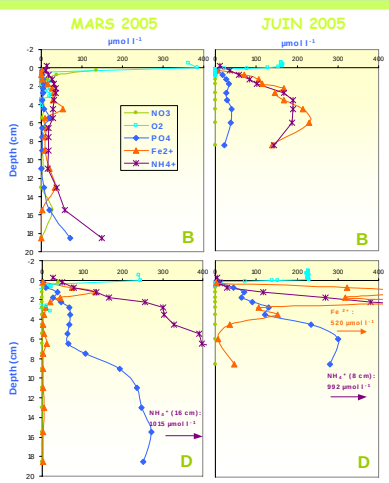
Seasonal variation of Orga-P in the sediment top layer (3 cm) was not significantly different (Friedman, n=24, 99 % confidence level) except at station F where a significant increase was observed in June. This can be related to phytoplankton growth.

A pattern with Fe-P decreasing in summer was observed at station C, X, D and F. This may be due to the reduction of Fe-P following an anoxia caused by the spring bloom.

➢ BIOAVAILABLE PHOSPHORUS on a **sedimentary layer of 3 cm** likely to be subjected to bioturbation or resuspension was calculated. The total load of potentially bioavailable phosphorus corresponds to **six years of external loadings**. This P could be released from sediments in the event of favourable environmental conditions (notably if anoxic conditions in the near bottom waters occurred).

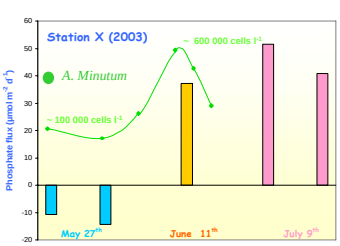


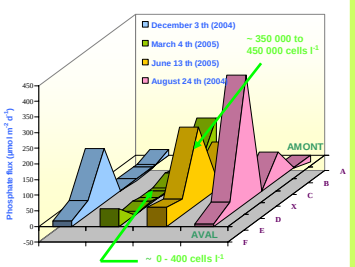
2- Pore water chemistry and flux calculation : benthic versus river fluxes



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 whatever the studied period. O_2 and NO_3^- depth penetrations and concentrations decreased in June after the bloom, whereas Fe^{2+} increased as Fe oxides were used as electron acceptors for the bacterially mediated oxidation of organic matter.

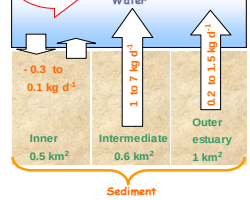
Diffusive fluxes were calculated from pore water profiles, using the Fick's first law (Krom and Berner, 1980) :





Results highlighted the heterogeneity of fluxes along the estuary, particularly in June and August. Very low phosphate fluxes (< 6 µmol m^{-2} d^{-1}) or even sediment uptakes were observed in the intermediate estuary both in May 2003 and in March 2005 before the maximum of *A. minutum cells densities*. A significant release (from about 50 to 400 µmol m^{-2} d^{-1}) occurred during and after the maximum of cells concentrations (350 000 - 600 000 cells l^{-1}). This could be a response of the sediment to the decrease in phosphate concentrations in the water column due to uptake by the phytoplanktonic community.

These data can be used to give a rough **estimate** of the role of **sediments** in the NUTRIENT BUDGET of the **estuary.**



Inputs of phosphate from sediments in the intermediate estuary ranged from 1 to 7 kg d^{-1}, which represented about **7-50 % of the external discharges** in June-August (~ 15 kg d^{-1}).

Conclusions

✓ **Phosphorus speciation results highlighted a decrease of bioavailable P (iron and organic bound) from inner part of the estuary seaward. Ratio of iron-bound P to iron-oxyhydroxides were lower in the inner and intermediate estuary (< 8) than in the outer site, suggesting saturation of sorption sites and greater P bioavailability. Pools of bioavailable P in the surficial sediment were about 6 times higher than the annual net-export of P (10 ton year⁻¹). Management measures to reduce nutrient inputs into estuarine systems should therefore consider that P availability may persist as a result of sediment supply, even after reducing the external point sources.**

✓ **Pore water and flux results exhibited the spatio-temporal heterogeneity of phosphate supplies from the sediments. This could partly be attributed to the fact that Penzé estuary like many other estuaries are highly dynamic environments (Sanders *et al*., 1997), in which sediments are subjected to great resuspension events. The highest phosphate supplies occurred in June and August in the intermediate area (up to 400 µmol m^{-2} d^{-1}) where they represented up to 50 % of external loadings. Its results further suggest that the pulse of phosphate coincided with occurrences of *A. minutum* reported in June.**

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References: Aminot and Kérouel, 2006, Ifremer publications, in press. ; Krom and Berner, 1980, Geochim. Cosmochim. Acta, 45, 207-266 ; Labry et al., 2004, XI conference on harmful algae, Cape Town, 15-19 November 2004 ; Maguer et al., 2004, Limnol. Oceanogr., 49(4), 1108-1114 ; Paludan and Jensen, 1995, Wetlands, 15, 365-373 ; Psenner et al., 1988, Arch. Hydrobiol. Beih. Ergebn. Limnol., 30, 98-103 ; Ruttenberg et al., 1992, Limnol. Oceanogr., 37 (7), 1460-1482 ; Sanders et al., 1997, J. Sea Res., 37(12), 3-23 ;