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Phosphorus dynamics and bioavailability in sediments of the Penzé Estuary (NW France): in relation to annual P-fluxes and occurrences of *Alexandrium Minutum*

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Abstract:

The macrotidal estuary of Penzé (Brittany, Western part of the Channel, France) has been subjected to recurrent annual toxic blooms of *Alexandrium minutum* since 1988. This study aims to specify the phosphorus dynamics and bioavailability in sediments in order to improve our understanding of *Alexandrium* occurrences. Sediment-P pools and diffusive phosphate fluxes were studied under similar hydrodynamic conditions, in the intermediate estuary in May, June and July 2003 and along the salinity gradient from August 2004 to June 2005. The results highlight a decrease in bioavailable phosphorus (iron and organic bound) from the inner part of the estuary seaward. The ratio of iron-bound phosphorus to iron-oxyhydroxides is lower in the inner and intermediate estuaries (5–8) than in the outer site (15), suggesting a saturation of sorption sites and greater phosphorus bioavailability in this area. Pools of bioavailable phosphorus in surficial sediments are about eight times higher than the annual net-export of P (7 ton year⁻¹). Phosphate releases from sediments are always lower than 5 $\mu\text{mol m}^{-2} \text{d}^{-1}$ in March. The highest supplies occur in June and August in the intermediate area (up to 400 $\mu\text{mol m}^{-2} \text{d}^{-1}$) where they represent up to 50% of river loadings. These results further suggest that phosphate pulses coincide with occurrences of *Alexandrium* reported in June.

Keywords: *Alexandrium minutum* - Estuary - Phosphate fluxes - Pore water - Sediment phosphorus - Sequential extraction

1. Introduction

Estuaries are generally regarded as highly eutrophic systems as a result of anthropogenic nutrient inputs. Among the many compounds usually supplied into the rivers and estuaries, phosphorus is important due to its buffering mechanism. The buffering mechanism of P is known for maintaining its concentrations close to constant values, providing an additional potential reservoir for primary production (Smil, 2000). Moreover, in such productive areas, sediments receive high concentrations of organic matter due to shallow water depths and river inputs. After sedimentation, organic particles are subjected to a continuous degradation and mixing process. The sediment may act as a phosphorus sink, thus liberating phosphate under specific conditions. This phenomenon is attributed mainly to the Fe(III)-bound-P dissolution when conditions change from oxic to anoxic, to the desorption of adsorbed phosphate when fine particles are resuspended (Froelich, 1988; Aminot *et al.*, 1993; Andrieux and Aminot, 1997; Andrieux-Loyer and Aminot, 2001) and to the assimilation of organic phosphorus by the bacterial community (Clavero *et al.*, 1999b; Avilés *et al.*, 2005). The released P may significantly increase the biologically available pool of P in the water, counteracting decreases in the external loads. As an illustration, in some estuaries, intrinsic supplies of phosphate by desorption, reduction or mineralization, may exceed external supplies by a factor 2 to 4 due to high concentrations in sediments (Schlungbaum and Nausch, 1990). Therefore, the knowledge of sedimentary phosphorus speciation and phosphate fluxes is essential in every study which aims to understand the functioning of a coastal system under anthropological constraints.

The Penzé estuary (North of Brittany, France) has been subjected to recurrent annual toxic blooms of the dinoflagellate *Alexandrium minutum* since 1988 (Erard-Le Denn, 1997). The conditions leading to the development of *Alexandrium minutum* (hydrology and nutrient concentrations) have been fairly well studied (Maguer *et al.*, 2004). The efflorescences reappear evenly under specific conditions (neap tide, temperature over 16 °C, and salinity between 26 and 28). However, the role of sediments in nutrient dynamics controlling the primary production is still poorly documented. Laboratory experiments on *Alexandrium minutum* growth control and one of its competitors -*Heterocapsa triquetra*- showed that *Alexandrium minutum* was only predominated in mixed culture when deprived of phosphate for 5 days and then subjected to a phosphate supply (Labry *et al.*, *in press*). It is therefore essential to verify if the sediment could potentially generate such phosphate supplies in the water column.

This study aims to point out the phosphorus dynamics and bioavailability in sediments in order to improve our understanding of *Alexandrium minutum* occurrences. To this end, seasonal variations of diffusive phosphate fluxes and phosphorus forms were studied along the salinity gradient. With these data we intend to answer two questions: (1) to what extent can the phosphorus sedimentary stock counterbalance a reduction in phosphate external loadings to prevent the bloom from fully developing, (2) to what extent can benthic fluxes contribute to phosphate enrichment of the water column.

2. Materials and methods

2.1. Study site

The Penzé River (28 km in length) drains an area of about 151 km² in North Brittany (figure 1a). The activities around the catchment area are essentially agricultural. This river has three major tributaries: the Coat Toulzac'h, the Eon and the Traon Gall. Its estuary is situated between the village of Penzé and the Morlaix Bay, covering a distance of 10 km (figure 1b). At high tide, the width of the channel is about 100 m, whereas at low tide, fresh waters go through a narrow channel about 10 m wide. The axis of the channel, the bottom of which consists of gravel, is situated between two muddy banks. The Penzé estuary is subjected to a macrotidal regime and the tidal range fluctuates between 1.8 m and 9.2 m. The water discharge at the village of Penzé ranges from 0.4 m³ s⁻¹ in summer to 15 m³ s⁻¹ in winter. Since 1989, nutrient measurements have shown a high nitrate content (768 ± 192 µmol l⁻¹) and lower concentrations in ammonium (14.3 ± 12.3 µmol l⁻¹), phosphate (5.4 ± 3.3 µmol l⁻¹) and silicate (185 ± 23 µmol l⁻¹; data from ECOFLUX, 2007). Water temperature in this system varies usually from 8 °C in winter to 20 °C in summer (Waeles, 2005).

2.2. Sampling

Samples were collected during the early summer 2003 in the intermediate estuary (st X) and from August 2004 to June 2005 along the salinity gradient (seven stations, from st A to st F plus st X). One core was sampled at each station except in May and July 2003 where samplings were duplicated. This study was carried out during similar hydrodynamic conditions (low river flow, neap tide, ebb tide). A parallel survey during a tidal cycle (June 2005) in the intermediate estuary (st X) showed that the highest phosphate diffusive fluxes occurred during neap tide (Bally *et al.*, in preparation). A summary of overlying physical-chemical water properties is given in table 1.

Sediment and its overlying water were collected by hand corer using PVC cores (id = 9 cm; h = 30 cm), as described in Mudroch and Azcue (1995). Any disturbance of the sediment-water interface was carefully avoided.

2.3. Overlying and pore water treatments

Overlying water was collected immediately after core recovery for further nutrient analyses. The profiles of pore-water oxygen were then measured using a miniaturized Clark-type oxygen sensor (Unisense OX500) coupled with a picoammeter (Unisense PA2000) and a micromanipulator (Unisense MM33). Oxygen profiles were only performed in March and June 2005 as the sensors were not available in August and December 2004. The in-situ temperature was maintained by using an insulating device.

Subsequently, the core was sliced into sixteen horizontal layers up to a total depth of 20 cm (0.5 cm for the top 3 cm, 1 cm up to 8 cm, 2 cm below, and 3 cm at the bottom) within 30 min. For every level, a sub-sample was centrifuged in a Whatman VectaSpin 20TM centrifuge tube filter (0.45 μm) under inert atmosphere (N_2) at 3000 rpm and 4 °C for 20 min in order to collect pore waters. The pore water was acidified to pH ~ 2. An aliquot was frozen for further nutrient analysis. Another aliquot was maintained at 4 °C for Fe^{2+} and Mn^{2+} analysis.

2.4. Sediment treatments

An aliquot of the wet sediment of known volume and weight was dried (5 days) and the weight loss was used to calculate porosity (Berner, 1980). Another sample was maintained at 4 °C for less than 15 days for sediment grain size determination. Finally, a sub-sample of wet sediment was frozen for the subsequent organic C analysis. Porosity, grain size and carbon determinations were only performed on the first three centimeters (6 layers), except in August when the whole core was analysed. The sediment remaining after the collection of the pore water was frozen at -25 °C for phosphorus speciation.

Sequential extraction of phosphorus pools and analysis

The major reservoirs of sedimentary P were determined using the widespread sequential method of Ruttenberg (1990, 1992). The main features are presented in table 2.

There are three differences compared to the original procedure of Ruttenberg (1992). Firstly, exchangeable P (Exch-P) was not extracted in step I with MgCl_2 but separately using the infinite dilution extrapolation (IDE) method (Aminot & Andrieux, 1996). Thus, step I extraction in this study includes easily exchangeable P and iron oxide-bound P (Fe-P). Secondly, we omitted citrate in the first step as it was shown to make a part of the calcium-bound phosphate soluble (Psenner, 1988). Thirdly, the MgCl_2 and H_2O washes were omitted except in the acetate buffer treatment (step II). These were originally used to avoid the secondary sorption of P on the residual solid surfaces during the extractions. This process was shown to be insignificant in the Citrate-Dithionite-Bicarbonate (CDB) and HCl extractions (Ruttenberg, 1992).

Organic P (Orga-P) was determined nonsequentially as the difference between 1 M HCl extractable P (24 h) before and after the ignition of the sediment (550 °C, 4 h; Aspila *et al.*, 1976). Total P is calculated as the sum of this organic P and the inorganic P determined with the sequential procedure (Slomp, 1996a). The inorganic P concentrations determined as the sum P-forms (Fe-bound P, authigenic P and detrital Ca-P) agreed well ($r^2 = 0.99$; $n = 379$) with inorganic P concentrations obtained with the 1 M HCl extraction in the one-step procedure.

The sedimentary inorganic carbon was removed with phosphoric acid (Cauwet, 1975) before organic carbon analysis.

The analysis of sediments for major elements (Total Fe and Ca) was performed by the Centre de Recherches Pétrographique et Chimique (CRPG/CNRS). The sample was dissolved by fusion with LiBO_2 and HNO_3 . These results are not shown in the present study as they are just used in a relation between Ca and Ca-P (see § IV.1) and in a relation with fine fraction (see § IV.2).

2.5. Analytical procedures

The analysis of sediment grain size was performed using LS 200 Beckman Coulter laser granulometry. Organic C was measured using a vario EL-III CN elemental analyser. Total Fe and Ca in sediments were measured by ICP-emission.

After thawing, the pore water was diluted tenfold, then analyzed using segmented flow analysis (SFA) for phosphate and nitrate (Aminot and Kérouel, 2007) and for ammonium (Kérouel and Aminot, 1997). Phosphorus forms extracts were also diluted tenfold and dithionite extracts were additionally bubbled with pure O_2 (30 ml min^{-1}) for one minute to enable phosphate determination.

Fe^{2+} in pore water and Fe concentrations in the Dithionite-Bicarbonate (DB) solutions were measured with the ferrozine method (Sarradin *et al.*, 2005) and Mn^{2+} with the leuco-malachite green method (Resing and Mottl, 1992), both adapted for SFA. The method of standard additions was used to check for potential interferences and to correct the results accordingly. DB-extractable Fe is used as a measurement of Fe bound in Fe oxides. These data allow the determination of Fe/P ratios in sediments. The analytical precision of the determinations was better than 2 %.

2.6. Calculated phosphate diffusive fluxes

Diffusive phosphate fluxes were calculated using the first Fick's law adapted for sediments (Berner,

1980): $F_d = -\phi \times D_s \times \left(\frac{dC}{dz}\right)$ (1), where F_d is the rate of efflux ($\mu\text{mol m}^{-2} \text{d}^{-1}$), ϕ is the sediment

porosity (dimensionless) of the upper sediment sample, D_s is the bulk diffusion coefficient ($\text{m}^2 \text{d}^{-1}$) and dC/dz is the concentration gradient at sediment-water interface ($\mu\text{mol m}^{-4}$).

dC/dz was calculated from linear regression on the concentration values at bottom water and just below the interface. The use of the sedimentary surface layer in the calculation of diffusive fluxes is in agreement with the fact that most organic matter decomposition takes place at or directly below the water-sediment interface (Aller, 1980; Ehrenhauss *et al.*, 2004). D_s was corrected for tortuosity, *i.e.*,

$D_s = \frac{D_0}{\theta \times F}$, where θ is the tortuosity (dimensionless), D_0 is the diffusion coefficient in water for PO_4^{3-}

($\text{m}^2 \text{d}^{-1}$) and F is the formation factor ($F = \phi^{-2}$, Manheim, 1970). The diffusion coefficient in water (D_0) is corrected for the in situ bottom water temperatures (Li and Gregory, 1974) and the value of θ is assumed to be equal to $\sqrt{1 - 2 \times \ln \phi}$ (Boudreau, 1996).

3. Results

As the same patterns were observed in 2003 and in 2004-2005 both for pore water and speciation results, only the 2004-2005 results are presented. Data from the 2003 surveys may be found in the 2003 IFREMER activity report (Anonymous, 2004) and in Gallioz, 2004.

3.1. Pore water profiles

Redox sensitive species (O_2 , NO_3^- , Fe^{2+} and Mn^{2+})

Oxygen concentrations in the bottom waters (figure 2) declined from about $360 \mu\text{mol l}^{-1}$ (st A) to about $200 \mu\text{mol l}^{-1}$ (st F) in March 2005. In June, concentrations varied from about $165 \mu\text{mol l}^{-1}$ (st B) to about $250 \mu\text{mol l}^{-1}$ (st A, X and D) in the inner and intermediate estuaries whereas concentrations of up to 316 and $325 \mu\text{mol l}^{-1}$ were observed in the outer estuary (st F and E) corresponding to a saturation of about 130 %. These saturations could be explained by the development of the phytoplankton community in the outer estuary (chlorophyll concentrations up to $20 \mu\text{g l}^{-1}$) which

consumes nutrients and carbon and release O_2 . The concentration profiles of O_2 showed a sharp negative concentration gradient presenting the sediment as a sink for dissolved oxygen whatever the season or the location. O_2 was always consumed within the first millimetres below the sediment-water interface. The penetration depths of dissolved oxygen profiles, ranged from 4 mm (st A, C) to 8 mm (st E, F) in March and from 1-2 mm (stations C, D, E, F and X) to 5-7 mm (st A and B) in June. These shallow penetration depths can be put down to the high reactivity of these sediments and to slow replenishment of oxygen (Sundby, 2006).

NO_3^- concentrations in the bottom waters decreased from the inner part of the estuary (st A) to the outer part of the estuary (st F) whatever the season. The lowest nitrate concentrations in the bottom waters always occurred in August for stations A to E (from $13 \mu\text{mol l}^{-1}$ at st E to $418 \mu\text{mol l}^{-1}$ at st A) or in June for station F ($6.5 \mu\text{mol l}^{-1}$). The highest concentrations were observed in March for stations A to F (from $32 \mu\text{mol l}^{-1}$ at st F to $744 \mu\text{mol l}^{-1}$ at st A) or in December for station X ($277 \mu\text{mol l}^{-1}$). The top sample of the pore water profiles was always impoverished in NO_3^- in relation to the bottom water, suggesting that the sediment is a sink of nitrate for the water column. NO_3^- dropped to concentrations close to zero below the oxic layer. However, nitrate could be sporadically present in the anaerobic part of the sediment.

No data were available for dissolved Fe and Mn in bottom waters. Mn^{2+} and Fe^{2+} pore water profiles indicated sediment dissolution of Mn and Fe oxides. Fe^{2+} profiles generally highlighted a sharp increase (up to 520 and $544 \mu\text{mol l}^{-1}$ at st D respectively in June and August) at the depth where NO_3^- disappeared, and a sharp decrease below 2-4 cm depth. On the contrary, Mn^{2+} profiles gradually increased and decreased with depth, concentrations never exceeding $18 \mu\text{mol l}^{-1}$. The profiles of Fe^{2+} were often more scattered than those of Mn^{2+} . Concentrations of Fe^{2+} and Mn^{2+} were greatly influenced by the seasons especially at stations B, X, D and E where concentrations significantly increased from March to June. The lowest Fe^{2+} and Mn^{2+} concentrations were observed before the productive period in March (st A, B, C, D, E) or in December (st X and F).

Phosphate and ammonium profiles

Phosphate concentrations in the bottom waters ranged from about $0.5 \pm 0.3 \mu\text{mol l}^{-1}$ (st F) to $3.5 \pm 1.3 \mu\text{mol l}^{-1}$ (st A). Phosphate pore water profiles generally exhibited a weak concentration gradient at stations A, B, C (inner estuary) and F (outer estuary) particularly in the first ten centimeters where concentrations did not exceed $50 \mu\text{mol l}^{-1}$ (figure 3). However, isolated phosphate peaks may occur at around 8 or 12-14 cm according to the station or the location.

Conversely, phosphate profiles generally presented a sharp concentration gradient up to 8-10 cm depth at stations X, E and even more markedly at station D (concentrations up to 300 - $314 \mu\text{mol l}^{-1}$ in June and August). Further down, either the concentrations continued to increase slightly or they gently decreased. Phosphate profiles highlighted seasonal variations with the highest concentration peaks occurring in June or August according to the station and the location.

Ammonium profiles displayed the same behaviour as phosphate profiles but with about five time higher concentration levels (figure 3). The highest concentrations of NH_4^+ and PO_4^{3-} were always observed in the intermediate estuary.

3.2. Solid fraction

Sediment characteristics (granulometry, porosity, Carbon and Nitrogen)

Sediment characteristics of surficial sediments (in the top 3 cm) are presented in table 3.

A grain-size characterization was performed using the classes defined in Wentworth (1922) and Bellair and Pomeroy (1977). Coefficients of variations were generally lower than 15 %, indicating a relatively stable grain-size nature of surficial sediments at each station over time. The relatively seasonal homogeneity in the sediment top layer was confirmed by using Friedman tests ($n=24$, 95 % confidence level) both for the lutite fraction ($< 62.5 \mu\text{m}$) and the sand fraction (62.5 - $2000 \mu\text{m}$). Station F presented the highest variabilities especially for the clay fractions ($< 3.9 \mu\text{m}$) which was relatively variable from one season to another (up to ± 20 %). According to the sedimentary characterization of Larsonneur (1977), the sediments were all silty sands. Nevertheless, the sediments at station A always presented the highest percentage of lutites (from 66 ± 3 % in March to 72 ± 2 % in December, June and August).

The vertical distributions of porosity (not shown) highlighted a decrease from the surface to the deeper layers (around 2-6 cm) whatever the season, in particular at stations B to F, and to a lesser extent at station A. The highest porosities (up to 85 %) always occurred at the upper estuary (station A) and the lowest (about 50-70 %) either in the outer estuary (st F) or in the intermediate estuary (st X). A pattern of decreasing porosity in June in surficial sediments (0-3 cm) was observed at stations A, B, C, D and E (Friedman tests, $n=24$, 95 % confidence level).

The vertical distributions of organic carbon (not shown) displayed a decrease or almost constant concentrations with depth, except at station B in August which presented a surficial deficit. The highest concentrations (about $4000 \mu\text{mol g}^{-1}$) always occurred at the upper estuary (st A) and the lowest (about $700 \mu\text{mol g}^{-1}$) either in the outer estuary (st F) or in the intermediate estuary (st C and X). A significant seasonal variability was observed at stations B, C, D and F with the highest concentrations in surficial sediments in June after the bloom (Friedman tests, $n = 24$, 95 % confidence level).

C/N and C/P molar ratios were quite variable further down the core, generally increasing with depth (respectively from about 9 to 12 and from about 250 to 550), and were considerably higher (table 3) than the Redfield ratio for marine organic matter of respectively 7:1 and 106:1 (Redfield, 1958).

P forms

The depth profiles of the seven sites showed differences both in the amount and proportion of the P pools (figure 4a, 4b and 4c). By and large, all sites had maximum concentrations of total P in the surficial sediment (ranging from $12\text{-}22 \mu\text{mol g}^{-1}$ at st F to $43\text{-}54 \mu\text{mol g}^{-1}$ at st A). The concentrations declined gradually with depth except in August in the intermediate and outer estuaries (st C, D, E and F) where concentrations exhibited a marked decrease from the surface to 0.75 cm depth. This decrease in total P was largely accounted for by a decrease in concentrations of Fe-P. Thus phosphate associated with iron hydroxides was a significant P pool in the upper part of these sediments and could represent from about 20 % (st X and F) to 57 % (st A) of total P. The highest amount and proportion of total P and Fe-P were always observed in the inner estuary (st A) and the lowest in the outer estuary (st F). A pattern of Fe-P decreasing in summer was observed at stations C, X, D and F.

Exchangeable phosphate (Exch-P) as determined by the IDE method (Aminot and Andrieux, 1996) is included in the Fe-P fraction. Exch-P concentrations (figure 5) declined from the inner estuary (about $7 \pm 1 \mu\text{mol g}^{-1}$ at st A) to the outer estuary (about $1.6 \pm 0.8 \mu\text{mol g}^{-1}$ at st F).

The concentration of Orga-P, calculated by subtracting inorganic P from total P should consequently be considered less precise than the concentrations of other phosphorus forms. The organic P content also generally decreased with depth (figure 4a, 4b, 4c). The highest concentrations in surficial sediments (about $11\text{-}17 \mu\text{mol g}^{-1}$) were always observed in the inner estuary (st A) and the lowest (about $2\text{-}3 \mu\text{mol g}^{-1}$) either in the outer estuary (st F) in August and March or in the intermediate estuary (st C and X) in December and June. The seasonal variation of Orga-P in the sediment top layer (3 cm) was not significantly different (Friedman, $n=24$, 95 % confidence level) except at station F where a significant increase was observed in June. Owing to the relatively wide concentration range, the Orga-P proportions in relation to total P were relatively variable (19-43 % on average), with the highest proportions encountered in August and June at stations E and F.

In coastal sediments, phosphorus associated with Ca is present in solids of various types and origins. The distinction between two groups of Ca-associated P was made in this study according to Ruttenberg (1993): on one hand, detrital fluoroapatite of igneous and metamorphic origin, and on the other hand, other forms of Ca-P such as biogenic skeletal debris, CaCO_3 incorporated phosphate and carbonate fluoroapatite precipitated from interstitial solutions. Generally speaking, almost all detrital Ca-P profiles (figure 4a, 4b, 4c) displayed relatively constant concentrations (about $4\text{-}5 \mu\text{mol g}^{-1}$) both with depth and along the estuary. Only stations E and F exhibited a gradual decrease in concentrations in March (respectively from 5.3 to $3.4 \mu\text{mol g}^{-1}$ and from 5.6 to $3.1 \mu\text{mol g}^{-1}$) and station A showed concentrations of up to $8.6 \mu\text{mol g}^{-1}$ (0.75 cm depth) in August. In spite of relatively constant concentrations, Ca-P proportions in relation to total P increased with greater marine influence (from 12-15 % to 50-60 % of total P on average) due to the lower contribution of Fe-associated P and organic P. As with almost all profiles of Authigenic P (figure 4a, 4b, 4c), concentrations showed a gradual decrease with depth or remained nearly constant. Only station A in December and June displayed an increase in concentrations (respectively from about $9 \mu\text{mol g}^{-1}$ (14 cm depth) to $12 \mu\text{mol g}^{-1}$ (18.5 cm depth) and from $8.6 \mu\text{mol g}^{-1}$ (0.5 cm depth) to $15 \mu\text{mol g}^{-1}$ (3.5 cm depth). Concentrations in surficial sediments (0.5 cm) always declined from the inner estuary ($8\text{-}12 \mu\text{mol g}^{-1}$ at st A) to the outer estuary ($1.5\text{-}2 \mu\text{mol g}^{-1}$ at st F). Authigenic Ca-P accounted for about 20-23 % of total P whatever the season, except at station F where it always represented about 14 % of total P.

3.3. Calculated phosphate diffusive fluxes

Phosphate benthic fluxes (F_d) calculated from pore water gradients using Equation (1) (§ II.6) ranged from $-21.5 \mu\text{mol m}^{-2} \text{d}^{-1}$ to $410 \mu\text{mol m}^{-2} \text{d}^{-1}$ over the whole estuary (figures 7 and 8). Very low phosphate fluxes ($<6 \mu\text{mol m}^{-2} \text{d}^{-1}$) or even sediment uptakes were observed in the intermediate estuary both in May 2003 and March 2005 prior to maximum *Alexandrium minutum* cell densities (figures 7, 8 and table 4). A significant release (from about 50 to $410 \mu\text{mol m}^{-2} \text{d}^{-1}$) occurred during and after maximum cell concentrations reported in the intermediate estuary (figures 7, 8 and table 4).

4. Discussion

4.1. Diagenetic processes in the sediments of the Penzé estuary

NH_4^+ and PO_4^{3-} pore water profiles in the present study indicate that there is nutrient regeneration. Such regeneration is driven mainly by organic matter decomposition which occurs more intensively in the intermediate and outer estuaries (st X, D and E) in June and August and even in December (st D and E). However, at some stations, nutrient profiles exhibit a vertical shape, especially in winter, reflecting low inputs of biodegradable organic matter. Several other parameters -both in the pore water and in the solid phase- confirm the occurrence of mineralization in spring in sediments of the Penzé estuary. First, O_2 , and subsequently NO_3^- are consumed, and their penetration depths decrease from March to June after the bloom. Also, Fe^{2+} and Mn^{2+} concentration levels generally increase from March to June, as Fe-oxides and Mn-oxides are used as electron acceptors (figure 2). Fe^{2+} generally appears at depths where nitrate concentrations are below the detection limit. This means that nitrate could be the primary oxidant for Fe^{2+} . Despite low concentration levels, Mn^{2+} appears below the detection limit of the bottom of the oxygen-bearing layer suggesting that O_2 is the primary oxidant of Mn^{2+} , which diffuses upwards. This was also observed in the muddy sediments of the Bay of Biscay (Hyacinthe *et al.*, 2001). With regard to solid phase, our data generally highlight the decrease in Orga-P and Orga-C concentrations with depth (figures not shown). This pattern is usual in depositional environments where the burial and mineralization of organic matter occur gradually in the deeper sediment layers (Morris and Bowden, 1986; Paludan and Morris, 1999). However, the distributions in sedimentary organic matter may sometimes be homogeneous which often points to a more intense bioturbation. Finally, the C/N and C/P ratios, higher than the Redfield ratios for phytoplankton, may reflect more rapid mineralization of N and P relative to C. Nevertheless, this difference with Redfield ratios may also reflect the presence of organic matter derived from more C-rich plant detritus. Currently, organic carbon contents in cultivated soils can reach $15000 \mu\text{mol g}^{-1}$ in the finest particles (Calvet, 2005).

Phosphorus behaves in a particular manner as its presence in interstitial waters is also controlled by the redox cycle of Fe which greatly affects its geochemistry after burial. In fact, Fe-oxides present in the oxic layer of the sediment can act as a trap for upwardly diffusing phosphate (Krom and Berner, 1980; Sundby *et al.*, 1992; Slomp *et al.*, 1996a). The Fe-P profiles in the Penzé estuary (figure 4a, 4b and 4c) show evidence of phosphorus enrichment due to Fe re-oxidation in sediment surficial layers. This is in agreement with observations made in other estuarine systems (Jensen and Thamdrup, 1993; Paludan and Morris, 1999; Coelho *et al.*, 2004). Fe-P decreases with depth and reaches stable values in sediments of the Penzé estuary. This is attributed to the reduction of Fe-oxides in the anoxic sediment layer, liberating the associated phosphate, in addition to the phosphate released during organic matter decomposition (Krom and Berner, 1980). Likewise, anoxia caused by the mineralization of organic matter following the sedimentation of the spring bloom, could explain the surficial Fe-P decrease in summer in the intermediate and outer estuaries. Furthermore, the release of PO_4^{3-} from Fe-P may contribute to the decrease of $\text{NH}_4^+/\text{PO}_4^{3-}$ ratios in surficial pore waters from March (about 8 to 18) to June (about 2 to 6) in this area.

At all stations Fe-P concentrations do not completely fall to zero even when there is no more NO_3^- and thus no more O_2 . Ruttenberg and Berner (1993), Anschutz *et al.* (1999) and Slomp *et al.* (1996) have also observed a clear persistence of Fe-P inside the reduced zone and concluded that Fe-oxides

could provide a temporary sink for P respectively in continental margin environments, in modern sediments of the Bay of Biscay and in the North sea sediments. This could imply that some Fe-oxide forms may well be protected from reduction, due to reduced iron compound coatings (Postma, 1993) and to the presence of surface bound P, Si and organics (Slomp *et al.*, 1996a). Fisher *et al.* (1982) have also mentioned the possibility of the precipitation of reduced minerals such as vivianite in an increasingly reduced environment. Moreover, Williams (1980) has shown that vivianite was extracted using dithionite.

Another type of diagenetic removal regarding phosphate is the formation of authigenic phases such as carbonate fluoroapatite (CFA) from phosphate released during the mineralization processes or the dissolution of iron oxides (Ruttenberg, 1990; Ruttenberg and Berner, 1993). The increase in authigenic P concentrations in relation to depth shows that CFA could form in the sediments of station A as already described in coastal marine sediments (Slomp *et al.*, 1996a). However, the relatively constant profiles observed at the other stations do not necessarily preclude the precipitation of CFA since this could be masked by bioturbation or could occur at the sediment-water interface (Van der Zee *et al.*, 2002).

Conversely, detrital Ca-P seems to be a more inert phosphorus forms as shown by smooth distributions whatever the sediment characteristics (*i. e.*, percentage of fine particles). Such pattern have already been reported in coastal environments (Andrieux-Loyer and Aminot, 2001; Morse and Cook, 1978) and suggests that surface effects are of minor importance and that calcium phosphate is mainly present within the matrix of the sediment minerals. This is illustrated by the absence of correlation ($r^2 < 0.2$) between detrital Ca-P and the fine fraction ($< 63 \mu\text{m}$) and between detrital Ca-P and Ca concentrations ($r^2 < 0.1$).

4.2. Sedimentary bioavailable Phosphorus

This study aims to improve our understanding of *Alexandrium minutum* events. Thus, the notion of bioavailability must be taken into account. Bioavailability has been assessed by bioassays (de Jonge *et al.*, 1993). However, our knowledge of phosphorus forms provides us with maximum levels of potentially bioavailable phosphorus. Authigenic and biogenic Ca-P in sediments are almost insoluble under the physico-chemical conditions of estuarine waters and cannot play a role in interstitial or overlying water enrichment (Williams *et al.*, 1980; Ruttenberg, 1992; Berner *et al.*, 1993; Jensen and Thamdrup, 1993). In the anoxic sediments of the Penzé estuary, phosphate may be released both from the reduction of Fe oxide-bound phosphate (Fe-P) and from the mineralization of organic matter (Orga-P).

The inner part of the estuary (figure 4a), with the greatest freshwater influence, always represented the largest sinks of potentially bioavailable P (Fe-P which includes Exch-P and Orga-P). This area is characterized by low current velocities and long residence times which allow a greater sedimentation of fine particles (Bassoulet, *pers. comm.*), rich in organic matter and in Fe-oxides. This is shown by the significant linear relationships between Orga-C or Fe_2O_3 and the $< 63 \mu\text{m}$ fraction (respectively $r^2 = 0.66$; $P < 0.01$ and $r^2 = 0.67$; $P < 0.01$; $n = 215$). Conversely, in the outer area of the estuary, iron-bound P (figure 4c) and exchangeable phosphate in surficial sediment (figure 5) were lower. This could be explained by two processes. First, the increase in pH along with higher salinity may produce the release of adsorbed P from the iron complexes due to competition with OH^- ions. Also, Fe oxides may be consumed during formation of pyrite (FeS_2), which can sequester a large fraction of sediment Fe which becomes unavailable for phosphate (Krom and Berner, 1980; Paludan and Morris, 1999; Coelho *et al.*, 2004). The importance of this Fe-S interaction would be greatest in marine sediments with significant sulphate reduction.

In addition, the particulate Fe/P ratios in oxic surficial layers (figure 6) suggest that the inner and intermediate areas are the most important in terms of P liberation. Particulate Fe/P ratios are considered to be indicators of free sorption sites for phosphate ions on iron-oxyhydroxides (Coelho *et al.*, 2004; Paludan and Jensen, 1995). Low Fe/P ratios (< 8) in the present study suggest less capacity to adsorb phosphate or even the saturation of sorption sites, resulting in phosphate fluxes to the overlying water, especially in the intermediate estuary. This could promote the occurrence of *Alexandrium minutum* and eutrophic conditions, especially in the inner and intermediate estuaries, despite management efforts to reduce phosphate loading from external sources.

Particulate Fe/P ratios generally increase with depth as the sediment become anoxic. This phenomenon is particularly marked in the intermediate estuary in March and June (from 4.5 to 18 at station D and from 5.3 to 11 at st X in December). According to Stumm (1992), the reduction-dissolution of Fe-oxides at the surface of minerals and clays proceeds in several steps. The last one, *i.e.*, detachment of Fe(II) ions from the matrix is slow. When Fe-oxides- PO_4 complexes are destroyed,

PO₄ is liberated while Fe(II) remains attached to the solid for a long time. Higher Fe/P ratios in deeper anoxic sediment layers especially in the intermediate estuary support the hypothesis that slow detachment of Fe(II) ions from the solid matrix is the rate determining process.

Bioavailable P concentrations were integrated with depth to obtain the total exchangeable P mass (Fe-P + Orga-P) on a sedimentary layer of 3 cm. This depth was chosen as it is likely to be subjected to bioturbation or resuspension (Bassoullet, *pers. comm.*). 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 about eight years of external loadings (7 ton year⁻¹), could be released from sediments in the event of favourable environmental conditions (notably if oxygen conditions in the near bottom waters deteriorated or if the oxic sediment layer was destroyed due to resuspension of sediments by flood, tidal currents or dredging).

4.3. Phosphate diffusive fluxes: benthic versus river fluxes

The present study highlight the heterogeneity of phosphate fluxes along the estuary, particularly in June and August. This could partly be attributed to the fact that the Penzé estuary, like many estuaries, are highly dynamic environments (Sanders *et al.*, 1997), in which sediments are subjected to substantial resuspension events. In addition, the present investigation shows the significant increase of phosphate diffusive fluxes from March to June especially in the intermediate estuary. Seasonality in benthic nutrient fluxes could be accounted for by an effect of temperature on both diffusion and metabolic activity of benthic organism (Clavero *et al.*, 2000). Another possible explanation for the flux enhancements could be that the sediment liberate phosphate in response to the decrease in concentrations in the water column due to an uptake by the phytoplanktonic community. The role of sediments in buffering phosphate concentrations has been described in other coastal environments. For example, Van Raaphorst *et al.* (1988) showed in the Dutch Wadden Zee that phosphate is removed from the water column to the sediment in autumn and winter when phosphate concentrations are high, and is released in spring and summer when phosphate concentration are lower due to the phytoplankton uptake.

These flux data can be used to give a rough estimate of the role played by the sediments in the nutrient budget of the estuary. Taking into account the studied area (about 2 km²), phosphate inputs from sediments ranged from about 2-4 kg d⁻¹ in June-July 2003, which represented 10-20 % of the external discharges (about 20 kg d⁻¹). In August 2004 and in June 2005, in the intermediate estuary (from Eon Bridge to Corde Bridge: about 0.6 km²), where the highest cell densities were measured, the inputs from sediments ranged from 1 to 7 kg d⁻¹ which represented about 7 to 50 % of the river loadings (about 15 kg d⁻¹). By considering an average flux (75 μmol m⁻² d⁻¹) on the whole estuary (2 km²), the contributions of the sediments were of the order of 5 kg d⁻¹ both in June and August corresponding to about 30 % of the external supplies. *Alexandrium minutum* requirements in nitrogen to form a bloom are supplied by the Penzé River, whose nitrogen levels are excessive (about 800 μmol l⁻¹; N/P superior to 100). Concerning phosphate, the situation is more complex. River inputs in phosphate are not sufficient to maintain the *Alexandrium minutum* bloom (Maguer *et al.*, 2004). The sediment could then supply the complementary phosphate required by *Alexandrium minutum*. However, the phosphorus supplies both from the river and the sediment are not sufficient to promote a bloom (Chapelle, *pers. comm.*). But it is necessary to bear in mind that diffusive fluxes have to be represented as a minimal threshold of the real contributions made by the sediment (Barbanti *et al.*, 1992). In fact, phosphate regenerated at the sediment-water interface, which directly diffuses back to the bottom water, like phosphate transport induced by bioturbation is not taken into account in calculations (Schenau and De Lange, 2001). To illustrate this idea, wide-scale divergences between diffusive fluxes and in-situ fluxes (benthic chamber) have already been reported and attributed either to bioturbation provoked by certain species of the benthic macrofauna (Callender, 1982) or to the release of gas bubbles which enhances transport during summer (Martens and Klump, 1980). However, in-situ measurements of nutrient fluxes in highly dynamic environments such as estuaries, can also be dubious as benthic chamber experiments isolate the sediments from the overlying hydrodynamics (Oldham and Lavery, 1999).

In addition, regeneration by mineralization and desorption of the particulate phosphorus -not taken into account in this study- could also be another source of phosphorus for *Alexandrium minutum* growth. As an example, studies of speciation in the Seine estuary showed that heavy loads of particles expelled from the estuary during spring floods, contain 50 % of bioavailable P and may therefore

significantly contribute to the enrichment of the Bay of Seine when phytoplankton is actively growing (Aminot *et al.*, 1993).

5. Conclusion

Our findings highlight the substantial sediment buffering capacity of the Penzé estuary system. The inner and intermediate areas are the most important in terms of P liberation, as suggested by the lower Fe/P ratio. Pools of bioavailable P in the surficial sediment are about 8 times higher than the annual net river input of P (7 ton year⁻¹). Pore water and flux results exhibit the spatio-temporal heterogeneity of phosphate supplies from the sediments. The highest phosphate supplies occurring in June and August in the intermediate estuary may represent up to 50 % of river loadings. In spite of the seasonal variability of diffusive fluxes along the estuary, these results further suggest that phosphate pulses coincide with occurrences of *Alexandrium minutum* reported in June. 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.

This study also confirms the need for more attention to be given to speciation and nutrient flux evaluations when investigating of the biogeochemical behaviour of nutrients. Further research should also be carried out into the nature, the behaviour and the liberation kinetics of the bioavailable phosphorus in coastal environments. Our results can also play a role in improving dynamic models of primary production by considering the internal sedimentary source of nutrients in order to produce a tool for management studies.

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Tables

Table 1

Summary of overlying physical-chemical water properties (river discharge, water depth, salinity, temperature) in 2003 in the intermediate estuary (st X) and in 2004-2005 along the estuary.

Sampling date	27.04.2003	11.06.2003	9.07.2003	24.08.2004	3.12.2004	4.03.2005	13.06.04
Penze outflow ($\text{m}^3 \text{s}^{-1}$)	1.26	0.67	0.46	0.96	1.66	3.53	0.92
Water depth (m)	0.8	0.7	0.7	0.2-1	0.2-1	0.4-1.2	0.3-1
Temperature ($^{\circ}\text{C}$)	15.0	20.0	23.7	17-17.8	6.7-8.5	4.7-6	17.9-18.3
Salinity	(1)* 30.2 (2)* 30.2	30	(1)* 29.1 (2)* 29.7	11.6-34.3	4.2-34.1	0-34.1	0-34.4

*(1): core 1; (2): core 2

Table 2

Sequential extraction method for P in sediments (after Psenner *et al.*, 1980; Ruttenberg, 1990; Aspila, 1992)

Step	Extractant and Protocol	Phase extracted
I) Adsorbed + iron-bound	0.1 mol l^{-1} Dithionite-Bicarbonate (DB) , 8 h, 20 $^{\circ}\text{C}$	Exchangeable or loosely sorbed P + easily reducible Fe-bound P
II) Authigenic	a) 1 mol l^{-1} Na-acetate buffer (pH = 4, 6 h, 20 $^{\circ}\text{C}$) b) washing with 1 mol l^{-1} MgCl_2 , (pH = 8, 0.5 h, 20 $^{\circ}\text{C}$)	Carbonate fluoroapatite (CFA) + biogenic hydroxyapatite + CaCO_3 -bound P
III) Detrital	1 mol l^{-1} HCl , overnight	Detrital fluoroapatite-bound P
IV) Organic	Ash at 550 $^{\circ}\text{C}$, then 1 mol l^{-1} HCl treatment overnight	Organic P

Table 3

Surficial sediment (in the top 3 cm) characteristics at each study site over the study period.

Station	A	B	C	X	D	E	F
n	24	24	24	12	24	24	24
Granulometry Silt + Clay (%)	72 (4)	57 (3)	46 (5)	45 (6)	51 (4)	56 (5)	50 (8)
Porosity (%)	80 (5)	69 (6)	60 (8)	58 (8)	61 (8)	62 (10)	58 (8)
C ($\mu\text{mol g}^{-1}$)	4056 (366)	2413 (937)	1170 (828)	1161 (919)	1382 (244)	1417 (316)	731 (353)
N ($\mu\text{mol g}^{-1}$)	327 (141)	186 (104)	110 (66)	113 (87)	137 (26)	150 (47)	87 (48)
Orga-P ($\mu\text{mol g}^{-1}$)	12 (2)	5.5 (0.2)	3.3 (1.3)	2.7 (0.5)	4.2 (1.2)	4.8 (1.8)	3.1 (2)
C/N	11 (1)	11 (1)	10 (1)	10 (1)	10 (1)	10 (1)	9 (1)
C/P	329 (38)	441 (155)	425 (191)	345 (77)	351 (96)	309 (49)	282 (188)

Mean (bold type) and standard deviation (in parentheses)
n= number of observations

Table 4

Cell maximum concentrations (l^{-1}) of *Alexandrium minutum* in 2004 and 2005 in the Penzé estuary.

	2004				2005		
Date	6/06	10/06	14/06	17/06	9/06	12/06	15/06
Cell l^{-1}	8800	175700	215698	26412	1160	64000	454400
					0		

Figures

Figure 1. Study area. (a) Main situation; (b) The Penzé estuary.

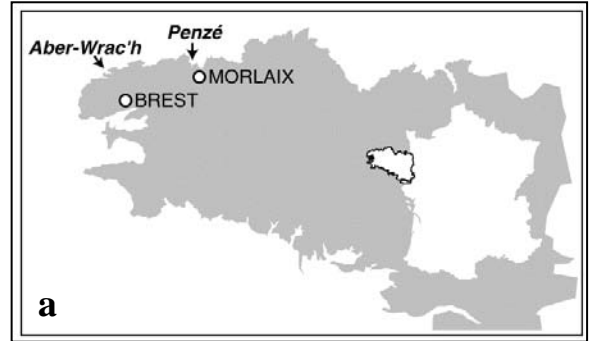
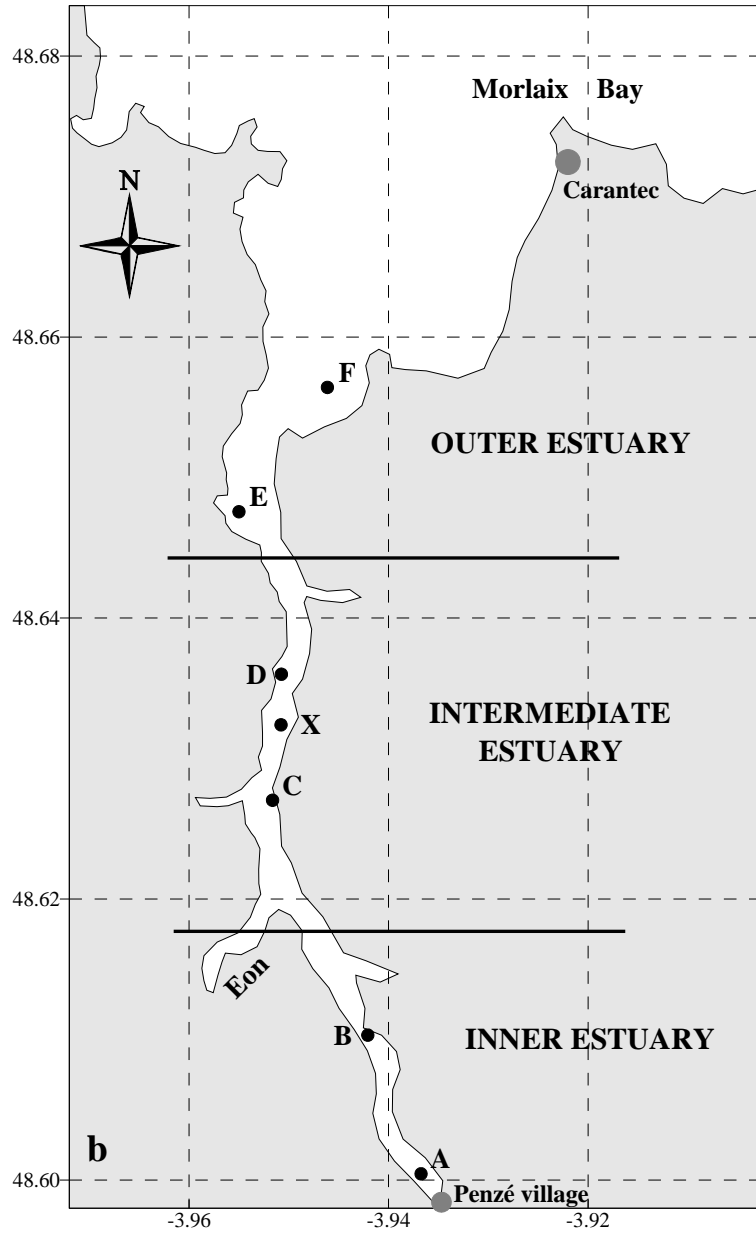


Figure 2. Vertical pore water profiles of the redox sensitive species, O_2 (x), NO_3^- (○), Fe^{2+} (●), Mn^{2+} (Δ), along the Penzé estuary (2004-2005). Oxygen sensors were only available in March and June 2005. Scales are the same for every graph. Only tick marks are indicated for intermediate scales not to overload the figures.

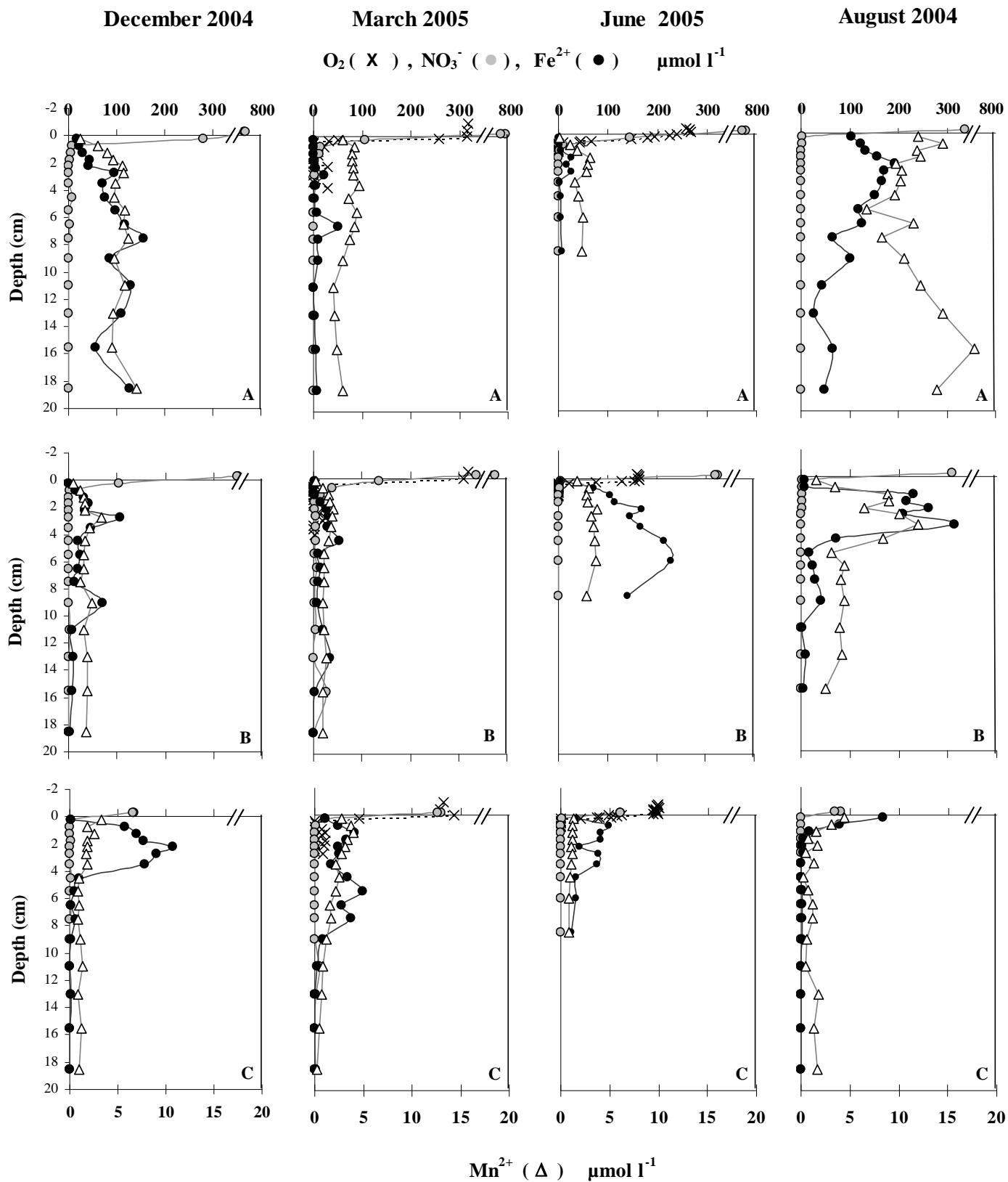


Figure 2 (continued)

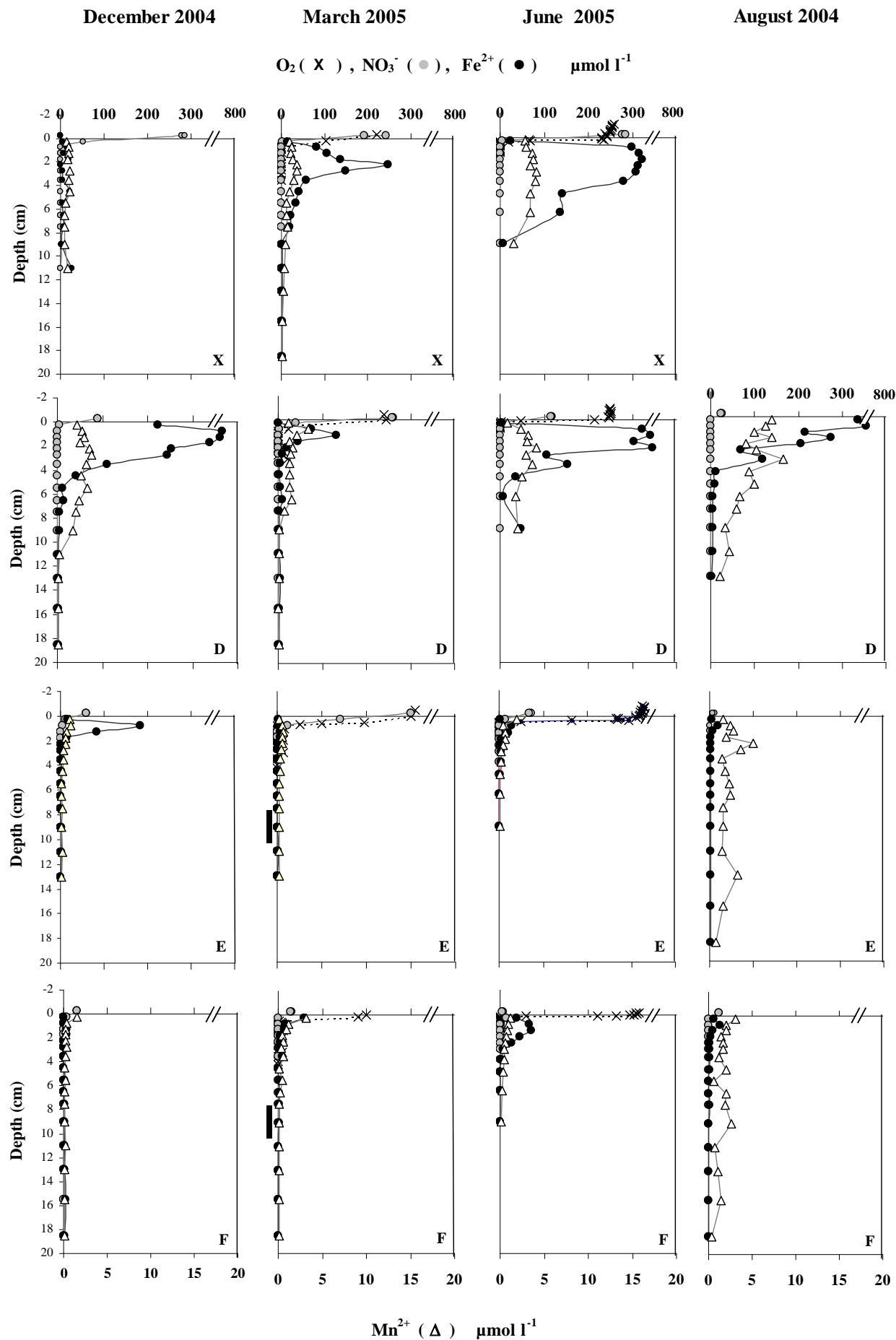
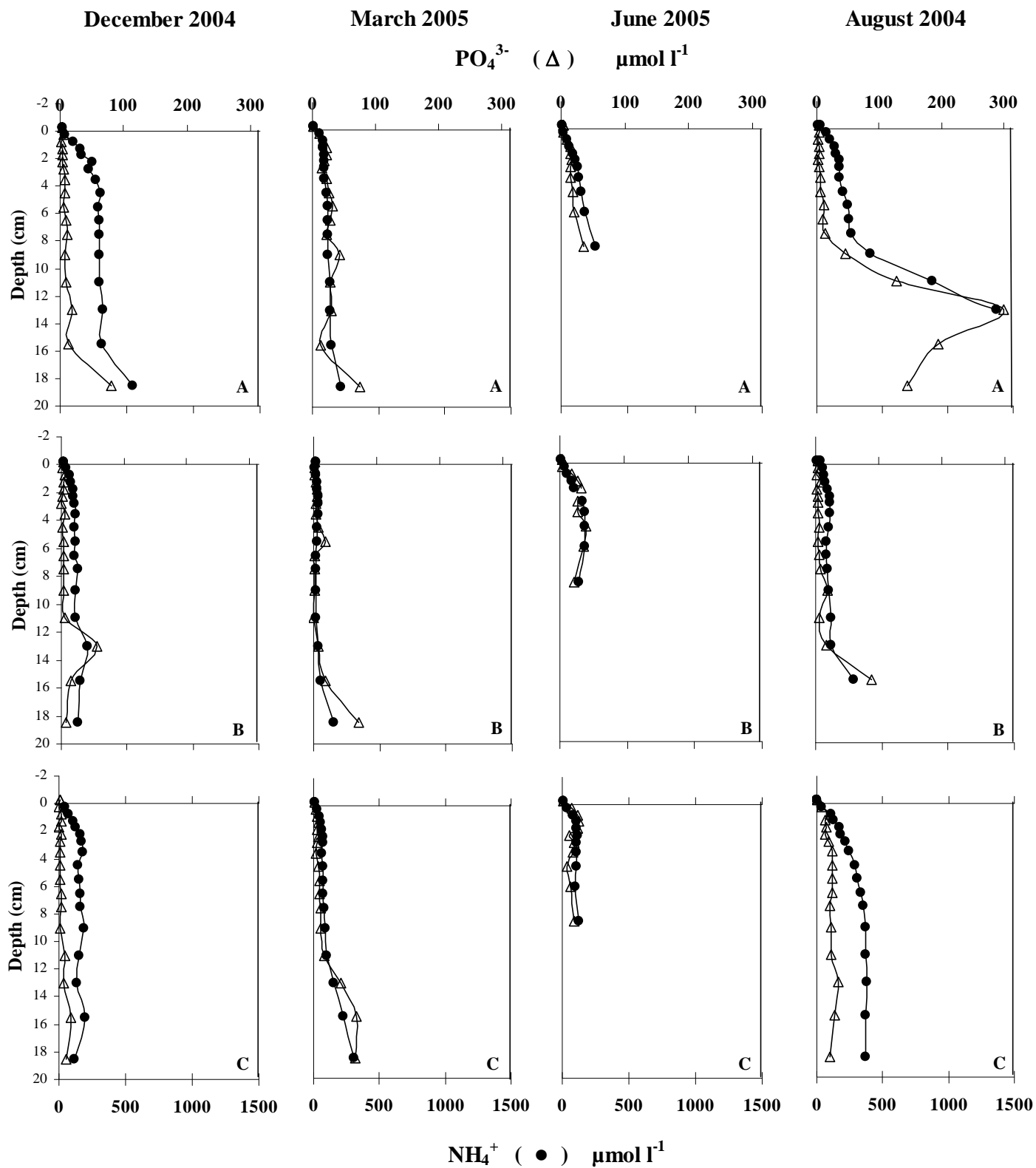


Figure 3. Vertical pore water profiles of NH_4^+ (●) and PO_4^{3-} (Δ) along the Penzé estuary (2004-2005). Scales are the same for every graph. Only tick marks are indicated for intermediate scales not to overload the figures.



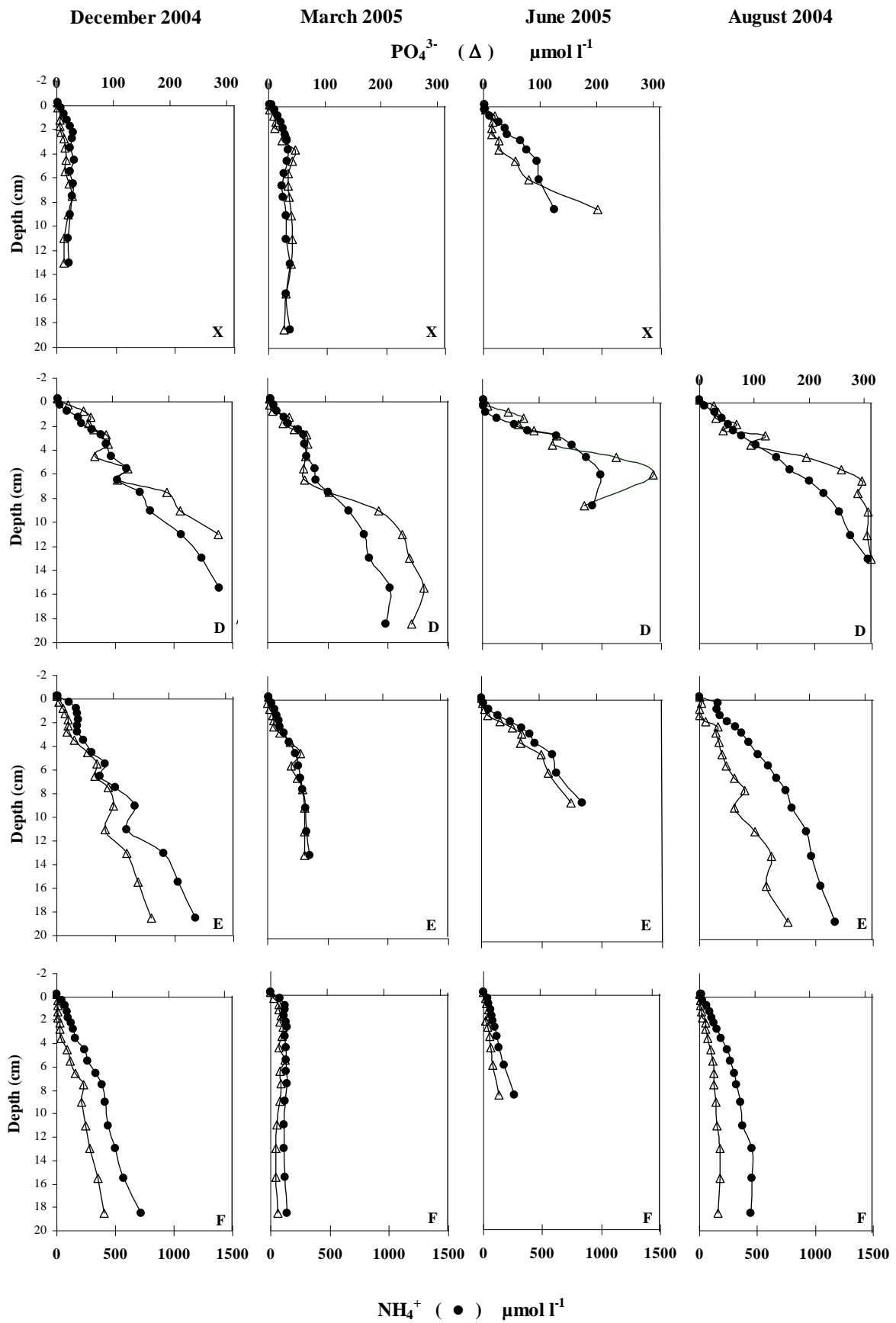


Figure 4a. Vertical distributions of phosphorus forms in sediments of the Penzé inner estuary (2004-2005). Scales are the same for every graph. Only tick marks are indicated for intermediate scales not to overload the figures.

Figure 4b. Vertical distribution of phosphorus forms in sediments of the Penzé intermediate estuary (2004-2005). Scales are the same for every graph. Only tick marks are indicated for intermediate scales not to overload the figures.

Figure 4c. Vertical distribution of phosphorus forms in sediments of the Penzé outer estuary (2004-2005). Scales are the same for every graph. Only tick marks are indicated for intermediate scales not to overload the figures.

Figure 4a

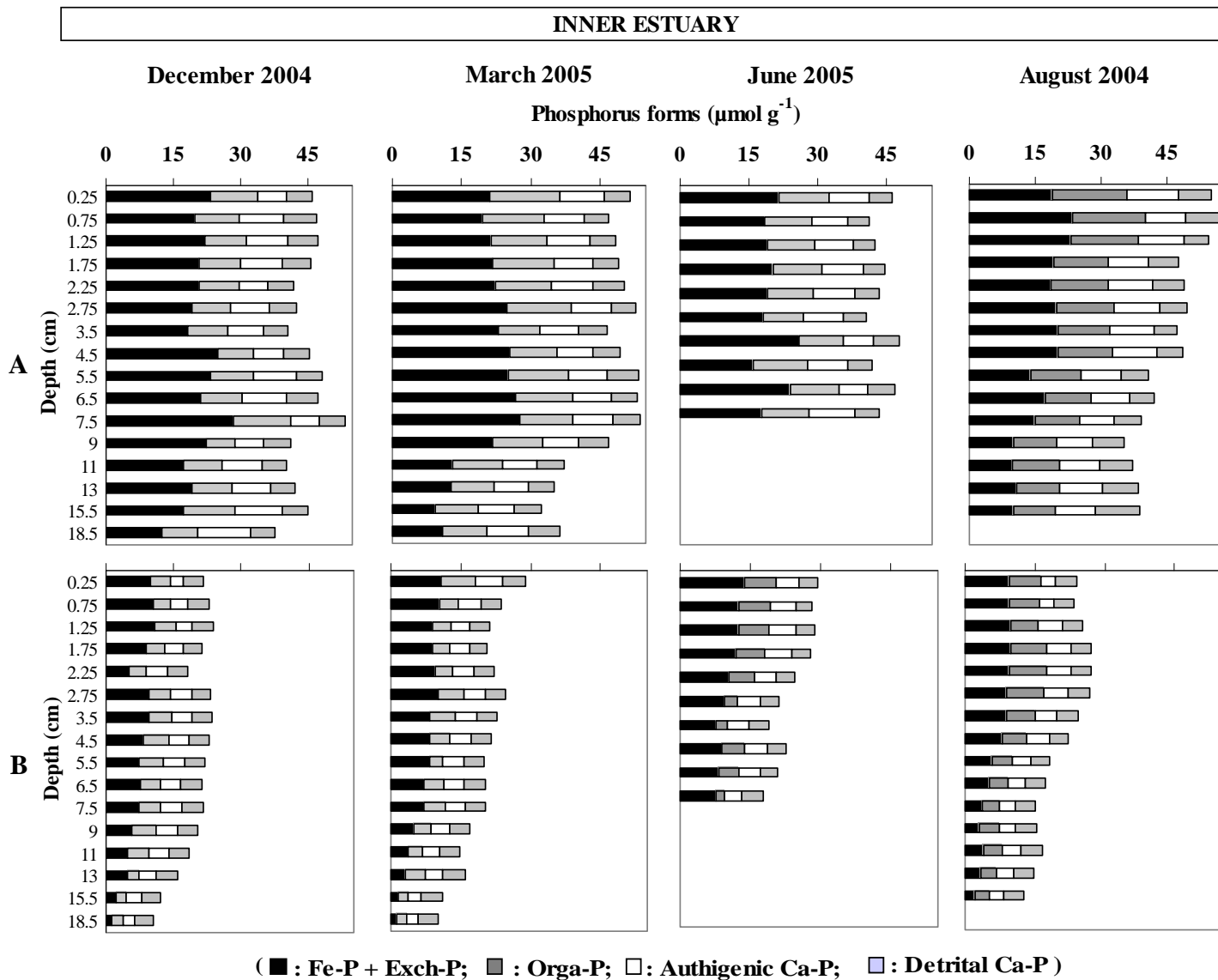


Figure 4b

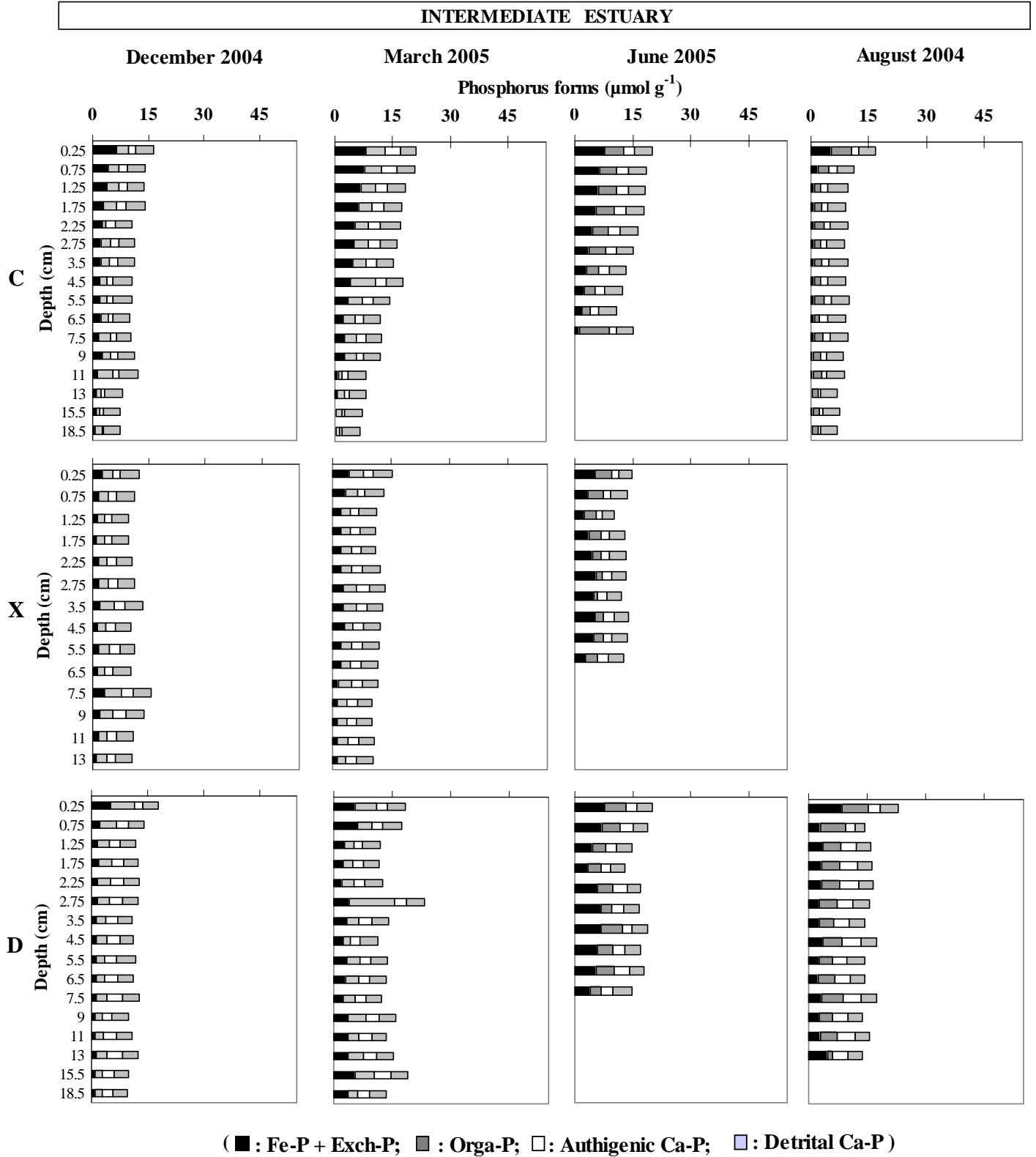


Figure 4c

OUTER ESTUARY

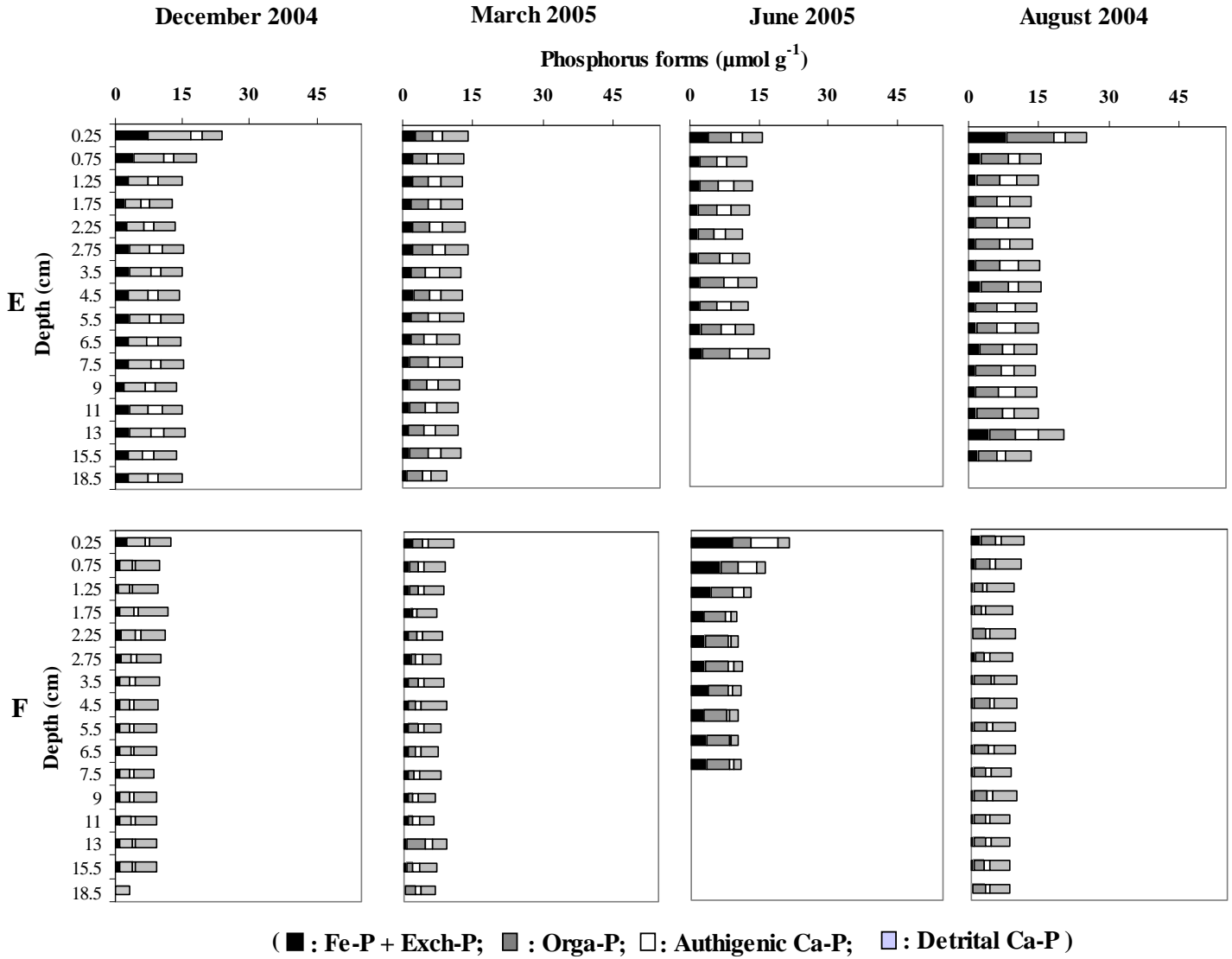


Figure 5. Exchangeable phosphate (Exch-P) in surficial sediments (0-0.5 cm) along the Penzé estuary (2004-2005).

Figure 5

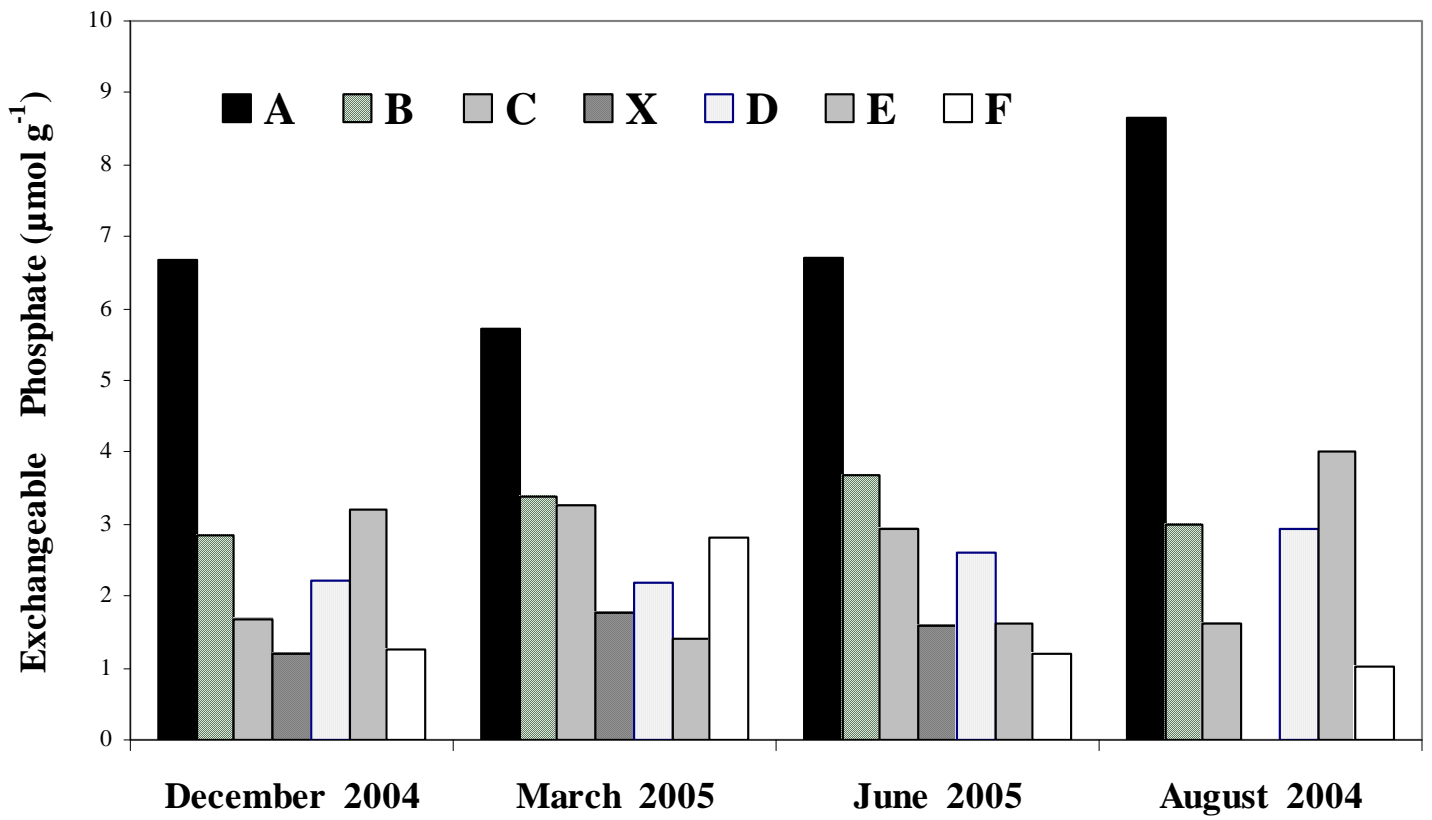


Figure 6. Particulate Fe/P ratios in oxic surficial sediments (0-0.5 cm) along the Penzé estuary (December 2004, March 2005, June 2005 and August 2004). *The Fe/P ratios under the dashed line (Fe/P = 8) suggest saturation of sorption sites.*

Figure 6

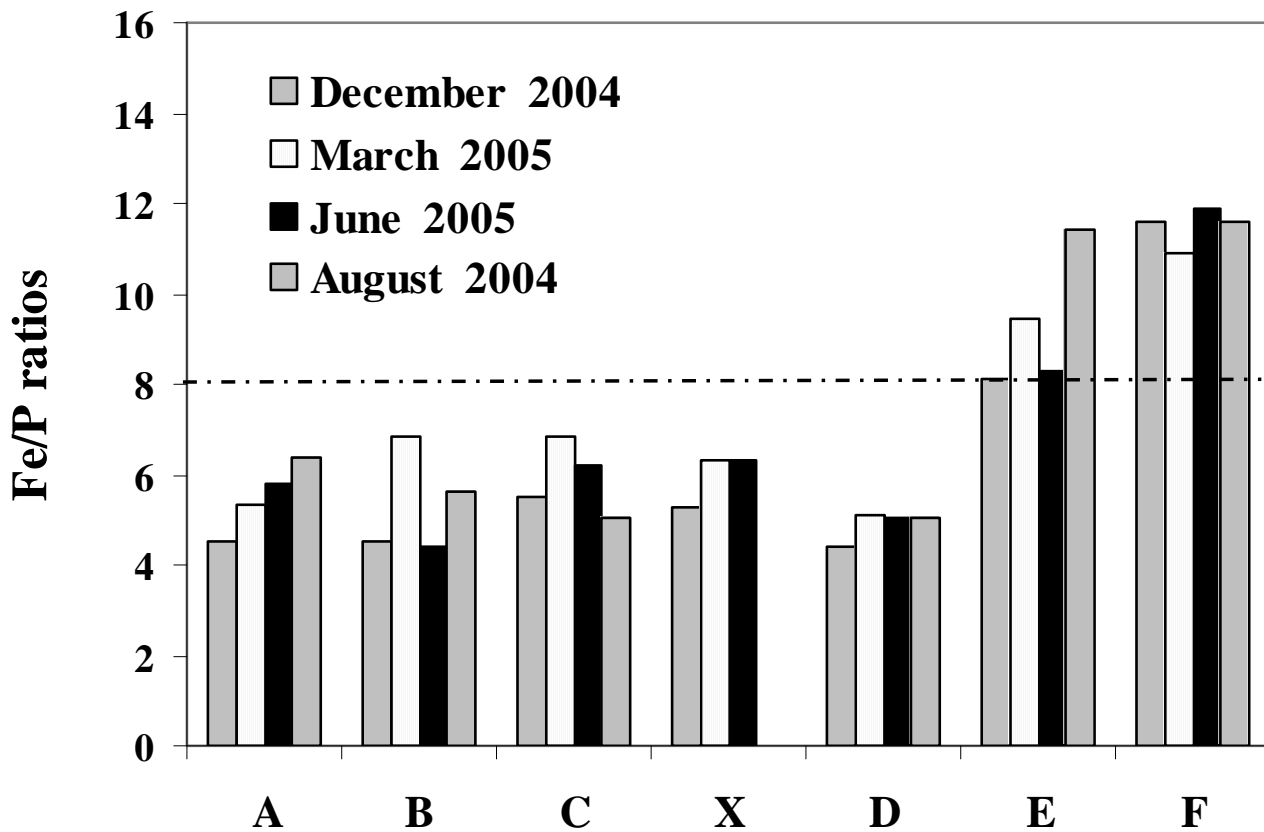


Figure 7. Phosphate diffusive flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$) and *Alexandrium Minutum* cell maximum densities (cell l^{-1}) in the Penzé intermediate estuary (st X), in May, June and July 2003. Flux evaluations were duplicated in May and July (core 1 and 2).

Figure 7

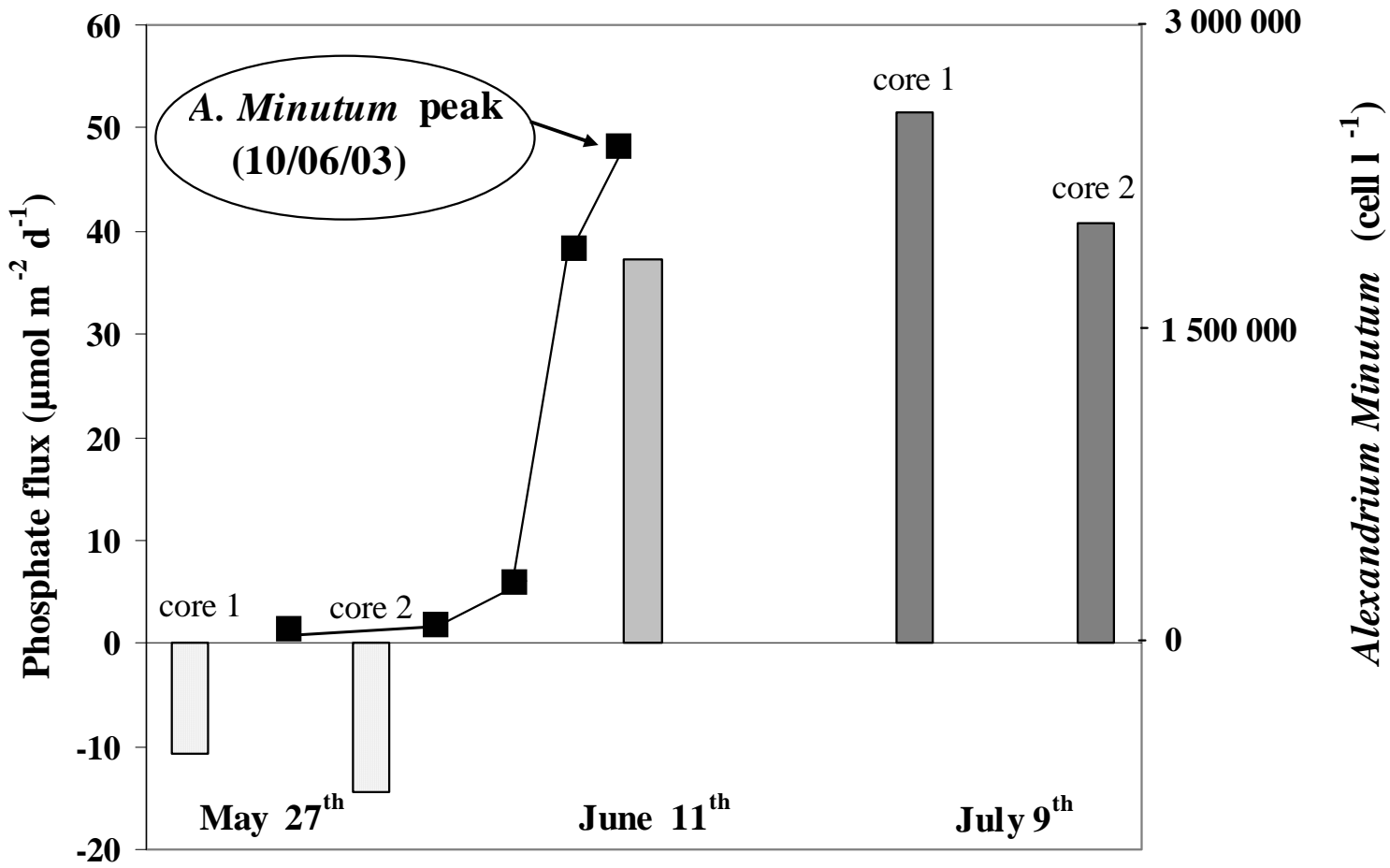


Figure 8. Phosphate diffusive flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$) along the Penzé estuary (2004-2005).

Figure 8

