



Phosphorus diagenesis in sediment of the Thau Lagoon

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Abstract

We describe the depth distribution of phosphorus in relation to the distribution of major redox species (dissolved O_2 , NO_3^- , NH_4^+ , Mn, and Fe, and particulate S, organic C, reactive Mn- and Fe-oxides) in modern sediments of two stations in the Thau Lagoon. Sediments close to the oyster bank zone are enriched in organic carbon and are highly bioturbated, while those outside the bank are less bioturbated and organic carbon levels are lower. In all sites, early diagenesis follows the well-accepted depth sequence of redox reactions of organic matter mineralization. The upper sediments of the station enriched in organic carbon contain high amounts of reactive particulate organic phosphorus that arrives at the sediment surface through biodeposition. Only a part of this phosphorus is released to the bottom water after mineralization, since more than 50% of total P is buried as an authigenic phosphate mineral. In the middle of the lagoon, outside the oyster bank zone, organic matter seems to be much more refractory, but the distribution of the major redox compounds indicates that this organic matter is partially mineralized. A portion of the phosphate and ammonium released during mineralization does not escape the sediment, since the concentration gradient is close to zero between 1 and 25 cm depth below the sediment–water interface. Pore water N and P are likely fixed by biological uptake. The characterisation and magnitude of this process require further study.

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1. Introduction

The oceanic phosphorus cycle depends on the inputs from rivers, and the ability of sediments to sequester and bury phosphorus (Froelich et al., 1982; Ruttenberg and Berner, 1993; Howarth et al., 1995). On shorter time scales, phosphorus sequestration by sediments affects the trophic state of lakes and lagoons, and the productivity of estuaries (Nixon, 1981; Caraco et al., 1990).

Coastal lagoons are a very common feature of coastal environments, occupying 13% of the world coastline. Because of their low water turnover and long residence time, many Mediterranean coastal lagoons are greatly affected by nutrient loads from their catchments (La Jeunesse and Elliott, 2004). The analysis of phosphorus compounds in sediments of the

Thau Lagoon indicates that the upper 5 cm layer of sediment is enriched in phosphorus (Moutin et al., 1993; Mesnage and Picot, 1995). Direct benthic flux measurements indicated that some phosphorus is remobilized to the water column (Mazouni et al., 1996). It has been documented that the Thau Lagoon system has suffered natural disturbance, caused by anoxic conditions in the bottom waters during summer, while low winds and high temperature lead to oxygen depletion (Souchu et al., 1998). The highest benthic fluxes of P towards the water column have been recorded during these periods. The release of phosphate is believed to be caused by the reductive dissolution of iron oxides.

Both the amount and the form of the phosphorus sequestered by sediments are affected by diagenesis. Near the sediment–water interface, where most of the freshly deposited organic matter is decomposed, phosphate is rapidly remineralized and released to the sediment pore water from which it can readily escape to the overlying water. Consequently, only a portion of the particulate phosphorus that reaches the

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sediment–water interface is actually buried with the accumulating sediment (Krom and Berner, 1980, 1981; Balzer, 1986; Sundby et al., 1992). Deeper in the sediment, organic phosphorus may be converted to apatite without loss of phosphorus from the sediment (Ruttenberg and Berner, 1993). Fe-bound P may also act as an intermediate between organic P and apatite P (Slomp et al., 1996b). Phosphorus sequestration is particularly important in coastal zones, and early diagenesis may have a great effect on phosphorus burial (Sundby et al., 1992; Jensen et al., 1995; Anschutz et al., 1998).

The vertical degradation sequence of organic matter proceeds by a sequential consumption of electron acceptors during oxidation of organic carbon (C-org) according to the energy yield per unit of reactive organic matter. Reduction of oxygen near the sediment–water interface is followed by reduction of nitrate, manganese- and reactive iron oxides, sulphate and finally carbon dioxide (Froelich et al., 1979; Postma and Jakobsen, 1996). Early diagenesis yields reduced products and creates chemical gradients and fluxes. The processes involved in re-oxidation of reduced products, particularly of N, Mn, Fe compounds, are still a matter of debate (Hulth et al., 1999; Anschutz et al., 2000; Hyacinthe et al., 2001). Secondary reactions that change the chemical speciation of iron affect the distribution of phosphorus (Anschutz et al., 1998). In addition, bioturbation can redistribute chemical species in the sediment, by transporting phosphorus associated with particulate material across redox gradients (Schink and Guinasso, 1977; Slomp et al., 1998). Therefore, the redox stratification of sediments is not simply restricted to a surficial oxic and a deeper anoxic layer. In this study, we present vertical profiles of extractable and dissolved phosphorus as well as major components of the redox system.

One important factor controlling the burial efficiency of phosphorus appears to be the adsorption capacity of the sediment for phosphate which generally decreases rapidly with depth below the sediment surface. This decrease has been attributed to the progressive reductive dissolution of iron oxides upon burial (Krom and Berner, 1980; Anschutz et al., 1998). Therefore, Fe-bound P is often the initial sink of P supplied by organic matter, but not the major final sink. That means it is important to carry out extractions that differentiate between Fe-bound P, Ca-bound P and organic P and to assess how the distributions change with depth to evaluate the fate of P that reaches the sediment surface. For this reason, we have examined the distribution of several operationally defined reactive phases of both iron and phosphorus. The results obtained from sediments of a coastal lagoon environment can be compared to sediments collected in open sea systems, and analyzed using the same extraction processes.

2. Methods

The study focussed on sediments of the Thau Lagoon located on the French Mediterranean coast (from 43°20' to 43°28' N, and from 3°32' to 3°42' E). Oyster banks represent about 1/5th of the surface of the lagoon. Sediment cores were collected at stations C4 and C5 in December 2001 and in April

2002 during cruises Microbent 1 and Microbent 2, respectively. The names of the cores are MB1-C4, MB1-C5, MB2-C4, and MB2-C5. Station C4 was located in the middle of the lagoon, and station C5 nearby a zone of oyster banks (Fig. 1). Sample coring was performed at 6 m water depth by divers with 10 cm i.d. PVC tubes, which allows sampling of sediment–water interface with minimum disturbance. Sediments at both sites consisted mostly of silt sized particles and shell debris.

High resolution vertical profiling of dissolved O₂ was carried out using Au/Hg microelectrodes as described previously by Brendel and Luther (1995) and Luther et al. (1998). A standard three-electrode voltammetric device was used for all electrochemical measurements with the microelectrode as working electrode, a platinum wire as counter electrode, and a saturated Ag/AgCl electrode as reference electrode. An Analytical Instrument Systems Inc. (AIS) model DLK-100 electrochemical analyser was used for all measurements. The counter and reference electrodes were inserted into the surface of the core. The microelectrode profiling was performed at *in situ* temperature less than 30 min upon the arrival of the sedimentary cores in the laboratory in order to measure pore water O₂. Although this device is capable of detecting dissolved Fe(II) and Mn(II), the pore water Fe(II) and Mn(II) concentrations were always below the detection limit (20 μM). Subsequently, the core used for O₂ profiling was sliced in thin horizontal sections (0.5 cm for the top 2 cm, and 1 cm below) within 2 h. A sub-sample of each slice was immediately sealed in a pre-weighed vial and frozen under inert atmosphere (N₂) for later determination of porosity and

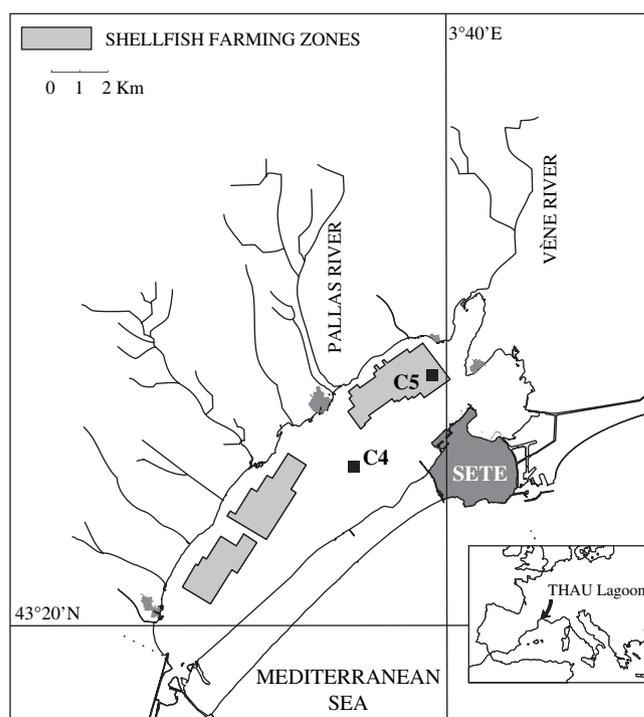


Fig. 1. Map of the Thau Lagoon, city of Sète, watershed boundary, and location of the stations C4 and C5.

chemical analyses of the solid fraction. Water content was determined after weighing before and after drying. Another sub-sample was centrifuged under N₂ at 5000 rpm for 20 min to extract pore water. Two aliquots of water were filtered (0.2 µm, surfactant-free cellulose acetate syringe filter) and frozen at –25 °C for nutrient analysis, and a third aliquot was filtered and acidified to pH 1.6 with ultrapure HNO₃ for dissolved Mn and Fe analysis.

The freeze-dried solid fraction was homogenised and the water content was used to correct the analyses for the presence of sea salt. Particulate organic carbon, total carbon and sulphur were measured on freeze-dried samples by infrared spectroscopy using a LECO C-S 125. Particulate organic carbon was measured after removal of carbonates with 2 M HCl from 50 mg of powdered sample. The precision of these analyses was ±3 µmol g⁻¹.

Samples were subjected to two different extraction techniques for the determination of reactive particulate P, Fe and Mn. The most easily reducible fraction was extracted with an ascorbate solution. The ascorbate reagent consists of a de-aerated solution of 10 g sodium citrate and 10 g sodium bicarbonate in 200 ml deionized water to which 4 g of ascorbic acid is slowly added for a final pH of 8 (Kostka and Luther, 1994; Anschutz et al., 1998). A second extraction on a separate aliquot was carried out with 1 N HCl to determine acid soluble P, Mn and Fe. For both procedures, about 100 mg of dry sample was leached with a 10 ml solution during 24 h while shaking continuously at room temperature. The centrifuged and filtered solution was then diluted in 0.2 N HCl and analyzed for Fe, Mn, and P. Phosphorus extracted with ascorbate (P_{ASC}) comes from amorphous iron oxides. The ascorbate solution is more selective than the citrate-dithionite (CDB) solution, which has been commonly used, to extract P associated with reactive Fe(III) phases. Anschutz et al. (1998) showed that the amount of phosphate extracted from marine sediments by the two reagents was similar, but more iron was extracted by the CDB reagent, probably because of its ability to dissolve crystalline iron oxides, which did not carry a lot of adsorbed P. Iron extracted with ascorbate (Fe_{ASC}) can partly result from the leaching of amorphous iron oxides originating from the oxidation of FeS during sample freeze-drying. Phosphorus extracted with 1 N HCl (P_{HCl}) comes from detrital and authigenic phosphate minerals, and from P associated with carbonates. Iron extracted with HCl (Fe_{HCl}) comes from the fraction extracted with ascorbate, FeS, some iron phyllosilicates and carbonates (Kostka and Luther, 1994). Specific tests on particulate-Mn extraction with ascorbate (Mn_{ASC}) and 1 N HCl (Mn_{HCl}) have shown that Mn_{HCl} represents the whole fraction of Mn-oxides and Mn associated with carbonates. Mn_{ASC} corresponds to the most easily reducible particles containing Mn(III,IV) (Anschutz et al., 2005). P was measured colorimetrically using a mixture of reagents adapted for each sample matrix. Mn and Fe were measured by flame atomic absorption spectrometry. The calibration lines for P, Mn, and Fe measurements were prepared with extracted blanks. Blank solutions were made with the leaching solutions that experienced the same treatment than the samples. Additionally, we

present data of total particle phosphorus, which was measured on sediments of the stations C4 and C5 by Elbaz-Poulichet (personal communication). The difference between P_{HCl} and total P represents mostly organic P (Ruttenberg, 1992).

Interstitial water compounds were analyzed using techniques adapted for small volumes of samples. Soluble reactive phosphate was determined colorimetrically as the molybdenum blue complex. Nitrate was measured by flow injection analysis (FIA) according to Anderson (1979). Ammonium was analyzed with the FIA method described by Hall and Aller (1992). Dissolved Fe was measured with the colorimetric method using ferrozine (Stookey, 1970). Dissolved Mn²⁺ was determined by atomic absorption spectrometry.

3. Results

3.1. Distribution of major diagenetic compounds

For both stations and at both periods of sampling, the pore water oxygen penetration depth was between 1 and 2.5 mm indicating that the upper sample for pore water extraction and solid analyses included the whole oxic zone and the top of the anoxic sediment. Concentrations of dissolved nitrate were always below 1 µM in bottom waters, and for most of the samples below the detection limit of 0.3 µM in pore water. Maximum concentrations of nitrate, lower than 5 µM, appeared just below the sediment–water interface in MB1-C4 and MB1-C5. The concentration of dissolved ammonium in bottom waters was below 5 µM during Microbent 1, in December 2001. The concentration was close to 10 µM during Microbent 2. Ammonium concentrations increased sharply within the first centimetres of the sediment pore waters. At station C4, and for both cruises (MB1 and MB2; Fig. 2), ammonium concentration remained close to 50–60 µM between 3 and 20 cm depth. Core MB1-C4, which was longer than core MB2-C4, showed that the concentrations of ammonium increased sharply below 25 cm depth, and reached about 600 µM at the bottom of the core (38 cm). The vertical profiles of dissolved ammonium continuously increased downward at station C5 (Fig. 3). The concentrations at depth were higher during cruise MB1 than during cruise MB2. For example, the concentration of ammonium at 10 cm depth was close to 400 µM during MB1, and 120 µM during MB2. Concentrations of pore water iron and manganese were very low in the cores of C4 and C5. They were generally close to or below the detection limit for the ferrozine method and flame atomic absorption (1 µM), and they were always below the detection limit of the voltammetric method with the polarographic mini-electrodes used for dissolved oxygen profiling. Localized peaks of dissolved Fe(II) occurred in core MB1-C4 at 10 and 15 cm depth (Fig. 2).

Particulate organic carbon concentrations were around 4 wt% in the top 4 cm of station C4, below which the concentration remained generally between 3 and 4 wt% (Fig. 4). At station C5, the concentration of organic C was 6.7 wt% in the top sample, and it decreased down to 3 wt% in the bottom sample (18 cm). Total particulate sulphur increased regularly at site

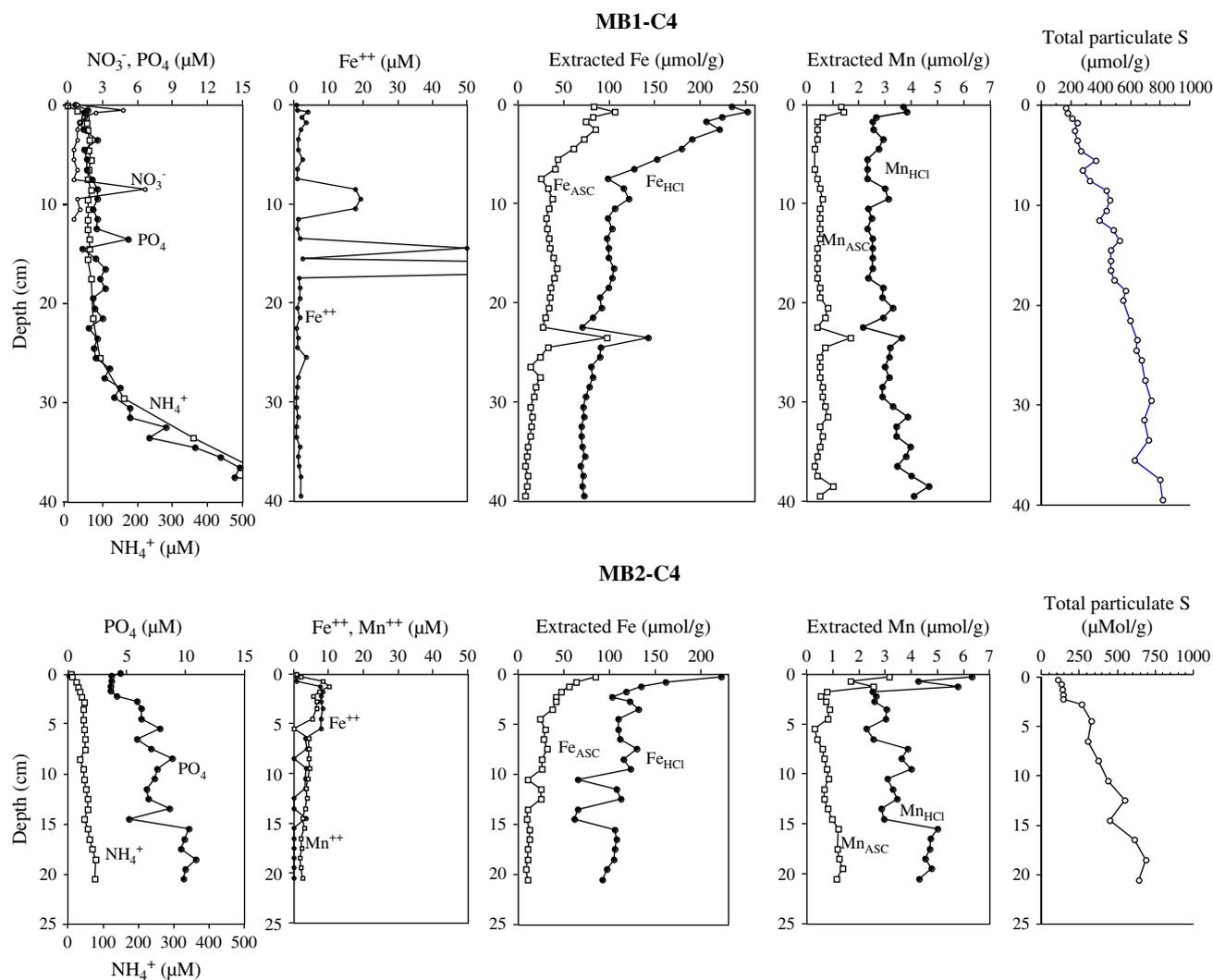


Fig. 2. Vertical profiles vs. depth in core MB1-C4 (top) and MB2-C4 (bottom) of dissolved phosphate, ammonium, nitrate, iron and manganese, particulate Fe and Mn extracted with ascorbate and 1 N HCl, and total particulate sulphur. The concentration units are $\mu\text{mol/L}$ (dissolved in the pore water) and $\mu\text{mol g}^{-1}$ (extracted from the solid phase sediment corrected for sea salt).

C4 from $140 \mu\text{mol g}^{-1}$ in the top sample to $800 \mu\text{mol g}^{-1}$ at 38 cm depth. The concentration of total particulate sulphur at C5 was $175 \mu\text{mol g}^{-1}$ in the top sample, but it reached concentration between 300 and $500 \mu\text{mol g}^{-1}$ below (from 0.5 to 20 cm depth).

The concentrations of both ascorbate extractable and 1 N HCl extractable iron were clearly highest in the surface layer of the cores of site C4 (Fig. 2). HCl extracted concentrations were always higher than ascorbate extracted Fe. The concentrations of Fe_{HCl} were above $200 \mu\text{mol g}^{-1}$ at the top of MB1-C4 and MB2-C4, and decreased down to $100 \mu\text{mol g}^{-1}$ at 6 cm depth in MB1-C4 and at 2 cm in MB2-C4. Fe_{HCl} concentration remained around $100 \mu\text{mol g}^{-1}$ at depth. The concentrations of Fe_{ASC} and Fe_{HCl} paralleled each other. The maximum concentrations at the surface were $110 \mu\text{mol g}^{-1}$ in MB1-C4 and $80 \mu\text{mol g}^{-1}$ in MB2-C4. Fe_{ASC} concentrations dropped to values lower than $40 \mu\text{mol g}^{-1}$ below 5 cm depth. Core MB1-C4 showed a sharp peak in the Fe_{ASC} and Fe_{HCl} profile at 23 cm depth, with a concentration of $60 \mu\text{mol g}^{-1}$ higher than the background concentration at

this depth (Fig. 2). The peak is not an artefact, since the HCl and ascorbate extraction were prepared from separate sub-samples. A similar peak was observed by Monna et al. (1997) in Thau Lagoon sediments, and was attributed to an exceptional flood event that occurred in 1875. The depth of this deposit is consistent with the sediment accumulation rate of about 0.2 mm y^{-1} at site C4 (Schmidt et al., 2007). Station C5 showed a 10 cm thick surface layer enriched in Fe_{ASC} , with values ranging between 100 and $60 \mu\text{mol g}^{-1}$ (Fig. 3). Fe_{ASC} concentrations decreased below to values close to $25 \mu\text{mol g}^{-1}$. The same profile was observed for iron extracted with HCl, but the concentrations were about $100 \mu\text{mol g}^{-1}$ higher than the Fe_{ASC} concentrations. Concentrations of particulate Mn were low in all the cores. Mn_{ASC} was lower or close to $1 \mu\text{mol g}^{-1}$, except for the top centimetre of cores from station C4, and the layer at 23 cm depth, which contained 1 or $2 \mu\text{mol g}^{-1}$ of Mn_{ASC} above the background concentration. Mn extracted with HCl represented about $3 \mu\text{mol g}^{-1}$ more Mn than Mn_{ASC} at the top of the cores. The difference increased slightly with depth.

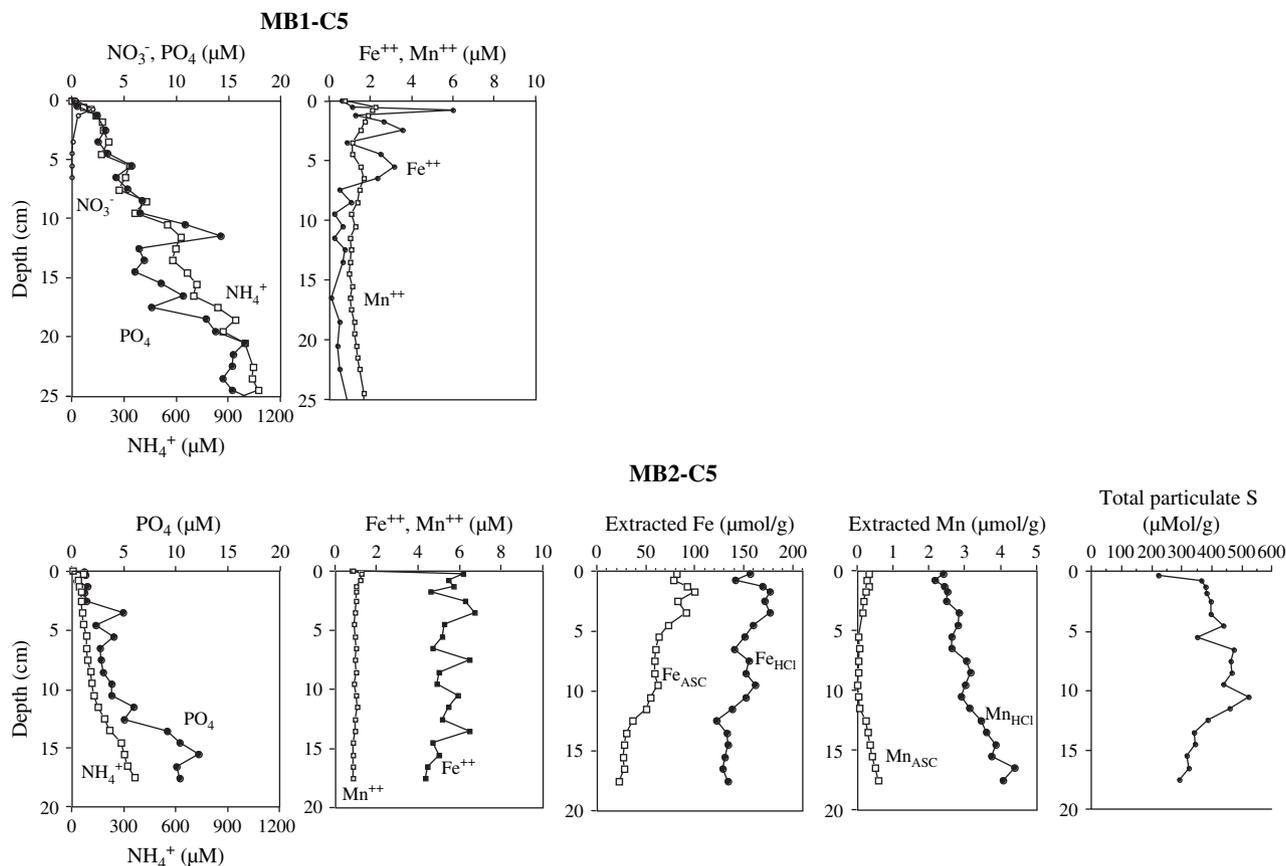


Fig. 3. Top: vertical profiles vs. depth in core MB1-C5 of dissolved phosphate, ammonium, nitrate, iron and manganese. The concentration units are $\mu\text{mol/L}$. Bottom: vertical profiles vs. depth in core MB2-C5 of dissolved phosphate, ammonium, nitrate, iron and manganese, particulate Fe and Mn extracted with ascorbate and 1 N HCl, and total particulate sulphur. The concentration units are $\mu\text{mol/L}$ (dissolved in the pore water) and $\mu\text{mol g}^{-1}$ (extracted from the solid phase sediment corrected for sea salt).

3.2. Phosphorus

Bottom water concentration of dissolved phosphate was below $0.5 \mu\text{M}$ in December 2001, and above $1 \mu\text{M}$ in April 2002. Unlike ammonium, the profiles of dissolved phosphate from MB1 and MB2 overlapped at C5, but not at C4. The pore water concentrations remained close to the bottom water concentrations, or they increased little, in the top 20 cm of station C4 (Fig. 2). They remained between 0 and $5 \mu\text{M}$ in core MB1-C4, and between 4 and $10 \mu\text{M}$ in core MB2-C4. The long core MB1-C4 showed that phosphate increased below 25 cm depth, and reached $20 \mu\text{M}$ at 38 cm depth. At station C5, the concentrations increased downward from the bottom water value to concentration above $10 \mu\text{M}$ below 15 cm depth (Fig. 3). The profiles of dissolved phosphate were more irregular than the smooth profiles of ammonium, but the general trend of dissolved phosphate profiles followed the profiles of dissolved ammonium.

Concentrations of total particulate phosphorus decreased slightly with depth from 35 to $25 \mu\text{mol g}^{-1}$ at station C4, and from 50 to $30 \mu\text{mol g}^{-1}$ at site C5 (Fig. 5). Higher concentrations of phosphorus at sites located inside oyster banks of the Thau Lagoon have also been reported by Mesnage and Picot (1995). The three cores studied for solid analyses

exhibited maximum concentrations of phosphorus extracted with ascorbate at the top of the cores, with concentrations between 11 and $15 \mu\text{mol g}^{-1}$. The concentrations reached a constant value of about $2.5 \mu\text{mol g}^{-1}$ below 5 cm depth at station C4, and decreasing concentrations from $5 \mu\text{mol g}^{-1}$ at 5 cm to $3 \mu\text{mol g}^{-1}$ at the bottom of core MB2-C5 (18 cm). At station C4, phosphorus extracted with HCl was about $8 \mu\text{mol g}^{-1}$ above P_{ASC} in the whole cores. The concentrations of P_{HCl} were much higher at station C5, with a concentration of $27.5 \mu\text{mol g}^{-1}$ in the upper sample, and concentrations above $20 \mu\text{mol g}^{-1}$ in the top 10 cm of the core MB2-C5. The concentrations decreased to about $15 \mu\text{mol g}^{-1}$ between 12 and 18 cm depth.

4. Discussion

4.1. The redox sequence of degradation of organic matter

We observe that the oxygen and nitrate concentrations decrease rapidly below the sediment surface. The disappearance of oxygen and nitrate is accompanied by a decline of Mn and Fe extracted with ascorbate (Figs. 2 and 3). This extracted fraction corresponds to Mn(III,IV)-oxides and oxyhydroxides

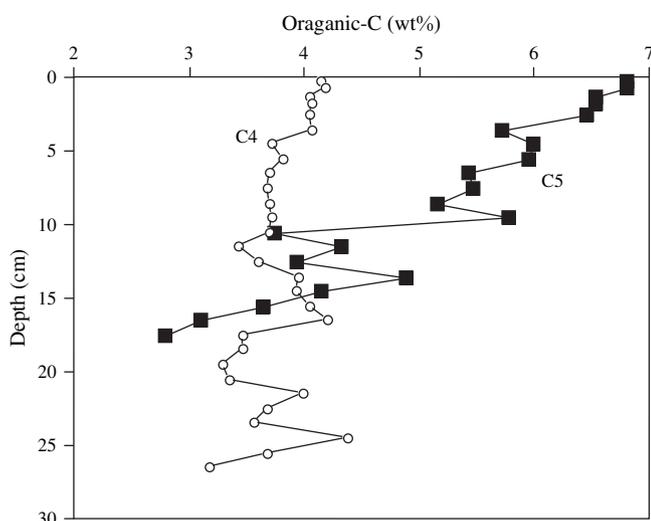


Fig. 4. Vertical profiles vs. depth of particulate organic carbon at benthic stations C4 and C5 during MB2, in wt%.

(Anschutz et al., 2005), and the most easily reducible Fe(III)-oxides or oxyhydroxides (Kostka and Luther, 1994). Total sulphur content increases with depth (Fig. 2). This distribution follows the well-established depth sequence of diagenetic reactions governed by the preferential use of the electron acceptor that yields the highest amount of free energy for the bacterially mediated oxidation of organic matter. Oxygen is reduced near the sediment–water interface, followed by the reduction of nitrate and manganese oxides, then reactive iron oxides, and sulphate (Froelich et al., 1979; Postma and Jakobsen, 1996). Reduction of sulphate produces dissolved sulphide a part of which precipitates as iron-sulphide and increases the particulate sulphur concentration.

O₂ consumption is attributed to oxic degradation of organic matter, and the re-oxidation of the products from the anaerobic degradation of organic matter (Canfield et al., 1993). The observed thickness of the oxic layer depends directly on the

C-org flux at the surface sediment. The peak of nitrate observed close to the oxic layer of MB1 cores (Figs. 2 and 3) is attributed to the succession of reactions that lead to the bacterial nitrification of organic N or ammonium that diffuses from below. The consumption of nitrate below the oxic layer suggests bacterial denitrification. NH₄⁺ is produced from anaerobic mineralization of organic N. The production of dissolved Mn²⁺ and Fe²⁺ in anaerobic sediments is attributed to reduction of manganese and iron oxides by bacteria or by reduced inorganic products such as sulphides. The peak of particulate Mn extracted by ascorbate or HCl can be attributed to detrital Mn-oxides and authigenic Mn-oxides that precipitate from the oxidation of dissolved Mn²⁺ that diffuses from below (Sundby, 1977). Mn_{ASC} can be attributed to all the forms of Mn(III) or Mn(IV) oxides or oxyhydroxides, which are all easily reducible (Anschutz et al., 2005). In sediments which are not mixed, the concentration of Mn_{ASC} decreases generally abruptly the bottom of the oxic layer (e.g. Hyacinthe et al., 2001). In all the cores, Mn_{ASC} concentrations decreased gradually, probably as the consequence of sediment mixing by bioturbation. Mn_{ASC} decreases to values close to zero, whereas Mn_{HCl} remains at concentrations above 2 μmol g⁻¹, which indicates that some Mn is buried in the solid fraction as an HCl leachable phase. The carbonate fraction is dissolved by 1 N-HCl extraction, but not by ascorbate extraction (pH = 8). Therefore, the low concentrations of dissolved Mn at depth could be related to the precipitation of secondary Mn-containing carbonates. The precipitation of authigenic carbonates is favoured by the production of alkalinity linked to anaerobic mineralization of organic carbon (Mucci et al., 1999).

The distribution of Fe_{ASC} (Figs. 2 and 3) is consistent with the assumption that the ascorbate reagent extracts only poorly crystalline oxides (Kostka and Luther, 1994). Fe_{ASC} concentration is highest near the oxic layer and decreases below. Fe-oxide phases may be used as terminal electron acceptors in bacterial oxidation of organic carbon or they may react with reduced sulphur to form FeS. The first hypothesis is supported by the

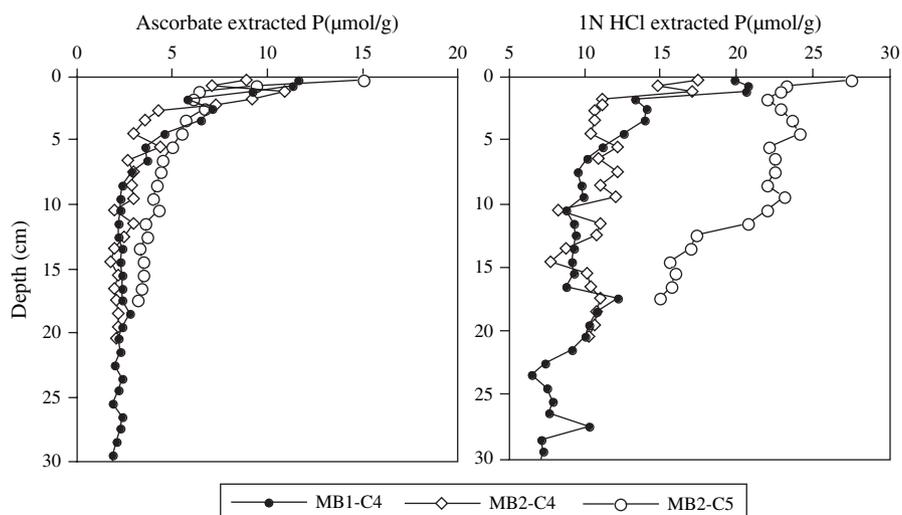


Fig. 5. Vertical profiles vs. depth of phosphorus extracted with ascorbate (left) and 1 N HCl (right) in cores MB1-C4, MB2-C4, and MB2-C5. The concentration units are μmol g⁻¹ (extracted from the solid phase sediment corrected for sea salt).

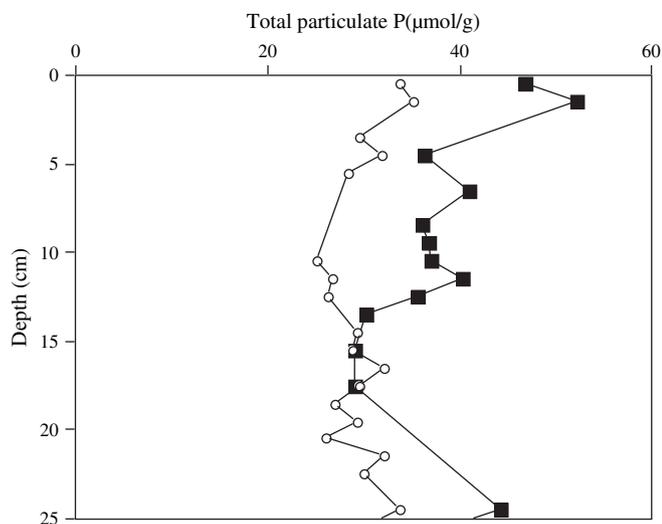


Fig. 6. Vertical profiles vs. depth of total particulate phosphorus at stations C4 and C5 (black squares). The concentration units are $\mu\text{mol g}^{-1}$.

occurrence of peaks of dissolved Fe(II) at the depth where Fe_{ASC} decreases. Iron from FeS can be extracted with the ascorbate solution (Kostka and Luther, 1994). This may explain the presence of Fe_{ASC} in the anoxic part of the cores. Total solid S is much more abundant than Fe_{ASC} indicating that S also comes from more refractory minerals than FeS, such as pyrite. Fe_{HCl} profiles are approximately parallel to the Fe_{ASC} profiles, which suggests that the decrease in Fe_{HCl} profiles observed below the oxic layer corresponds to the reduction of the most reactive fraction of solid Fe(III) (the Fe_{ASC} fraction). The additional part can consist of Fe-phases that are less reactive toward sulphide (Canfield et al., 1992) or toward bacterial reduction (Postma and Jakobsen, 1996). The particulate sulphur that was measured in the oxic part of the cores can arise from the mixing upward transport by bioturbation of refractory pyrite produced deeper in the sediment. The thickness of the layer mixed by bioturbation at stations C4 and C5, as determined with ^{210}Pb excess activities, has been determined by Schmidt et al. (2007). It represents the upper 10 cm at C5 and the upper 2–3 cm at C4.

4.2. The distribution of particulate phosphorus

Phosphorus extracted with ascorbate shows high concentrations at the top of the cores, and decreases below (Fig. 5). These data support the notion that phosphorus is associated with poorly crystalline Fe(III) phases present at the top of the sediment (Sundby et al., 1992; Slomp et al., 1996a,b). The Fe:P ratio in the P_{ASC} enriched layer is between 5 and 14, which is within the range of values noted in several continental margins (Slomp et al., 1996a; Anschutz et al., 1998, 1999) (Fig. 7), but the Fe:P ratio does not show a linear relationship within this range of value. The low and relatively invariant Fe:P ratios suggest the existence of an iron oxide phase with very high adsorption capacity, i.e. a very large specific surface area. Canfield et al. (1992), Raiswell (1993) and Van der Zee et al. (2003) have shown that ferrihydrite and

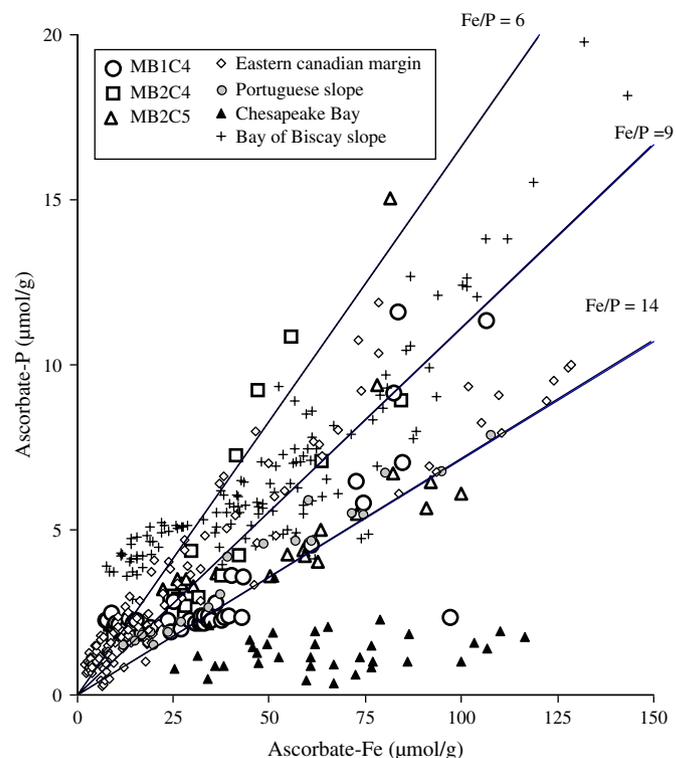


Fig. 7. Plot of ascorbate extractable Fe vs. ascorbate extractable P for the sediments from the Thau Lagoon (stations MB1-C4, MB2-C4, and MB2-C5), the Bay of Biscay continental slope (Anschutz et al., 1999), the Eastern Canadian continental margin, the Portuguese continental slope, and the Chesapeake Bay (Anschutz et al., 1998). The plot shows nearly linear relationships with values of the Fe/P ratio between 6 and 14 for the continental margin and slope sediments. No relationship could be discerned for the anoxic sediments from Chesapeake Bay. Most of the plots are between 6 and 14 for the Thau Lagoon stations, but the relationship is not linear.

nanogoethite were the most reactive iron oxide phases present in marine sediment. This suggests that the phosphate bearing phase extracted with ascorbate is most likely ferrihydrite or nanogoethite with most of the sorption sites occupied by phosphate. P_{ASC} decreases rapidly with depth, which suggests that the phosphorus bearing poorly crystalline Fe-oxide is reduced in the anaerobic sediment. In agreement with this, we observe that the contents of ascorbate extractable phosphorus and iron decrease simultaneously with depth in the sediment of station C4 (Fig. 2). At station C5, Fe_{ASC} remains high in the upper 10 cm (Fig. 3), whereas P_{ASC} decreases in the first cm (Fig. 5). This paradox suggests that below 1 cm depth Fe_{ASC} is rather extracted from FeS, which has a low adsorption capacity for phosphorus (Krom and Berner, 1981). High concentrations of particulate sulphur below 1 cm depth at station C5 support this hypothesis. Absence of relationship between Fe and P extracted by ascorbate, with high Fe_{ASC} and low P_{ASC} was also observed in FeS-rich sediment of the seasonally anoxic Chesapeake Bay. Water column of the Thau Lagoon remains oxygenated most of the time, but it becomes anoxic some years, at the end of summer, when high temperature of water, absence of wind, and accumulation of organic matter in quantities that exceed capacity of mineralization coincide

(Souchu et al., 1998). These characteristics probably explain non-linearity of the Fe:P ratio, and intermediate position of Thau Lagoon plot, between the Chesapeake Bay and the margin and slope sediments (Fig. 7).

Phosphorus extracted with 1 N HCl (Fig. 5) comes from the fraction extracted with ascorbate, with an additional contribution of igneous, biogenic (fish debris), or authigenic phosphate minerals (Ruttenberg, 1992). At station C4, P_{HCl} consists of almost a constant concentration above P_{ASC} , which suggests that it comes from the dissolution of P associated with Fe(III) minerals (the P_{ASC} fraction), and the dissolution of detrital igneous and biogenic phosphate phases with constant concentration in the cores (Fig. 5). At station C5, the concentration of P_{HCl} is much higher than at station C4, particularly in the upper 10 cm, whereas the concentrations of P_{ASC} are about the same. Several mechanisms may be called upon to explain this: (1) the deposition of detrital phosphate minerals is higher at C5; (2) the deposition of biogenic apatite is higher at C5; and (3) authigenic phosphate mineral precipitates at C5, but not at C4. The layer enriched with P_{HCl} also corresponds to the layer enriched with organic carbon (Fig. 4). According to the sedimentation rate of 0.15 mm y^{-1} (Monna et al., 1997; Schmidt et al., 2007), the enriched layer corresponds to the last 70–100 years of deposition, and represents the period of oyster farming activities close to the C5 station. Therefore, the high carbon content at the top of C5 core must be linked to an increased export of organic matter, due probably to oyster faeces biodeposition. High concentrations of P_{HCl} must be related to the high organic carbon content. Since 1 N HCl does not leach organic P, the excess of P_{HCl} probably comes from authigenic inorganic P that precipitates after the mineralization of organic P during early diagenesis. Authigenesis of phosphate minerals is favoured in conditions that prevail at station C5, that is, high labile organic matter flux and significant mineralization of C-org under anaerobic condition (Ruttenberg and Berner, 1993).

Organic phosphorus (P-org) can be quantified from the difference between total solid phosphorus (Fig. 6) and P_{HCl} . P-org represents $17\text{--}25 \mu\text{mol g}^{-1}$ at C4. At station C5, P-org is close to $30 \mu\text{mol g}^{-1}$ in the upper 3 cm, and close to $15 \mu\text{mol g}^{-1}$ below. Organic P represents between 30 and 70% of the total solid P in the first decimetre of sediment of the Thau Lagoon. This result was also found by Mesnage and Picot (1995). These values can be compared to the theoretical concentration of P-org, which can be calculated considering that the organic matter has a Redfield ratio of C:P = 106:1. For C4, the calculation gives a theoretical P-org between 32 and $25 \mu\text{mol g}^{-1}$, and for C5 the values decrease from 53 at the top of the core to 21 at 18 cm depth. The higher theoretical values suggest that the bulk sedimentary organic matter is depleted in P relative to the living marine organic matter, as frequently observed in marine sediments.

4.3. Pore-water phosphate

Dissolved phosphate concentrations increase below the sediment–water interface (Figs. 2 and 3). The positive

gradient from the sediment–water interface to the sediment must trigger a diffusive flux of phosphate toward the water column, as deduced by Mazouni et al. (1996). Because of the very thin thickness of the oxic layer, it not possible to calculate here an accurate flux of phosphate using Fick's first law, and the vertical resolution of our sampling. The release of phosphate to pore waters mostly originates from two processes. The first reason why phosphorus is released to the pore water is that the sediment loses its capacity to adsorb phosphate as it undergoes burial. The loss of adsorption capacity has been attributed to the progressive reductive dissolution of amorphous iron in the anoxic subsurface sediment layers (Krom and Berner, 1980; Sundby et al., 1992; Jensen et al., 1995). The second process is the aerobic and anaerobic mineralization of organic matter during early diagenesis, which produces dissolved phosphate. The profiles of major redox species show that these processes occur in the studied sediments. The reactions of organic matter mineralization are also responsible for the release of ammonium in pore waters, as observed in the cores.

The ratio between dissolved ammonium and phosphate (NH_4/PO_4) can provide information about the processes of phosphate release and uptake in the sedimentary cores (Ruttenberg and Berner, 1993; Schuffert et al., 1994). A constant NH_4/PO_4 ratio indicates a stoichiometric nutrient regeneration due to organic matter mineralization. Variable ratios suggest that reactions of P removal or addition take place. The ratio is about 20–30 in core MB1–C4, and between 6 and 9 in MB2–C4. NH_4/PO_4 is between 60 and 110 in MB1–C5 and between 20 and 35 in MB2–C5. The ratios are variable and do not represent the Redfield ratio of N:P = 16, indicating that the mineralization of marine organic matter alone cannot explain the profiles. The ratios are much higher during MB1 (December 2001) than during MB2 (April 2002), and for a given period, they are higher at C5 than at C4. Higher NH_4/PO_4 ratio at C5 suggests that a reaction of P removal occurs, which agrees with an authigenic precipitation of a phosphate mineral, as observed from the 1 N HCl extraction in C5.

The variable NH_4/PO_4 ratios are due to separate ammonium profiles at C5 between MB1 and MB2, whereas the profiles of dissolved phosphate remains the same between both periods. At C4, the opposite is observed, i.e. overlapping ammonium profiles, and distinct phosphate profiles. Therefore, the phosphate at C4 and ammonium at C5 are not at steady state. Organic matter mineralization, iron oxide dissolution, and authigenic P-mineral precipitation are insufficient to explain the divergent behaviour of ammonium and phosphate in the different cores. One must also invoke reactions where ammonium is involved. Moreover the profiles of ammonium and phosphate in MB1–C4 (Fig. 2) show a significant rupture in their slope at 25 cm depth. The profiles indicate that the pore water concentrations of both ammonium and phosphate are controlled by a reactions of removal above about 25 cm depth. The adsorption of phosphate, for example at the level enriched with Fe_{ASC} at 23 cm depth, could explain the dissolved phosphate removal, but not the ammonium profile,

and P_{ASC} does not show a simultaneous enrichment with Fe_{ASC} at this depth, which exclude this hypothesis. Parallel non-steady state profiles suggest that phosphate and ammonium react together in the sediment column. It was pointed out that some phosphate precipitated as authigenic apatite. Ammonium can be involved in redox reactions in the anoxic part of the sediment, when oxidizing particles, such as Mn(III,IV) oxides or oxyhydroxides, are advected through bioturbation at depth (Anschutz et al., 2000; Hyacinthe et al., 2001). The depth of biological mixing at C4 is only 2–3 cm below the sediment–water interface (Schmidt et al., 2007), which is not enough to supply Mn-oxides down to 25 cm. Simultaneous uptake of ammonium and phosphate occurs when organic matter is produced through autotrophic processes. We can speculate that the uptake of N and P within the anoxic sediment could be the result of biologic production by lithotrophic bacteria. This hypothesis needs, however, further studies. The benthic utilization of pore water nutrient can varies with time because of temperature, or macrofauna activity, which could explain the change of the NH_4/PO_4 ratio. It can also varies spatially because of the different N and P content of organic matter between C4 and C5, which is the initial source of ammonium and phosphate for pore waters.

5. Conclusions

The distribution of phosphorus in the sediment of the Thau Lagoon shows us how several processes can affect one single element during early diagenesis, and how the magnitude of these processes may vary spatially or with time in coastal regions. This variation also indicates that the study of P cycle in one lagoon cannot be representative of lagoons altogether. As already observed in continental margin sediments, the major reactions of phosphate release are the mineralization of organic phosphorus and the reductive dissolution of ascorbate extractable iron (III) phases. The reactions of phosphate removal from pore waters are adsorption on iron oxides, precipitation as an authigenic phosphate mineral, and biological uptake within the sedimentary column. In the sediments described in this study, less reactive phosphorus is buried than present at the sediment–water interface. The balance of the reactions in the sediment of the Thau Lagoon depends on the station location. The upper sediments of the station located close to the oyster banks contain high amount of reactive particulate phosphorus. This fraction consists mostly of organic phosphorus that arrives at the sediment surface through biodeposition. Only a part of this phosphorus is released to the bottom water after mineralization, since more than 50% of the total P is buried as HCl extracted P, which consists mostly of an authigenic phosphate mineral. In the middle of the lagoon organic matter seems to be much more refractory, but the distribution of the major redox compounds indicates that a part of this organic matter is mineralized. A part of the phosphate released is fixed in the sediment by an unknown process that requires further study.

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