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Deposition and fate of reactive Fe, Mn, P, and C in suspended particulate matter in the Bay of Biscay

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ABSTRACT

Hydrographic structure of the water column, dissolved nutrient concentrations and the distribution of suspended particulate matter were recorded from CDT measurements and Niskin bottles sampling on the continental slope of the Bay of Biscay and on the axis of Capbreton canyon. Ascorbate extraction was applied here for the first time on marine suspended particles to determine the content of reactive Fe- and Mn-oxides, and P associated with Fe-oxides. Hydrographic structure of the south-eastern part of the Bay of Biscay did not change during the last three decades. Particulate organic carbon (POC) contents dropped strongly with depth, showing that organic matter mineralization was efficient in the water column. Organic matter mineralized in the water column had a Redfield N:P ratio. POC percent of particles collected at depth were higher during a bloom period, suggesting that some new organic matter reached the bottom. Contents of Fe and Mn extracted with the ascorbate leaching solution showed that suspended particles originated from the Gironde estuary, one of the major sources of particles in the Bay of Biscay. Intermediate and deeper nepheloid layers occurred in the Capbreton canyon. Particles of nepheloid layers were enriched in Mn- and Fe-oxides because they originated from resuspension of surface sediment.

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1. Introduction

Studying the sediments that accumulated on margins is essential to evaluate global biogeochemical cycles (Walsh, 1988; Mantoura et al., 1991; Wollast, 1998). However, continental margins are complex environments, where it is difficult to rely directly on benthic processes to vertical particle fluxes from water column to sediment. In the last decades, several experiments focused on the relationship between sea surface production and flux of particles in deep waters, taking into account the role of mineralization and lateral advection, including hydrodynamics and sedimentary processes. These multi-disciplinary programs intended to quantify carbon cycle on margins. Several programs concluded that resuspended and advected material was particularly significant on continental slopes and submarine canyons (e.g., McCave, 1986; Gardner, 1989; Lampitt et al., 1995; Antia et al., 1999; Lapouyade and Durrieu de Madron, 2001).

The objective of the present work was to report new data on the hydrographical structure of the south-eastern part of the Bay of Biscay, and to study the spatial distribution and composition of

suspended particulate matter (SPM) in samples collected on the Bay of Biscay slope and the canyon of Capbreton. Heussner et al. (1999) reported that the composition of suspended particles in the Bay of Biscay remained steady in traps positioned on the slope close to the bottom because particles originated from permanent resuspension and lateral advection of sediment. Thus, the sampling strategy was conceived so as to obtain a view of the vertical and spatial distribution and composition of SPM, rather than to record the particle flux at a single station with a trap. For that, we decided to sample particles on filtered waters on vertical profiles at selected stations. The study focused on diagenetically reactive compounds, in particular organic C, reactive Fe- and Mn-oxides, and P associated with Fe-oxides. The idea was to examine the origin, the reactivity, and the preservation of these compounds in the water column before their further transformation during sediment diagenesis.

2. Study area and sampling

The Bay of Biscay is a semi-enclosed basin at the eastern side of the North Atlantic Ocean. Patterns of surface waters are strongly constrained by seasonal variations of thermocline and mixed layer and river runoff (Puillat et al., 2004). Below surface waters, Northern Atlantic Central Waters (NACW) is present down to 800 m depth. Between 800 and 1200 m, a branch of Mediterranean

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Outflow Waters (MOW) is present. Hydrographic stations located between 140 and 1000 m depths have been selected to compose a SE–NW transect, ranging from the outer shelf to bathyal open slope environments (stations 1, 3, 4, and 5; Fig. 1; Table 1), and on the axis of Capbreton canyon (stations 2, 6, and 7).

Fifty samples were collected during two cruises, in February 2002 and March 2003 (Table 1). Water samples were taken using a multi-sampler/carousel CTD profiler (Sea Bird Technology). Water samples were collected during the ascent of the carousel. The CTD was equipped with a dissolved oxygen sensor, a transmissiometer, the sensing device for turbidity estimate, and an altimeter, which gave the precise position of the device relative

to seafloor. During the second cruise a fluorimeter sensor was added. Water samples were collected at the surface (10 m depth), close to the bottom (5 m above the seafloor), and at intermediate depths, where nepheloid layers were located during CTD descend. Two or three 12 l bottles were sampled at each depth in order to collect enough particles.

A part of the collected water was filtered on a 0.2 μm surfactant-free cellulose acetate syringe filter for nutrient analysis. Dissolved inorganic phosphate (DIP) and silicon concentrations were measured onboard within 4 h according to Strickland and Parsons (1972). Nitrate was measured by flow injection analysis (FIA) according to Anderson (1979). The rest of the collected material was separated into two aliquots filtered onboard through pre-weighed filters: one through precombusted (500 °C for 3 h) GF/F filters to evaluate SPM and organic carbon (POC) concentrations, and the other was filtered through 0.4 μm cellulose acetate membranes for selective leaching to extract the most reactive part of Fe (III) phases, all Mn (III, IV) oxides and oxyhydroxides, and the co-precipitated or adsorbed P (Anschutz et al., 1998, 2005). For that, filters were leached for 24 h with 3 ml of ascorbate reagent consisting of 50 g NaHCO_3 , 50 g Na-citrate, and 20 g ascorbic acid in 1 l H_2O with a final pH of 8. At the beginning, filters and leaching solution were placed into an ultrasonic bath for 15 min. Aliquots of centrifuged solution were then diluted ten times with a 0.2 M HCl solution for Fe, Mn, and P analysis.

Iron and manganese were analysed using flame atomic absorption spectrometry. The precision estimated from replicates was $\pm 3\%$ for Mn and $\pm 7\%$ for Fe. Accuracy was better than 10%. Extracted phosphorus was measured by the molybdate blue method especially adapted for the diluted ascorbate matrix (Anschutz et al., 1998). Analytical error was lower than 10% from replicate samples. Final contents are given in $\mu\text{mol g}^{-1}$ of dry suspended particle. POC was determined by infrared spectroscopy after dry combustion using a LECO C-S 125. POC was measured after removal of carbonates with 2 M HCl.

3. Results and discussion

3.1. CTD profiles and nutrients

In 2002, surface waters were mixed in the upper 250 m (Fig. 2), with rather homogeneous temperatures (12.5 ± 0.1 °C), salinities (35.5 ± 0.1), and oxygen concentrations (245 ± 15 μM). Surface waters (20 m) at station 1 were under the influence of the river Adour plume, with a salinity of 34 and a temperature of 12 °C. The influence of cold fresh waters was noticeable for all stations visited in 2003, where salinities were less than 35.5 in the upper 100 m. Most of the temperature, salinity, and dissolved oxygen depth profiles overlapped below 300 m depth (Fig. 2), and were characteristic of water masses of the southern Bay of Biscay. NACW were present down to 800 m depth. Below, MOW were characterised by high salinity (35.80–35.85, Le Floch, 1968) and low oxygen concentrations for the Bay of Biscay ($170 \mu\text{mol l}^{-1}$, Le Floch, 1968; $190 \mu\text{mol l}^{-1}$, Hyacinthe et al., 2001). CTD profiles showed a similar stratification below 300 m depth than those reported by Ogawa and Tauzin (1973). Ogawa and Tauzin (1973) noted, nevertheless, sporadic low oxygen concentrations at the bottom of the canyon, which were not observed in the present study. We noted, however, that the oxygen concentration was shifted to slightly lower values at station 2 in winter 2002 and not in 2003. This suggests that water oxygenation is unsteady in the Capbreton canyon.

Concentration vs. depth profiles of DIP, nitrate, and silicon showed standard profiles, with low values at the surface, and an

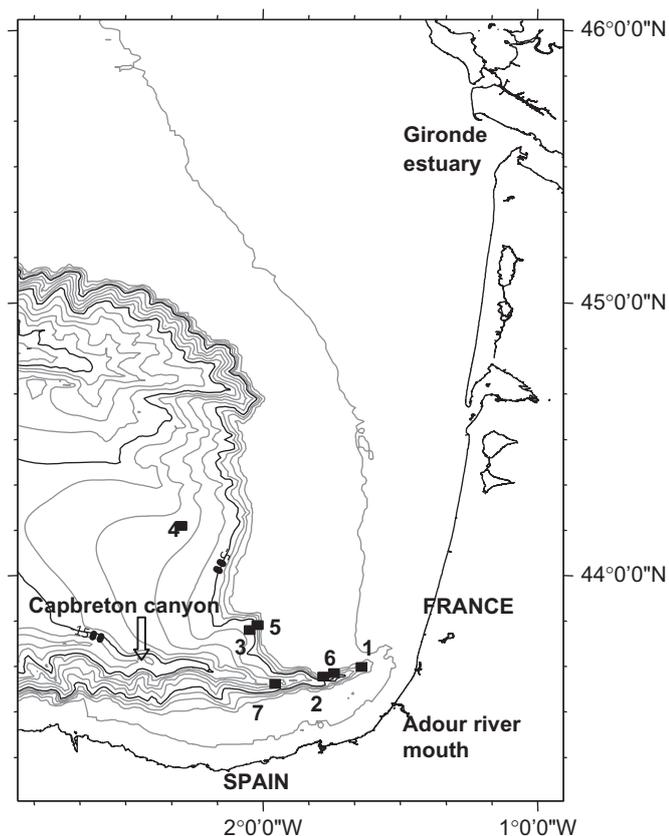


Fig. 1. Map of the south-eastern part of the Bay of Biscay showing location of stations.

Table 1

Location and water depth of the studied stations.

PROTAGO 1		February 2002				
	Station 1	Station 2	Station 3	Station 4	Station 5	
	slope	canyon	slope	slope	slope	
Position	43°42.045N 1°33.996W	43°42.045N 1°43.218W	43°48.986N 2°03.096W	44°08.985N 2°19.971W	43°49.501N 2°02.840W	
Depth (m)	146	671	585	990	396	
PROTAGO 2		March 2003				
	Station 1	Station 2	Station 3	Station 6	Station 7	
	Slope	canyon	slope	canyon	canyon	
Position	43°42.067N 1°34.165W	43°37.580N 1°43.240W	43°48.423N 2°03.247W	43°38.080N 1°41.700W	43°36.373N 1°54.090W	
Depth (m)	155	635	615	575	1030	

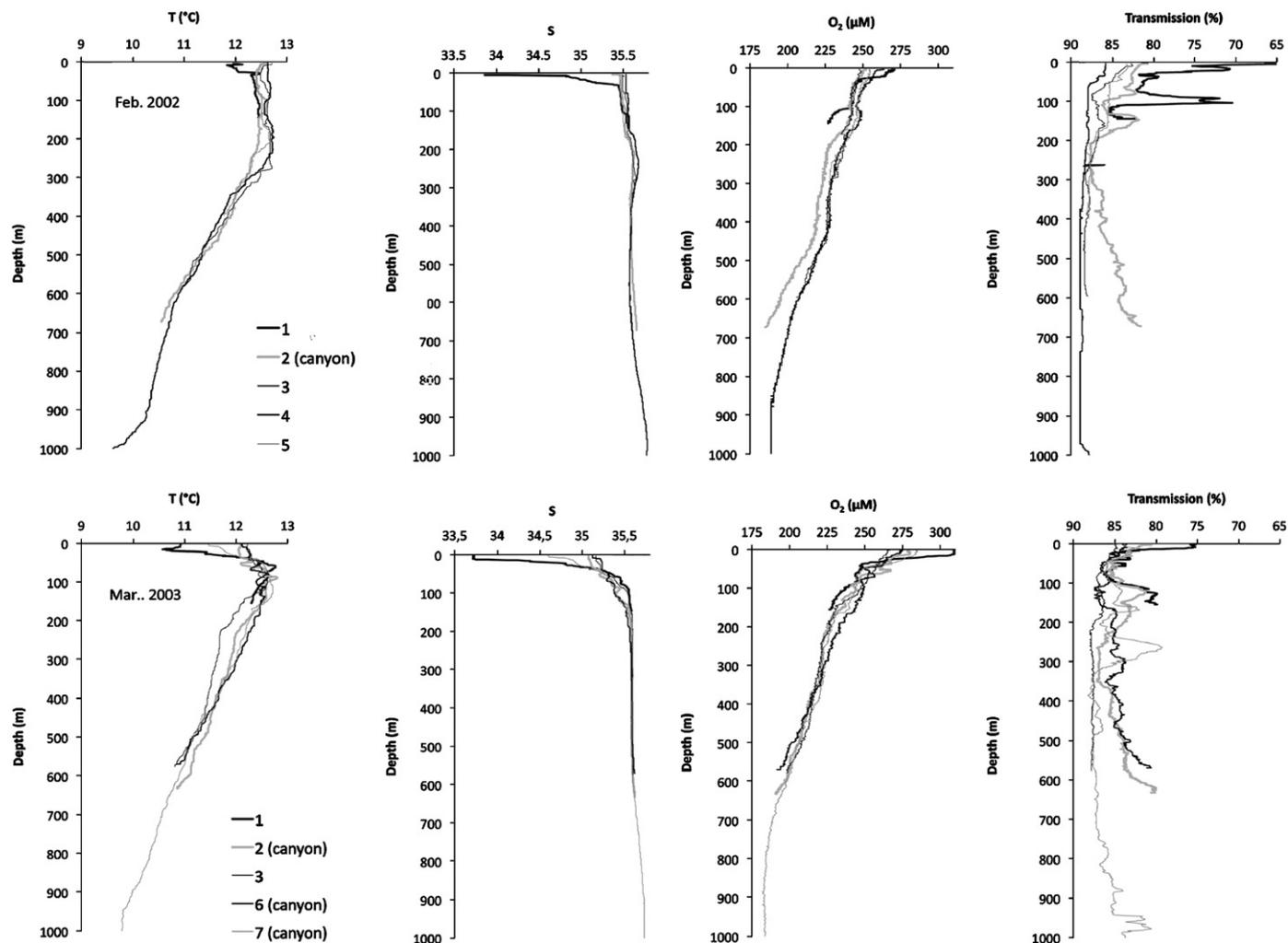


Fig. 2. Profiles of salinity, temperature, dissolved oxygen and transmissionmetry vs. depth in the water column of stations sampled in February 2002 (top) and March 2003 (bottom). Stations 2, 6, and 7 are located in the Capbreton canyon.

increase in concentration with depth (Fig. 3). Nutrient concentrations in the shallowest samples were low, but generally higher in February 2002 than in March 2003, probably because of the thick mixing zone in 2002. Surface waters at station 1, which contained a freshwater end-member, were enriched in nutrients as well. Except station 1, profiles from February 2002 and March 2003 were similar. Dissolved silicon concentrations were generally close to $1 \mu\text{M}$ at the surface, and they increased to reach about $5 \mu\text{M}$ at 750 m depth. DIP concentrations started at the top with concentrations lower than $0.25 \mu\text{M}$, and increased with depth linearly to values of $1 \mu\text{M}$ at 750 m depth. Nitrate concentrations increased from 2 to $4 \mu\text{M}$ at the surface to about $16 \mu\text{M}$ at 750 m depth. The $\text{NO}_3^-:\text{DIP}$ ratio was between 14 and 18 below the mixing zone, and was centred on the Redfield N:P ratio of 16, suggesting that organic matter mineralized during SPM settling and at the bottom of the water column is of planktonic origin.

3.2. Suspended particulate matter

Concentrations of SPM were lower than 2mg l^{-1} for the samples collected at open slope stations. Concentrations were between 3 and 6mg l^{-1} for samples collected at the surface and in nepheloid layers of Capbreton canyon. Turbidity profiles, as estimated by percent transmission profiles, showed that the

turbidity was the highest at the top and at the bottom of profiles (Fig. 2). Surface nepheloid layers were associated with chlorophyll maximum, as reported from fluorimetry profiles recorded in March 2003. Station 1 had the highest turbidity. Turbidity maximum at the surface was associated with the Adour river plume. Stations 3, 4, and 5 (open slope) had the lowest particle concentrations within NACW and MOW. Minor nepheloid layers occurred between 100 and 200 m depths, and 20 m above the bottom. Stations 2, 6, 7, and 8 located on Capbreton canyon had large nepheloid layers between 100 and 300 m depths. These layers were located at the depth of bathymetric slope inflections, suggesting detachment of bottom nepheloid layers, as observed at Goban Spur during OMEX 1 (Van Weering et al., 2002). Turbidity increased progressively in the deepest 300 m to reach values at the bottom as high as in surface waters, showing that SPM focusing towards the canyon axis occurred.

3.3. Particle chemistry

3.3.1. Organic carbon

Organic carbon contents of SPM showed different patterns in February 2002 and in March 2003 (Fig. 3). They were close to 2.5 dw% (dry weight %) in surface samples collected in winter 2002. At stations 2, 3, 4, and 5 POC contents of SPM decreased

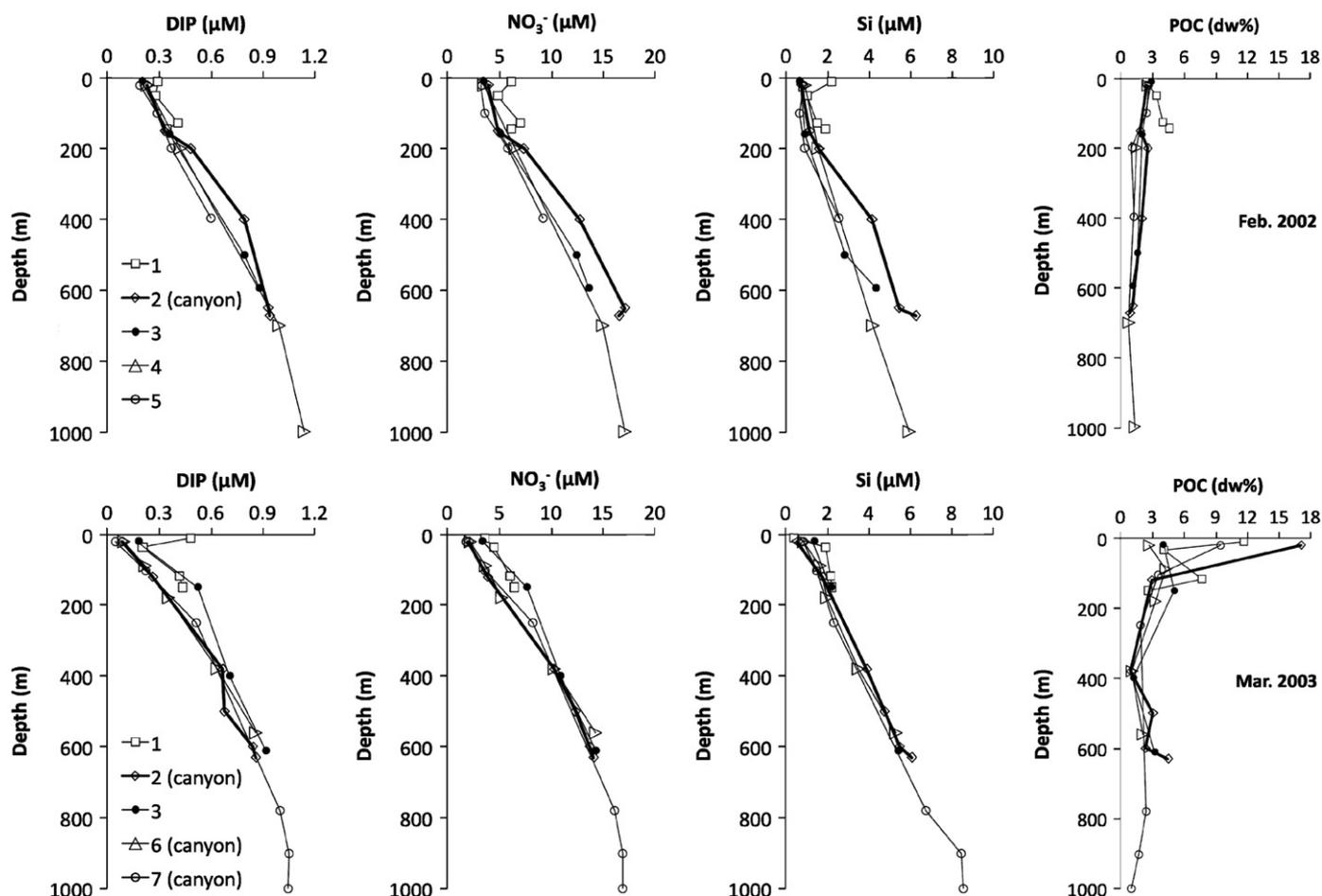


Fig. 3. Depth profiles of dissolved nitrate, phosphate, and silicon concentration (in μM), and particulate organic carbon (POC) content of suspended particles (in dry weight %) in February 2002 (top) and March 2003 (bottom).

down to about 1dw% close to the bottom. Percent of POC measured in shallower samples in 2002 was close to, or higher than, values from the main tributaries of the southern Bay of Biscay. Etcheber et al. (2007) measured a steady content of 1.5dw% in the Gironde estuary SPM and a mean content of 3.0dw% in the Adour river. POC content increased with depth, reaching 4.6dw% at the bottom of station 1, at 150m depth. The POC content was higher at the surface in March 2003 than in February 2002, in agreement with an early spring bloom as observed in other years by Laborde et al. (1999) and Huret et al. (2007). Surface SPM contained more than 4dw% POC at all stations, except for station 6, and reached 17dw% at station 2. Contents of POC decreased strongly with depth, showing that organic matter mineralization was efficient in the water column. This observation is concomitant with slightly lower oxygen concentration at depth in March 2003. Particles were, however, more enriched in POC in 2003 than in 2002, suggesting that export of organic matter occurred and some new organic matter reached the bottom.

3.3.2. Ascorbate extractions

The ascorbate reagent is well known to extract reactive Mn-oxides, the most reactive part of iron oxides, and P associated with these oxides. Ascorbate has been used for marine sediments (e.g. Kostka and Luther, 1994; Chaillou et al., 2002; Anschutz et al., 2005) and estuarine suspended particles (Deborde et al., 2007). It has been applied here for the first time on marine suspended particles. Fe-asc contents varied between 5 and $60\mu\text{mol g}^{-1}$ in

SPM (Fig. 4). The highest contents were detected in samples with high turbidities, at station 1 and in Capbreton canyon. Mn-asc contents ranged between 0 and $24\mu\text{mol g}^{-1}$. The highest contents were measured in sample of the canyon axis as well. P-asc was measured only in February 2002. We observed a similar overall shape for P-asc and Fe-asc profiles, with P-asc contents varying between 0 and $11\mu\text{mol g}^{-1}$.

Fe-asc was generally less than the content of $30\text{--}50\mu\text{mol g}^{-1}$ measured in suspended particles of either the Gironde estuary (Deborde et al., 2007), one of the major sources of particles in the Bay of Biscay, or the nearer Adour estuary (unpublished data). Fe-asc was the lowest in surface samples and at stations distant of the coast because of riverine particle dilution by biogenic marine particles. Phosphorus extracted with ascorbate corresponds to the fraction of phosphorus adsorbed on reactive Fe(III)-oxides leached with ascorbate. Except for surface samples, the Fe-asc:P-asc ratio was between 5 and 12 (Fig. 4). This value is close to the ratio of 10 measured in the Gironde estuary (Deborde et al., 2007) and the ratio of 5 measured in the Adour estuary (unpublished), which corroborate the idea that iron oxides originate from these estuaries. Fe-asc:P-asc ratio was lower than 5 in SPM of surface samples at slope stations 3, 4, and 5. They contained probably a mixture of Fe(III)-oxides originating from land and an additional fraction of P leachable with ascorbate. This part could have corresponded to a P fraction loosely adsorbed on particles. Deborde et al. (2007) reported that this fraction decreased by about 60%, but not totally, along the salinity gradient of the Gironde estuary. At stations 3, 4, and 5, the relative proportion of

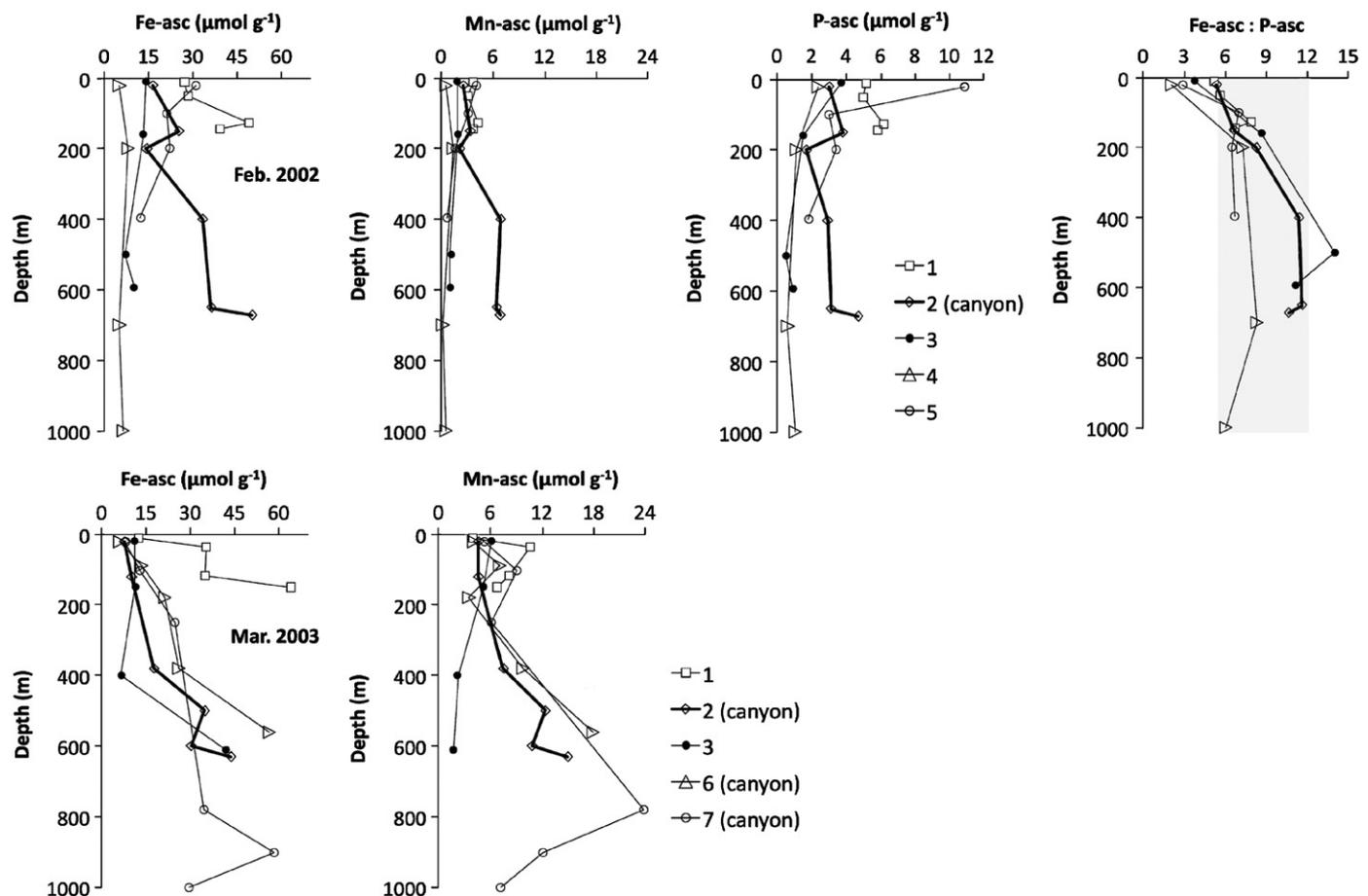


Fig. 4. Profiles of ascorbate extracted Fe and Mn contents (Fe-asc and Mn-asc in $\mu\text{mol g}^{-1}$) of suspended particles from waters sampled in February 2002 (top) and March 2003 (bottom). Additional profiles of ascorbate extracted P (P-asc) and $\text{Fe-asc}:\text{P-asc}$ ratio (top right). The grey area corresponds to the range of $\text{Fe-asc}:\text{P-asc}$ of the Gironde estuary and Adour river suspended particles.

P-asc decreased downwards, suggesting that the loosely sorbed P fraction was used in the photic zone, and thus it was a bioavailable fraction.

As for Fe-asc , contents of Mn-asc were lower than for the Gironde and Adour particles (5.5 and $9 \mu\text{mol g}^{-1}$, respectively) in surface particles and at remote stations, probably because of the dilution with biogenic particles. Particles of Capbreton nepheloid layers were significantly enriched in Mn-asc relative to riverine particles. Surface sediments of the Capbreton canyon contain between 10 and $20 \mu\text{mol g}^{-1}$ of Mn-asc (Hyacinthe et al., 2001). They are enriched in Mn-asc through early diagenesis processes. Thus, nepheloid layers originated probably from resuspension of surface sediment. Resuspension of particle in Capbreton canyon is probably triggered by the combination of internal waves (Dickson and McCave, 1986; Pingree and New, 1995) and steep slopes (e.g. Puig and Palanques, 1998).

4. Conclusion

Processes that govern the distribution of biogenic reactive compounds in water column and in suspended particle control sediment composition and benthic processes. In the Bay of Biscay, fresh marine organic matter is mineralized in the water column, but some fresh organic matter reach the sediment surface during bloom. Thus, benthic processes are probably unsteady at the studied stations. Resuspension of sediment particles has been evidenced in the Capbreton canyon, but not on the open slope.

Redeposition deeper down of suspended sediment engender a focusing of Mn-oxide and Fe-oxide-rich particles and an increase in metal oxides content of sediments down slope, towards the canyon axis. Thus, resuspension plays a role in the distribution of oxidant, and consequently, in the pathways of organic matter mineralization in sediments.

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