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Oxygen and organic carbon fluxes in sediments of the Bay of Biscay

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ABSTRACT

The relationship between particulate organic carbon (POC) concentrations measured in modern sediment and fluxes of exported POC to the sediment surface needs to be understood in order to use POC content as a proxy of paleo-environmental conditions. The objective of our study was to compare POC concentrations, POC mineralization rates calculated from O_2 consumption and POC burial rates. Benthic O_2 distributions were determined in 58 fine-grained sediment cores collected at different periods at 14 stations in the southeastern part of the Bay of Biscay with depths ranging from 140 to 2800 m. Depth-dependent volume-specific oxygen consumption rates were used to assess rates of aerobic oxidation of organic matter (OM), assuming that O_2 consumption solely was related to heterotrophic activity at the sediment–water interface. Heterogeneity of benthic O_2 fluxes denoted changes in time and space of fresh organic material sedimentation. The most labile fraction of exported POC engendered a steep decrease in concentration in the upper 5 mm of vertical O_2 profiles. The rupture in the gradient of O_2 microprofile may be related to the bioturbation-induced mixing depth of fast-decaying carbon. Average diffusive O_2 fluxes showed that this fast-decaying OM flux was much higher than buried POC, although diffusive O_2 fluxes underestimated the total sediment oxygen demand, and thus the fast-decaying OM flux to the sediment surface. Sedimentary POC burial was calculated from sediment mass accumulation rate and the organic carbon content measured at the top of the sediment. The proportion of buried POC relative to total exported POC ranged at the most between 50% and 10%, depending on station location. Therefore, for a narrow geographic area like the Bay of Biscay, burial efficiency of POC was variable. A fraction of buried POC consisted of slow-decaying OM that was mineralized within the upper decimetres of sediment through oxic and anoxic processes. This fraction was deduced from the decrease with depth in POC concentration. At sites located below 500 m water depth, where the fast-decaying carbon did not reach the anoxic sediment, the slow-decaying pool may control the O_2 penetration depth. Only refractory organic material was fossilized in sedimentary records at locations where labile OM did not reach the anoxic portion of the sediment.

1. Introduction

Knowledge of the oceanic budget of marine carbon is essential for the topical subject of climate change. The rate of carbon transfer across atmosphere–water and sediment–water interfaces controls current and future atmospheric CO_2 concentrations. The understanding and estimate of flux processes and the characterization of factors that may alter them, enable us to improve the interpretation of past changes from sedimentary records (Wefer et al., 1999).

It is commonly accepted that the flux of particulate matter to the sea floor represents the magnitude of surface primary production over an oceanographic province. But roughly 90% of the organic matter that is produced in the euphotic layer is degraded in the water column (Suess, 1980). Only a small fraction of particulate organic carbon (POC) reaches the seafloor, representing 1.5% of primary production in the open ocean and values reaching 17% on continental slopes (Wollast, 1998). The most part of exported POC is oxidized through diagenetic reactions (Lampitt and Antia, 1997; Schlitzer, 2002; Wenzhöfer and Glud, 2002).

The export of POC to the sediment surface is not steady in a short time-scale, since phytodetritus pulses may reach the sea floor after bloom events (Witte et al., 2003). Sediment traps are commonly used to quantify directly the POC flux to the seafloor with a high temporal resolution. Also this approach needs to consider hydrodynamic conditions, resuspension, swimmers, and the OM degradation within the trap to obtain accurate POC exports. An alternative approach is to use the sediment oxygen consumption and burial rates of organic carbon to estimate POC fluxes (Jahnke, 1996; Sauter et al., 2001; Seiter et al., 2005). This method may display lower temporal variability (Martin and Bender, 1988; Sayles et al., 1994;

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Smith et al., 1992), but temporal dynamics following settlement of fresh OM have been evidenced (Witte et al., 2003; Sachs et al., 2009). The preservation of sedimentary OM depends on surface water productivity, sediment accumulation rate, bottom water oxygen concentration, organic matter source, resuspension, and the magnitude of lateral transport from continental margins. The buried fraction represents eventually a minor proportion of the primary production along the continental shelves and slopes and in the open oceans (Canfield, 1994; Hedges and Keil, 1995).

Organic matter that reaches sediments is mineralized according to a depth sequence of redox reactions that control sediment diagenesis and benthic fluxes (Froelich et al., 1979; Canfield et al., 1993). The initial oxidant of organic carbon is oxygen because it is energetically the most favourable electron acceptor. The proportion of organic matter oxidation with oxygen ranges from nearly 100% in deep-sea sediments to only a few percent in organic-rich rapidly accumulating coastal sediments for which anoxic processes dominate (Bender and Heggie, 1984; Canfield et al., 1993). The major part of reduced species produced by anaerobic processes during early diagenesis are ultimately reoxidized by oxygen (e.g., Wenzhöfer and Glud, 2002). Dissolved oxygen penetration depth in sediments is thus controlled by aerobic heterotrophic activity, reoxidation of reduced compounds produced by anaerobic mineralization, and transport by diffusion, advection and bioturbation (Burdige, 2007). In the absence of a photosynthetic benthic community, the oxygen required by all of these reactions can only be supplied by transport through the sediment–water interface.

In deep-sea and continental margin sediments, sediment oxygen consumption is often mainly controlled by the OM reaching the seafloor. Consequently, the benthic O_2 flux at the sediment–water interface provides a suitable tool to determine the OM mineralization rates in marine sediments (Epping et al., 2002; Sauter et al., 2001; Wenzhöfer and Glud, 2002). The sediment O_2 uptake is measured ex situ or in situ either directly by incubation of enclosed sediment cores or indirectly, from the O_2 concentration gradients recorded in the surface sediment (Epping et al., 2002; Lansard et al., 2008; Rabouille et al., 2003; Sauter et al., 2001; Wenzhöfer and Glud, 2002). Diffusive oxygen uptake underestimates the total sediment community oxygen consumption, which takes into account benthic faunal activities, particularly in shallow sediments (Archer and Devol, 1992; Glud and Blackburn, 2002; Glud et al., 1994; Hulth et al., 1994). A review of advantages and drawbacks of these different approaches is presented by Glud (2008).

In this paper we present a database that compiles the oxygen and particulate organic carbon (POC) profiles on the slope and canyons of the Bay of Biscay. Benthic O_2 uptake rates were calculated from sediment O_2 concentration profiles measured onboard ship. This allows us to (i) define the spatio-temporal changes of the oxygen uptake and oxygen penetration depth (OPD) in the Bay of Biscay, (ii) compare diffusive oxygen flux and OPD to POC content, (iii) calculate averaged fluxes, and (iv) estimate a minimal value of POC fluxes to the sediment and define the proportion of these fluxes associated with mineralization and burial. The conclusive purpose is to have a better idea of the relationship between the POC concentrations in modern sediment and the flux of exported POC to the sediment surface.

2. Material and methods

2.1. Study area

The Bay of Biscay database consists of 104 studied cores, for which vertical profiles of redox-sensitive properties have been measured. The distribution of oxygen and carbon was studied in 58 undisturbed cores collected at 14 stations between 140 and 2800 m water depths in the southeastern part of the bay on the Aquitaine margin slope (stations A, B, D, F, WH, 11, 12 and 13), in the canyon of Capbreton (stations C, C', K, E and J), and in the northeastern part, in the canyon of Cap Ferret (station I) (Fig. 1; Table 1), during 13 cruises from 1997 to 2006. Temporal changes were assessed at stations A, B, and D, which were sampled more than ten times in different seasons (Table 2). The other stations

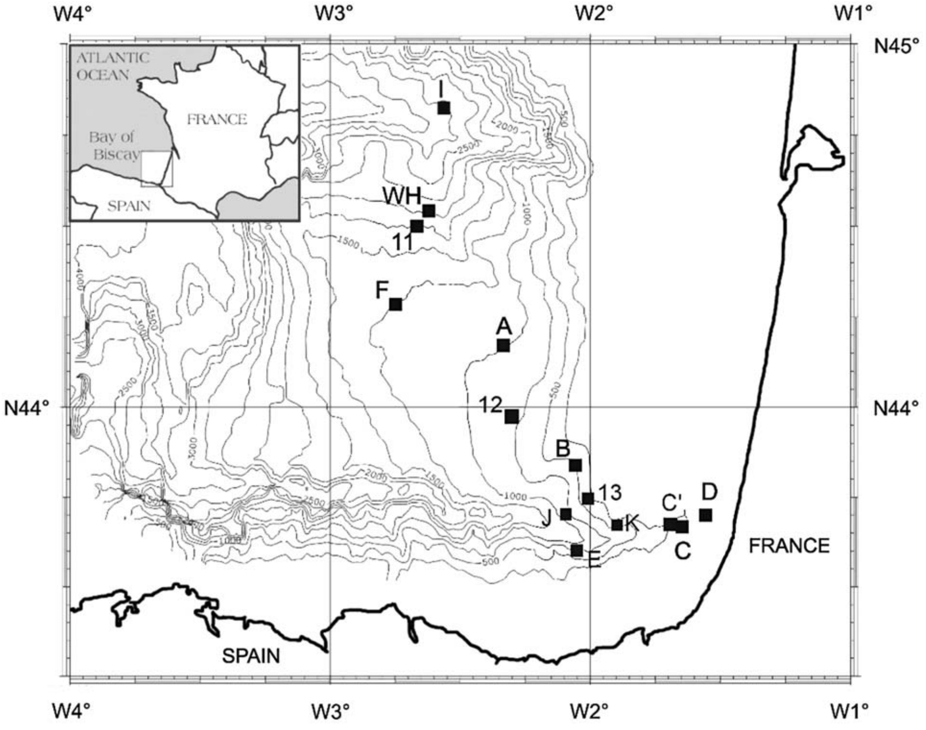

Fig. 1. Map of the southeastern part of the Bay of Biscay showing the location of the stations.

were sampled less frequently. At all stations, the sediment consisted of mud composed of silico-clastic clay and silt and less than 30% carbonates (Hyacinthe et al., 2001). The deepest stations were influenced by North Atlantic deep waters (4 °C), those shallower than 1200 m by warmer layer of Mediterranean outflow waters and of Northern Atlantic central waters (10–12 °C).

2.2. Sampling and sample processing

Cores were collected by means of a Barnett multi-corer designed to sample eight cores in 10 cm diameter and 80-cm-long plexiglass tube. Each core contained the upper few decimetres of the sediment, the overlying bottom water (between 2 and 5 l, depending on the corer penetration into the sediment), and the undisturbed sediment–water interface. Overlying water of two cores was collected immediately after core recovery for dissolved O_2 measurements in duplicate by Winkler titration (Strickland and Parsons, 1972). Cores studied were collected between 1997 and 2006. At early stages of the program, the O_2 profiles were obtained without knowing more recent works on the effect of core pre-incubation period on O_2 gradient at the sediment surface (e.g. Epping et al., 2002; Hall et al., 2007; Glud, 2008). Glud (2008) indicated that artefacts that affect the benthic O_2 distribution were mainly explained by improper establishment of in situ conditions during the onboard measurements. Fortunately, at that time our target was to reduce sediment disturbance during core retrieval so that the sediment never left significantly in situ conditions until onboard measurement of dissolved oxygen profile. Accordingly, we attempted to minimize carefully the time between core extraction and profiling. The corer was winched up at a speed of about 75 m min^{-1}. Profiling began less than 10 min after the arrival of the core onboard, that is about 15 min after core extraction at the shallowest station D, and less than 1 h after core extraction at the deepest station I. Measurements were performed after reestablishment of in situ temperature (Epping et al., 2002; Glud et al., 1994; Sauter et al., 2001). This time was short, because for most of the stations, in situ temperature was between 10 and 12 °C, which was the interval of temperature of the whole water column above 1000 m depth in winter, and between 1000 and 100 m depth in summer (Anschutz and Chaillou, 2009). The record of temperature as soon as cores reached the deck indicated that the sediment remained always very close to in situ temperature (within 2 °C), except for the sediment collected at station I, for which the difference between in situ temperature (4 °C) and temperature onboard was sometimes 7 °C. Consequently, diffusive oxygen uptakes calculated at station I (2800 m) were less robust, because they could have been overestimated. This is in agreement with Glud et al. (1999), who showed that laboratory and in situ microprofiles measurements were similar at stations above 2470 m water depth, while they were different at the deeper investigated stations. In 2005, to control the quality of the profiles measured onboard, we compared at stations 12 and K such profiles recorded in triplicate, and profiles from the same cores after several days incubation, while bubbling overlying water with air at in situ temperature.

Table 1
Study site characteristics.

Area/stations	*Position*		*Water depth (m)*
A	44°10.24′N	2°20.06′W	1000
B	43°50.31′N	2°03.47′W	550
C	43°40.08′N	1°38.87′W	250
C′	43°39.57′N	1°39.14′W	350
D	43°42.00′N	1°33.45′W	140
E	43°46.06′N	1°48.03′W	750
F	44°17.10′N	2°44.95′W	1250
WH	44°32.52′N	2°37.23′W	2000
I	44°49.46′N	2°33.78′W	2800
J	43°38.05′N	1°52.23′W	850
K	43°37.73′N	1°43.62′W	650
11	44°27.76′N	2°39.46′W	1600
12	43°59.98′N	2°15.12′W	800
13	43°42.21′N	1°59.56′W	375

Table 2
Volumetric consumption of O_2 of the upper oxic layer calculated from the PROFILE model (value reported in mmol m^{-2} d^{-1}).

Station Depth (m)	**D 140**	**C 250**	**C′ 350**	**13 375**	**B 550**	**K 650**	**E 750**	**12 800**	**J 850**	**A 1000**	**F 1250**	**11 1500**	**WH 2000**	**I 2800**
10/97	3.8	3.7			2.3					3.4				
	8.4	3.0								3.2				
01/98	13.6	11.4			10.0		6.3			6.6	2.0			
		11.0			6.2					7.2				
										7.7				
06/98	6.7	8.8			3.9		2.3			7.0				
	6.8						3.0			6.5				
07/98	8.1				4.9		4.2			2.2				
10/98	13.2	10.1			6.2		3.4			4.4			4.4	
	11.9	9.1			3.4					4.8			2.8	
	16.7													
12/98	5.8	5.8			6.1		6.1			2.6				
		4.1			10.8					4.0				
01/99	10.5		4.1		5.9		6.3			1.3				3.3
	9.7		4.3				5.5			1.5				2.7
04/98	9.5				4.4		2.8							
							3.7							
06/99	9.2				3.4				8.2	3.0				3.0
	11.3				4.4				6.3	5.6				3.8
05/00	10.8				2.8	7.1	12.6			3.9				
	10.6						6.1			2.6				
05/04	16.4				2.8					3.3		4.1	4.0	
	10.1				4.3					2.7		4.5	3.4	
08/05				12.2		7.3		7.3						
						7.9		7.0						
Average	10.2	7.5	4.2	12.2	5.1	7.4	5.2	7.1	7.3	4.2	2.0	4.3	3.6	3.2
SD	3.3	3.3	0.1		2.4	0.4	2.8	0.2	1.3	2.0		0.3	0.7	0.5

Profiles obtained with and without pre-treatment showed very similar overall shape and oxygen penetration depth.

Profiles of pore water O_2 were measured using a guarded Clark-type microelectrode (Revsbech, 1989). The sensor tip diameter of 100 μm enables to record dissolved O_2 with a vertical resolution of 500 μm using a micromanipulator. This resolution was appropriate for recording concentration gradients in the studied cores. Equilibration of the electrode lasted less than 20 s at each depth. Overlying water was gently stirred immediately before profiling for the cores collected at shallower stations, whereas there was no stirring for deep-sea sediments in order to prevent atmospheric contamination. Stirring influences the thickness of the diffusive boundary layer (DBL). However, Reimers and Glud (2000) showed that the DBL impedance became almost negligible when the O_2 penetration depth was >2 mm, what was always the case in our study. The sediment–water interface was defined visually from the inflection of the O_2 profile (Jørgensen and Revsbech, 1985). The O_2 penetration depth (OPD) was determined as the depth for which the microelectrode zero signal was reached. During the cruise in August 2005, additional O_2 profiles were measured by voltammetry. We used solid-state voltammetric microelectrodes made by sealing a 100 μm gold wire in glass tube and plating mercury onto the polished exposed gold surface as described by Brendel and Luther (1995). Oxygen was determined using Linear Sweep Voltammetry (LSV), scanning from -0.1 to -1.7 V at rate of 200 mV s^{-1}. Detection limits at 99% of confidence limit for O_2, was 3 μmol l^{-1}. All electrodes were calibrated at in situ temperature with the bottom water oxygen concentration and the zero signal in the anoxic sediment. The voltammetric method gave similar profiles than those of Clark-type microelectrodes. Then, the cores were sliced in thin horizontal sections (0.5 cm thick for the upper 2 cm, 1 cm from 2 to 8 cm, and 2 cm below this). For each depth interval, a sub-sample was immediately sealed in a pre-weighed vial, and frozen for analyses of porosity and solid fraction. Occasionally, surface sediment from a sister core was collected for excess ^{210}Pb ($^{210}Pb_{xs}$) and excess ^{234}Th ($^{234}Th_{xs}$) analyses.

2.3. Analyses

Porosity was calculated from particle density and water content determined by comparison of the weights of wet and freeze-dried sediment. The density of whole particles was estimated at 2.65 (Berner, 1980), which is the mean density of alumino-silicate and calcium carbonate minerals. Porosity profiles were fitted to the equation

$$\phi_z = (\phi_0 - \phi_\infty)\exp(-\alpha z) + \phi_\infty \qquad (1)$$

where z is the sediment depth, α the depth attenuation coefficient for porosity, ϕ_0 and ϕ_∞ the sediment porosity at the sediment–water interface and at a infinite depth in the sediment, respectively. The estimated values for α, ϕ_0 and ϕ_∞ were used for the diffusive oxygen fluxes calculations with the PROFILE software (Berg et al., 1998).

Particulate organic carbon concentration was measured on freeze-dried material by infrared spectroscopy using a LECO C-S 125, after removal of carbonates with 2 M HCl from 50 mg of powdered sample (Etcheber et al., 1999). Maximum sediment mass accumulation rates and biodiffusion coefficients were estimated from vertical profiles of $^{210}Pb_{xs}$ (half-life = 22.3 years) and $^{234}Th_{xs}$ (half-life = 24.1 days). Activities of ^{210}Pb and ^{234}Th were determined in about 5 g of freeze-dried material sealed in a counting vial, by high-resolution and low-background gamma spectrometry with a semiplanar and a well-type detector for 4–24 h. The uppermost sediment layers were analyzed for ^{234}Th by counting the 63.3 KeV gamma emission. These measurements were completed within 1 month after sampling and corrected for radioactive decay that occurred from sample collection to counting. Sediment layers were investigated downcore until a rather constant ^{234}Th activity was reached. This activity was considered as the supported activity and used to calculate the $^{234}Th_{xs}$. The $^{234}Th_{xs}$ inventories were calculated from depth a to depth b according to:

$$I = \sum_{a}^{b} A_z(1-\phi_z)\Delta_z \cdot \rho \qquad (2)$$

where I is the inventory of $^{234}Th_{xs}$, Δ_z the depth intervals between depths a and b, A_z the excess activity of ^{234}Th for Δ_z, ϕ_z the porosity for Δ_z, and ρ the particle density.

2.4. Flux calculations

2.4.1. Sediment oxygen uptake

Sediment O_2 uptake rates were assessed by means of the numerical model PROFILE that uses a curve fitting approach by adjusting the computed O_2 profile to the measured one (Berg et al., 1998). This approach enables to consider the entire vertical distribution of dissolved oxygen and to use the porosity gradient within the sediment. The two boundary conditions used for calculation are the oxygen concentration at the sediment–water interface and zero oxygen concentration at the bottom of the oxic zone. The bulk sediment molecular diffusion coefficient (Ds) was assumed to be equal to $D_s = D_o/(1+3(1-\phi))$ (Rasmussen and Jørgensen, 1992) where ϕ is the sediment porosity and D_0 is the diffusion coefficient in water (Broecker and Peng, 1974) at in situ temperature (Li and Gregory, 1974). The vertical transport processes include also bioturbation. Bioturbation is classically described as an eddy-diffusive transport process occurring within a surface mixed layer (Goldberg and Koide, 1962). Surface sediments can be characterized by a mixed layer of thickness L with both constant biodiffusion coefficient (Db) and a constant burial rate. The mixed-layer depth is commonly defined as the depth of strong gradient inflection along the ^{210}Pb profile. Biodiffusion coefficients are computed from ^{234}Th profiles. Such profiles were not obtained at the same time resolution as dissolved O_2 profiles. At the shallow stations, like stations D and C, vertical $^{210}Pb_{xs}$ profiles showed almost no gradient (Anschutz et al., 1999; Hyacinthe et al., 2001; Chaillou et al., 2002, 2006, Mouret et al., 2009; Schmidt et al., 2009), meaning that the thickness of the bioturbated layer exceeds the length of the cores. Here, bioturbation dominated over sedimentation, making it impossible to discriminate between biodiffusion coefficient and burial rates from radioisotopic profiles. Accordingly, we did not determine the Db at the shallow stations. At the deeper stations, by contrast, the bioturbated layer was thinner ($L \leq 1$ cm). Activities of $^{234}Th_{xs}$, recorded in the surface layers of the cores decreased strongly with depth, to below the detection limit at 1 cm depth for most of the cores. The values recorded in the upper 0.5 cm showed temporal variations for a given station. The corresponding biodiffusion coefficients ranged from 0.08 to 14.8 cm^2 $year^{-1}$ (Mouret et al., 2009). The maximal value was assessed at station B in May 2000. It was 30 times lower than molecular diffusion coefficient Ds of dissolved O_2. Indeed, most of the tracer-derived Db were two or three order of magnitude lower than Ds, suggesting that for the deeper stations studied here, particle biodiffusion had a low effect on O_2 fluxes. However, bioturbation on solutes can be many times stronger than on solids. According to Berg et al. (2001), solute biodiffusivity can be twelve times higher than the tracer-derived Db, which makes Db for dissolved O_2 still lower than Ds. Considering all the points discussed above we decided eventually to base our calculation of

O_2 consumption only on molecular diffusion. Therefore, our assessment gave minimal values of sediment oxygen uptake.

2.4.2. POC fluxes

The flux of fast-decaying POC was deduced assuming that a fraction of O_2 volume-specific uptake was used for aerobic heterotrophic respiration of a Redfield-type organic matter. This assumption introduced some limitations and requested to define the fraction of O_2 used for heterotrophic activity.

First, it is well known that the nature of POC that reaches the seafloor is not primary Redfield-type organic matter. Settling organic matter has commonly higher C/P or C/N ratios than fresh planktonic material. However, the O/C ratio of oxic respiration is not affected significantly (Boyd and Trull, 2007), and the rate of mineralization of fast-decaying POC was assumed to be 106/138 of a fraction of O_2 uptake.

Second, within the oxic zone proportions of oxygen are used to oxidize refractory carbon and oxidize reduced compounds (Mn(II), Fe(II), S(−II), NH_4^+) at the oxic/anoxic boundary. This last part dominates in coastal sediments (Jørgensen, 2000; Soetaert et al., 1996; Thamdrup and Canfield, 2000). It should be subtracted from oxygen consumption in our assessment of the relative proportion of fast-decaying carbon. This fraction could be estimated from the sum of reduced compound fluxes towards the oxic zone (Berg et al., 2003). Information are available in our database for this approach, but to rely on reduced compound fluxes to estimate oxygen fluxes, several secondary reactions have to be taken into account (e.g., Anschutz et al., 2000; Hyacinthe et al., 2001; Berg et al., 2003) because reduced compounds are not oxidized with oxygen only. For instance, Fe(II), S(−II), and NH_4^+ may be oxidized with Mn-oxides. Hyacinthe et al. (2001) estimated that the diffusive flux of reduced compounds amounted to less than 7% of the flux of dissolved oxygen across the sediment/water interface at stations B, A, and I, meaning that for deep stations, the uptake of O_2 by aerobic respiration dominated. For our purpose we assumed that the volume-specific oxygen uptake of the lower oxic layer was controlled by slow-decaying POC and oxidation of reduced compounds. Consequently, we assumed that the defined pool of O_2 used to oxidized fast-decaying POC solely was the oxygen uptake of the upper oxic layer. The volumetric consumption of O_2 of the upper oxic layer was calculated from the PROFILE model, and expressed in flux unit. This upper box of oxygen profiles was clearly separated from below by an inflexion of the curvature in most of the profiles recorded in sediments collected deeper than 500 m. At those shallower stations, for which the whole oxic layer was thinner than 1.5 cm, our approach was not accurate, because the resolution of the profiles did not enable us to separate the fluxes at the top and at the bottom of the oxic layer. Therefore, we did not calculate fast-decaying carbon at theses stations.

Third, oxygen uptake rate used for calculation represents only a fraction of the total sediment community oxygen consumption, which includes also benthic faunal activities and resuspension (Archer and Devol, 1992; Glud and Blackburn, 2002; Glud et al., 1994; Hulth et al., 1994). Solute biodiffusion is lower than molecular diffusion at the deep slope stations studied. Therefore the use of diffusion calculations from ex situ profiles may provide a reasonable lower limit of fast-decaying carbon input.

The pool of fast-decaying carbon, which triggers the oxygen flux at the sediment–water interface, is not buried but it becomes recycled to CO_2. We named "buried POC" the POC that was not converted to CO_2 at the sediment surface. It approximately corresponded to all the POC content of the surface samples. Buried POC fluxes were calculated using POC content in the upper centimetre and the sediment mass accumulation rates. The "fossilized POC" flux represented the flux deduced from the mass accumulation rates and POC concentrations at the bottom of the studied cores. Then, the slow-decaying POC flux was deduced from the difference between buried POC flux and fossilized POC flux.

Sediment transport processes are characterized by sediment mass accumulation rates and bioturbation. These processes at the stations studied have been discussed thoroughly in previous works (Hyacinthe et al., 2001; Chaillou et al., 2002, 2006; Mouret et al., 2009; Schmidt et al., 2009). At the shallow stations, like stations D and C, vertical $^{210}Pb_{xs}$ profiles showed almost no gradient. Here, bioturbation dominates over sedimentation. Therefore, we did not determine the accumulation rates at the shallow stations. At the deeper stations, surface $^{210}Pb_{xs}$ activities were close to 1000 Bq kg^{-1} and the values decreased exponentially downcore to reach values lower than 100 Bq kg^{-1} at depths varying from 4 cm at station I to 10 cm at station B. Values of sediment mass accumulation rates deduced from $^{210}Pb_{xs}$ activities (Anschutz et al., 1999; Chaillou et al., 2002; Hyacinthe et al., 2001), as well from sediment traps (Heussner et al., 1999; Schmidt et al., 2009), and from a model based on steady-state manganese diagenesis (Mouret et al., 2009) were obtained for sediments of stations B (550 m), A (1000 m), F (1250 m), 11 (1600 m), WH (2000 m), and I (2800 m), with values of 54, 34, 44, 7, 9, 18, and 15 mg cm^{-2} yr^{-1}, respectively. Hemi-pelagic sedimentation rates were not obtained for sediments of the Capbreton canyon because they consisted of turbidite accumulations.

3. Results

3.1. Oxygen profiles

Bottom waters of the Bay of Biscay are well oxygenated with oxygen concentrations of between 180 and 250 μmol l^{-1}, i.e., always more than 80% oxygen saturation. Stations at between 800 and 1200 m water depth present typically the lowest values because they are under the influence of Mediterranean waters (Ogawa and Tauzin, 1973). Oxygen penetration depths vary from 5 mm at the shallow stations (e.g. site D) to 6 cm at the deeper stations (e.g. sites F and WH; Fig. 2). We clearly observe two types of oxygen profiles. At the deeper stations, profiles are characterized by a steep decrease in oxygen concentration in the upper 5 mm, and by a smoother decrease downwards to anoxia. At those stations for which OPD is limited to a few mm (e.g. station D), vertical oxygen distributions are only characterized by a sharp decrease in oxygen concentrations. Canyon stations are characterized by OPD lower than that of slope stations of similar water depth (e.g. stations B and K; Fig. 2). Time series of oxygen profiles are only available for stations D, C, B, and A. Volumetric oxygen consumption of the upper oxic layer shows temporal variation (Table 2). Oxygen fluxes do not display consistent seasonal differences. Average oxygen consumption are between 2.0 mmol m^{-2} d^{-1} at station F (1250 m) to more than 10 mmol m^{-2} d^{-1} at station D (140 m) and 13 (375 m). Not surprisingly, the highest diffusive oxygen uptake rates are observed in the shallow station sediments (D, C, C', 13, B and K).

3.2. POC profiles

Particulate organic carbon (POC) contents of surficial sediments decrease from above 2 dw% (dry weight %) at the shallowest stations (D, C, C', and G) to values close 1.0 dw% at the deepest stations (A, F, 11, I, and WH) (Table 3). Vertical profiles at stations A, B, F, I, WH, and 11 reveal commonly higher

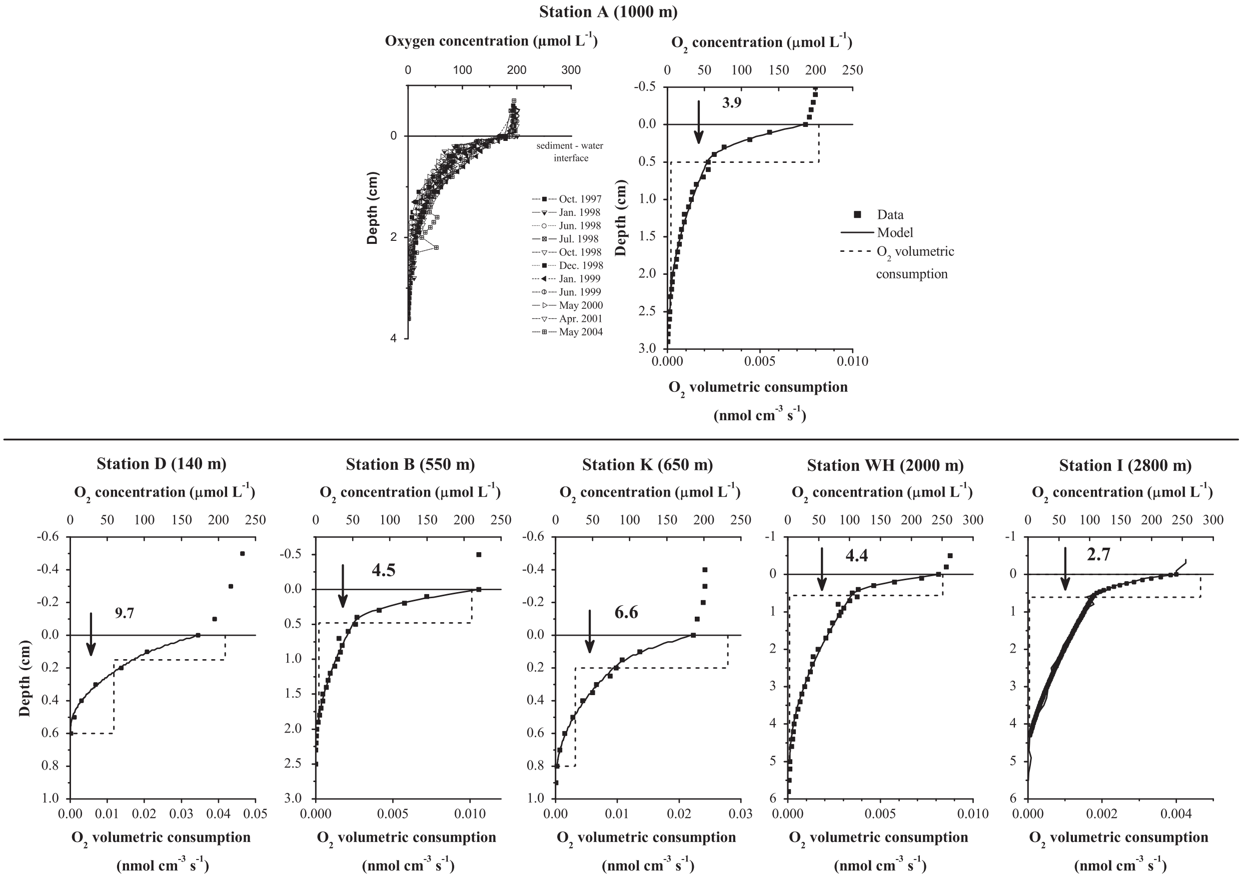

Fig. 2. Selected O_2 microprofiles at six different stations. Output of the PROFILE model (Berg et al., 1998) show the curve fitting and the volumetric O_2 uptake. The numbers and black arrows indicate the diffusive flux of O_2 (mmol m^2 d^{-1}) across the sediment-water interface. A example of temporal variation of O_2 profiles is shown for station A sediments. The 0-value at the ordinate indicates the relative position of the estimated sediment surface.

Table 3
POC content (value in percent) of superficial sediments (first half centimetre). Name of cruises (first line) refers to month/year.

	10/97	01/98	01/99	04/99	06/99	05/04	Average
D (140 m)	2.01	2.05	2.23	2.12	2.32	2.17	**2.15**
C (250 m)	1.85	2.09					**1.97**
C′ (350 m)			2.20				**2.20**
G (400 m)		2.00					**2.00**
B (550 m)	1.77	1.51	1.48	1.61	1.83	1.86	**1.68**
E (750 m)		1.98	1.74				**1.86**
A (1000 m)	1.11	1.00	1.14			1.31	**1.14**
F (1250 m)		0.72					**0.72**
11 (1600 m)						1.29	**1.29**
WH (2000 m)						1.09	**1.09**
I (2800 m)			1.20		1.39		**1.30**

POC concentrations at the top than that at a few centimetres below (Fig. 3 and 4). By contrast, vertical profiles at stations D, C, and C’ show almost no gradient. Vertical profiles at stations E and K are heavily scattered. These stations are all located along the axis of the Capbreton Canyon, the sediments of which consist of a succession of centimetre to decimetre thick turbidite sequences (Mulder et al., 2001). Here, variation of POC content are caused by transient processes of sedimentation, and grain size sorting of particles (Anschutz et al., 2002; Chaillou et al., 2008).

3.3. *POC fluxes*

The estimation of fast-decaying POC flux is derived from our assumption that volume-specific oxygen uptake at the sediment surface was related to aerobic respiration of Redfield-type POC. Therefore, the highest fluxes are calculated for the shallowest sediments and the lowest flux are determined at station F (Table 4). Buried POC fluxes are estimated only at those stations for which sediment accumulation rates are available. The flux is 109 μmol cm^{-2} yr^{-1} at station B, and less than 33 μmol cm^{-2} yr^{-1} at the other stations (A, F, 11, WH, and I). The sum of fluxes of fast decaying POC and buried POC encompasses theoretically the total POC flux to the sediment surface. Total POC flux is 235 μmol cm^{-2} yr^{-1} at station B, and ranges between 77 and 137 μmol cm^{-2} yr^{-1} at the other stations. Fossilized POC flux deduced from bottom core POC content represents between one half and two thirds of buried POC flux, and only between 30% (station B) and 4% (station 11) of the total POC flux (Table 4). By difference, the slow-decaying POC flux represents between one half and one third of the buried POC flux.

4. Discussion

4.1. *Oxygen fluxes*

Temporal changes in diffusive oxygen fluxes at a given station could not be related to any other recorded parameter, nor interpreted clearly in terms of seasonality, inter-annual variability or spatial heterogeneity. Microscale patchiness in O_2 distribution may suffice to explain the observed variability (e.g. Glud et al., 2009). Also, these changes may be associated with pulses in exported flux and rapid turnover of fast-decaying organic material to the sediment surface. Intermittent fluxes of particles to the

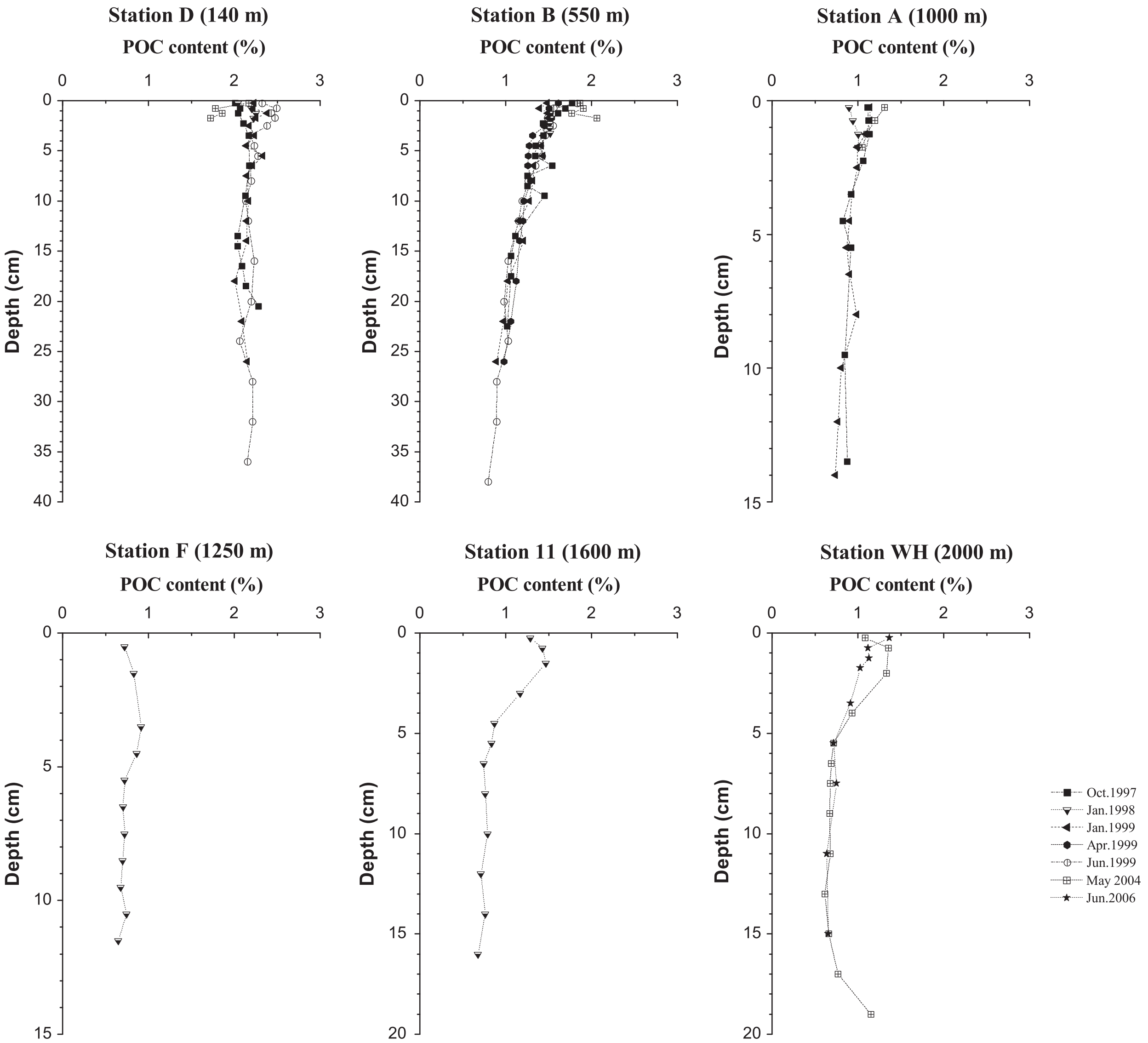

Fig. 3. Vertical POC profiles in dry weight percent for the stations on the slope (D, B, A, F, 11 and WH). Distinct symbols represent the different cruises.

sediment are indeed illustrated by variation of $^{234}Th_{xs}$ inventories (Fig. 5). The pool of fast-decaying carbon that may explain oxygen flux variations is probably minor compared to the whole organic carbon content of the sediment, because Grémare et al. (2005) found no significant temporal changes at the studied stations in totally and enzymatically hydrolyzable amino acids, which are indicators of the organic matter lability. Also, Etcheber et al. (1999) observed no significant seasonal evolution of POC at the sediment surface in the Bay of Biscay, attributing this pattern to a quick mineralization of sedimented labile POC. Averaged diffusive oxygen fluxes were the highest at the shallower stations, meaning that the export of labile organic carbon to the sediment must be significant.

4.2. Oxygen penetration depth

Sediments in productive coastal environments are commonly characterized by millimetric OPD compared to centimetric or decimetric OPD found in deep ocean sediments (Glud et al., 1994). OPD is controlled by the balance between downward flux of oxygen from the overlying water and oxygen consumption through POC and reduced compounds oxidation. Oxygen is transported to sediments by molecular diffusion, by bioturbating and irrigating activities of benthic organisms.

Fig. 6 shows that the OPD is linked to the water column depth. The OPD is regulated by organic carbon degradation, and therefore by organic carbon content and carbon rain rate to the sediments (Emerson et al., 1985; Gehlen et al., 1997). The exported organic carbon flux typically decreases strongly with water depth, as the material is mineralized in the water column (Antia et al., 1999; Berger et al., 1989; Betzer et al., 1984; Martin et al., 1987; Pace et al., 1987; Suess, 1980). Martin and Sayles (2003) reported the relationship between the OPD and water depth on three continental margins: Northeast Atlantic (Lohse et al., 1998), Northwest Atlantic (Martin and Sayles, 2003) and Northeast Pacific (Reimers et al., 1992). The OPD is lower in the Pacific zone because bottom water is older and depleted in oxygen, and because of high rain rates of organic carbon. Our results reflect and enrich the relation obtained previously in Northeast Atlantic (Lohse et al., 1998). Our data reveal the ODP variability for a given depth in the Bay of Biscay. The patchiness or seasonal variations of organic matter inputs may explain these variations.

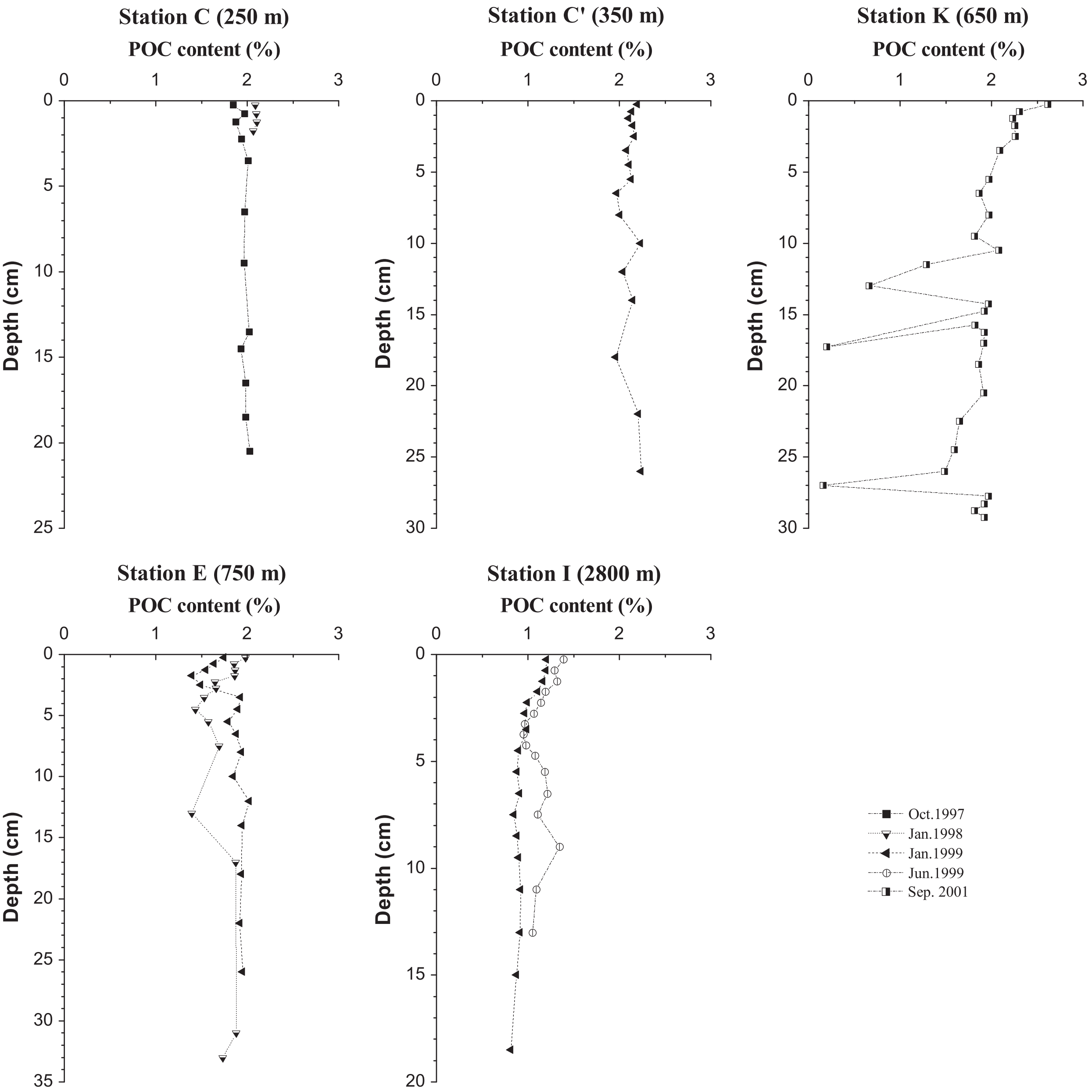

Fig. 4. Vertical POC profiles in dry weight percent for the stations of the canyons of Cap Ferret (I) and of Capbreton (C, C', K and E). Distinct symbols represent the different cruises.

Table 4
Fast-decaying POC fluxes calculated from mean volumetric oxygen consumption transformed with Redfield ratio, buried POC estimated with mean surface POC contents and accumulation rates. Total POC fluxes are the sum of these two fluxes. Fossilized POC fluxes calculated from mean bottom core POC content. Slow-decaying POC fluxes are the difference between the two last.

	D 140 m	B 550 m	A 1000 m	F 1250 m	11 1500 m	WH 2000 m	I 2800 m
Mean Oxygen Flux (mmol m^{-2} d^{-1})	10.2	5.1	4.2	2.0	4.3	3.6	3.2
Fast-decaying POC flux (μmol cm^{-2} yr^{-1})	285	126	104	51	101	97	81
Accumulation rate (mg cm^{-2} yr^{-1})		78	36	44	7	14	17
Mean surface POC content (μmol g^{-1})	1792	1400	933	600	1075	1142	1150
Buried POC flux (μmol cm^{-2} yr^{-1})		109	33	26	7	16	19
Total POC flux (μmol cm^{-2} yr^{-1})		235	137	77	108	113	100
Mean bottom POC content (μmol g^{-1})	1660	780	594	450	540	570	850
Fossilized POC flux (μmol cm^{-2} yr^{-1})		61	21	20	3.8	8	14
Slow-decaying POC flux (μmol cm^{-2} yr^{-1})		48	12	6	3.2	8	5

Lower OPD at canyon stations (Fig. 6) suggests that the flux or lability of organic matter is higher in canyon sediments than that in slope sediments. OPD could have been as well influenced by sediment mixing and modification of labile organic matter distribution. High particle fluxes to canyon sediments is supported by ^{234}Th$_{xs}$ data (Fig. 5). This radionuclide

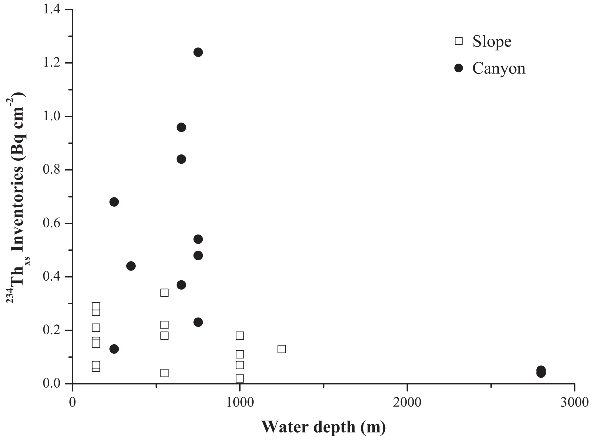

Fig. 5. ^{234}Th$_{xs}$ inventories as a function of water depth. The open squares represent plots of slope stations, and closed dots represent canyon of Capbreton stations.

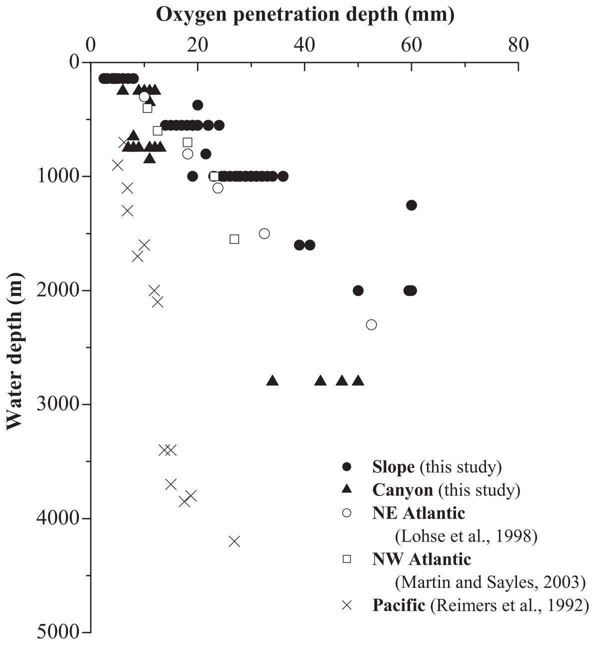

Fig. 6. Oxygen penetration depth vs. water depth. The open dots represent data of Lohse et al. (1998) in the Northeast Atlantic, the open squares, data of Martin and Sayles (2003) in the Northwest Atlantic, and the crosses, data of Reimers et al. (1992) in the Pacific. Closed dots are oxygen penetration depths (OPD) of the stations located on the Bay of Biscay slope, and closed triangles are ODP of the canyon of Capbreton stations.

is a good tracer of particle inputs on a period of 100 days (Aller and DeMaster, 1984; Smith et al., 1993; Smoak et al., 1996; Waples et al., 2006). Inventories of ^{234}Th$_{xs}$ at the canyon stations shallower than 1000 m water depth exceeded inventories at the slope stations (Fig. 5). This indicates that more particles, and probably more organic matter, reached the bottom of the upper canyon. Focusing towards Capbreton canyon axis of resuspended particles has been documented (Anschutz and Chaillou, 2009). Particles resuspension in submarine canyons is triggered by the combination of internal waves (Dickson and McCave, 1986; Pingree and New, 1995) and steep slopes (e.g. McPhee-Shaw et al., 2004; Puig and Palanques, 1998).

4.3. Surface POC vs. diffusive oxygen flux

Fig. 7a presents the relationship between the diffusive oxygen fluxes and POC concentrations of surface sediments. Both parameters correlate positively (p=0.007, n=26). However, the proportion of oxygen fluxes accounted for by changes in POC concentrations remains limited (r^2=0.428). The sediment oxygen consumption rate depends mainly on the rate of aerobic respiration, which in turn, depends on the flux of labile organic matter (Gehlen et al., 1997; Katsev et al., 2006). The relationship between sedimentary POC and benthic aerobic respiration cannot rely only on the use of global descriptors of organic matter, but must rather consider labile POC. An important part of the sedimentary POC is either refractory by nature (i.e., continental organic detritus) or extensively degraded, and thus cannot be easily absorbed by benthic fauna (Plante and Jumars, 1992; Plante and Mayer, 1994; Plante and Shriver, 1998a, 1998b). POC in superficial sediments corresponds to a mixture between fast-decaying POC and more refractory carbon. The occurrence of fast-decaying carbon within the sediment column depends on the depth of sediment mixing. The contribution of fast-decaying carbon to POC decreases with depth below the sediment–water interface (e.g. Berg et al., 2003; Boudreau and Ruddick, 1991), and probably becomes insignificant below the depth of sediment mixing by bioturbation. At the shallow stations C and D, the thickness of the bioturbated layer exceeds the length of the cores, meaning that labile organic matter is supplied below the oxic layer in this case. At the deeper stations, the well-mixed layer ($\leq$1 cm) is thinner than the oxic layer. The well-mixed-layer depth is defined as the depth of strong gradient inflection along the ^{210}Pb profile. Even if mixing may occur below this depth, the long-period (22.3 years) tracer ^{210}Pb activity shows below 1 cm depth a decrease that fits radioactive decay (Anschutz et al., 1999; Hyacinthe et al., 2001; Chaillou et al., 2002, 2006, Mouret et al., 2009; Schmidt et al., 2009). Thus, mixing below 1 cm depth is probably very slow, and most likely slower than fast-decaying carbon mineralization kinetics. Therefore fast-decaying carbon probably disappears below this upper cm layer, which accounts for the diminution in oxygen consumption rate associated with the second curvature of oxygen profiles. In the following discussion, we attempt to decipher the relationship between the diffusive oxygen flux and the different categories of organic matter, and to define the potential implications for further interpretation of sedimentary POC content.

4.4. POC fluxes

The diffusive oxygen flux used for calculations of fast-decaying carbon flux represents indeed only a fraction of the total sediment community oxygen consumption, which takes into account macrofauna activity (Glud and Blackburn, 2002; Smith, 1978). Actually, because macrofaunal activities transport pore waters faster than molecular diffusion, microorganism respiration and metabolism is underestimated. The sum of the buried POC and fast-decaying POC flux encompasses theoretically a value, which is a minimal value, of the total POC flux to the sediment. For slope stations for which the sediment mass accumulation rate and diffusive oxygen flux are available (Table 4), the total POC flux calculated in this way exceeds largely the buried POC flux (Fig. 8). This suggests that the mean concentration of organic carbon of sinking particles is higher than the concentration measured in surface sediment. Previous sediment trap data confirm this observation (Etcheber et al., 1999; Schmidt et al., 2009). Analyses of sediment trap material located close to station I (2800 m) and at station WH (2000 m) revealed a range of POC

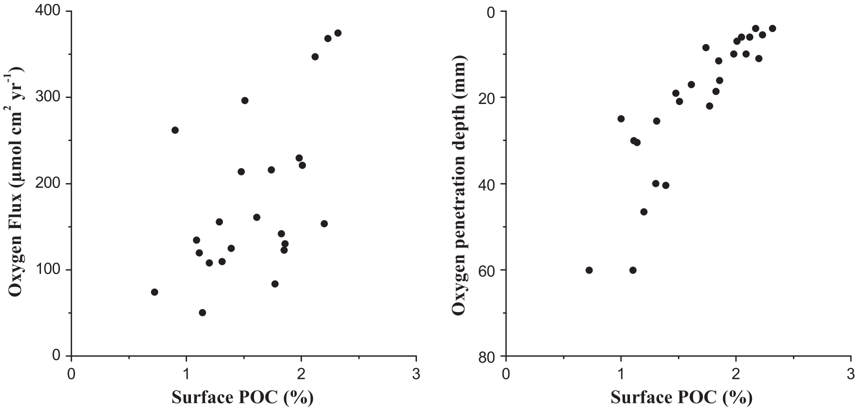

Fig. 7. Relationship between surface POC (content of POC in the upper half centimetre) and oxygen flux (a), and relationship between surface POC and oxygen penetration depth (b).

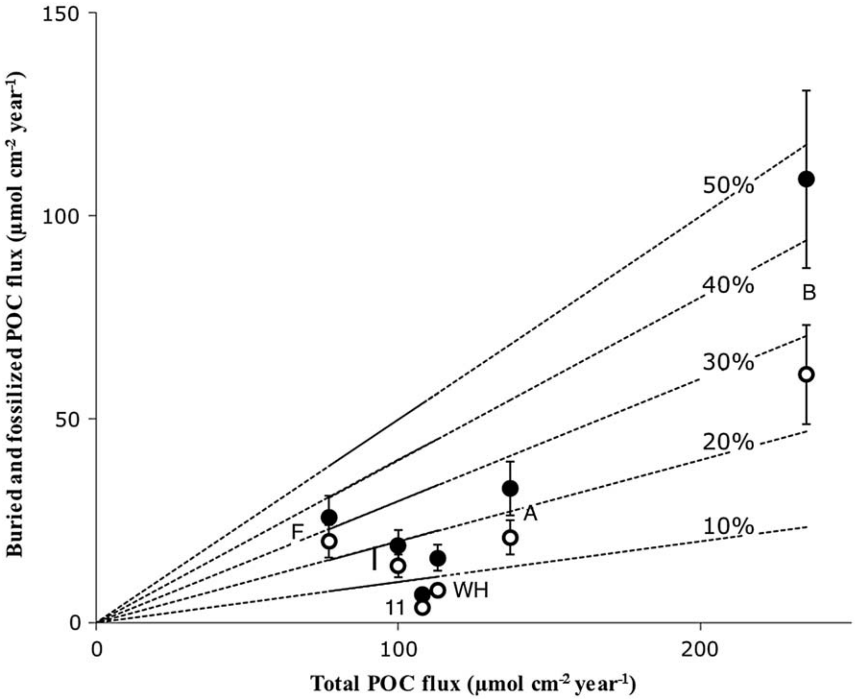

Fig. 8. Total POC fluxes estimate vs. buried POC fluxes (closed dots) and fossilized POC fluxes (open dots) for the stations B, A, F, 11, WH and I. Dashed lines show 10, 20, 30, 40 and 50% of burial efficiency.

content between 3% and 10% for the sinking particles whereas the mean POC content in sediments was only of 1.4 dw% in the first half centimetre. Therefore, the POC content of surface sediments represents only a minor proportion of the settling POC.

Our results reveal that the mean surface sediment POC concentrations represent only a reduced fraction of the total POC flux that arrives at the sediment surface at studies sites. At the deepest stations, the fast-decaying POC flux is much higher than the buried POC flux, suggesting that the sharp oxygen gradient is triggered by a fraction of labile POC that is quickly converted into CO_2, and recurrently replaced by new inputs. This can be easily illustrated by an example. At station I, for instance, the upper cm has a particle content of 344 mg cm^{-2}, as deduced from the measurement of water and solid fraction contents. This represents about 20 years of sedimentation with a mass accumulation rate of 17 mg cm^{-2} yr^{-1}. The POC content is estimated to 395 µmol, i.e. 1.38 dw% of 344 mg. The rate of organic carbon mineralization deduced from the average diffusive oxygen flux is about 81 µmol cm^{-2} yr^{-1} (Table 4). Consequently, it only would take 5 years to consume all measured organic carbon if we exclude fresh inputs. This shows first, that the stock of surface POC is mostly composed of slow-decaying or refractory carbon. Second, the fast-decaying organic carbon that is responsible for the steep gradient of oxygen at the sediment surface has a high turnover.

Variations of oxygen fluxes detected at stations for which time-series are available suggest seasonality of fresh organic material sedimentation. The highest fluxes probably occur after input of labile POC. The lowest fluxes show that high sediment oxygen consumption is not maintained between two successive episodes of labile POC input, suggesting that the fresh material is almost mineralized within a few weeks or months as observed after pulses in pelagic food supply at the abyssal sea floor (Pfannkuche, 1993; Smith et al., 2002; Witte et al., 2003). Fresh and labile organic carbon is consumed either in the upper mm of sediment once deposited at the seafloor, or deeper in the sediment after mixing through bioturbation (Jahnke et al., 1982). The rupture in the curvature of oxygen profiles observed at deep stations (Fig. 2) may be related to the depth of mixing, i.e. to the depth of fast-decaying POC occurrence. The sharp gradient close to the sediment–water interface occurs where fast-decaying POC is mixed with slow-decaying POC. Below, the gentle gradient results from aerobic mineralization of slow-decaying POC only. Hence, fresh fast-decaying POC never reaches anoxic sediment at the stations that display two curvatures in dissolved oxygen profiles, which is in agreement with the thickness of the bioturbation-induced mixed layer deduced from vertical $^{210}Pb_{xs}$ profiles (Mouret et al., 2009). Since the depth of the gradient inflection is not deeper than the depth at which $^{234}Th_{xs}$ is detected, we can deduce that the residence time of fast-decaying POC is of the order of magnitude of $^{234}Th_{xs}$ activity, i.e. few weeks or months.

POC content of the oxic layer and oxygen penetration depth correlated negatively (r^2=0.758, $p<0.0001$, n=26; Fig. 7b). OPD is controlled largely by the more refractory material (i.e., the one accounted for by the second curvature of oxygen profiles), and not by the most labile fraction of POC.

The proportion of buried POC measured at the top of the sediment column relative to total POC flux depends on station location, ranging from about 50% at station B to about 10% at station 11 (Fig. 8). These are maximum percentage, because total POC flux values are underestimated. For a narrow geographic area like the Bay of Biscay, POC concentration in surface sediment is not proportionate to exported POC flux to the sediment, because it does not represent a predetermined fraction of POC exported to the sediment. There is no significant relationship between the calculated portion of buried POC and characteristics like water depth or surface POC concentration. Both properties probably control partly buried POC concentration, together with several other characteristics like origin of organic matter and lithogenic material, macro- and meïo-benthic communities, or sedimentation rates. A variety of environmental properties define the proportion of residual POC relative to total POC flux, explaining the observed spatial variability. Moreover, this suggests that the fraction of residual POC at a given location may change with time. Then, the evolution of POC concentration in a paleo-environmental record cannot be directly interpreted as exported POC flux evolution.

The fossilized POC flux does not really correspond to the buried POC flux deduced from POC concentrations in the upper layer because POC concentrations decrease with depth at most of the studied stations. A 3.5 m long Kullenberg core collected at station B (Mouret et al., unpublished results) showed that POC concentration did not change significantly below 30 cm depth. For deeper station sediment, a steady POC concentration seems to be reached within the length of the sediment cores. Consequently, the fossilized POC fluxes were calculated from POC concentrations measured in the sediment core bottom (Fig. 8). Here again, the fossilized POC flux is a variable proportion of the total POC flux depending on station, ranging from 30% at station F to 5% at station 11. Again, these are maximum percentage. The proportion of fossilized POC flux corresponds to the organic carbon burial efficiency defined by Canfield (1994) or Hedges and Keil (1995). Betts and Holland (1991) and Canfield (1994) showed that burial efficiencies correlated directly with sediment accumulation rates. Values deduced from Table 4 describe a rough linear relation, where the burial efficiency (in %) is 0.46 × the sediment mass accumulation rate (in $mg\,cm^{-2}\,yr^{-1}$). But because the correlation is weak (r^2=0.66, n=6) the fossilized carbon cannot be considered as a direct proxy of exported carbon.

The observed decrease in organic carbon concentrations in the studied sediments is the result of mineralization of POC through early diagenesis processes. Fossilized POC amounts to between 40% (station B) and 80% (station F) of buried POC, meaning that surface POC content is more refractory at deeper stations. Shallow station cores (i.e., stations D, C, and C') contain well-mixed sediment with high concentrations of POC. Here, the refractory POC, the slow-decaying POC, and the fast-decaying POC likely occur together in the anoxic portion of the sediment. Because of mixing, it becomes difficult to estimate the sediment mass accumulation rate from short-living radionuclides at these stations, and therefore the part of residual POC relative to exported POC cannot be estimated. As the exposure time of POC to well-oxygenated bottom water is shorter at these shallow stations than that at deeper stations, POC is supposed to be less degraded (Hartnett et al., 1998; Reimers, 1989), and the residual POC flux may represent here a larger fraction of the exported flux than that at the deeper stations.

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