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Seasonal dynamics of carbon recycling in coastal sediments influenced by rivers: assessing the impact of flood inputs in the Rhône River prodelta

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Abstract

The biogeochemical fate of the particulate organic inputs from the Rhône River was studied on a seasonal basis by measuring sediment oxygen uptake rates in the prodelta, both during normal and flood regimes. On a selected set of 10 stations in the prodelta and nearby continental shelf, in situ and laboratory measurements of sediment oxygen demand were performed in early spring and summer 2007 and late spring and winter 2008. In and ex situ sediment Diffusive Oxygen Uptakes (DOU) did not show any significant differences except for shallowest organic rich stations. DOU rates show highest values concentrated close to the river mouth (approx. 20 $mmolO_2 m^{-2} d^{-1}$) and decrease offshore to values around 4.5 $mmolO_2 m^{-2} d^{-1}$ preferentially in a south west direction, most likely as the result of the preferential transport of the finest riverine material. Total Oxygen Uptake (TOU) obtained from core incubation showed the same spatial pattern with an averaged TOU/DOU ratio of 1.2±0.4.

Over different seasons, spring summer and late fall, benthic mineralization rates presented this same stable spatial pattern.

A flood of the Rhône River occurred in June 2008 and brought up to 30 cm of new soft muddy deposit. Right after this flood, sediment DOU rates close to the river mouth dropped from around 15–20 $mmolO_2 m^{-2} d^{-1}$ to values close to 10 $mmolO_2 m^{-2} d^{-1}$, in response to the deposition near the river outlet of low reactivity organic matter associated to fine material. Six months later, the oxygen distribution had relaxed back to its initial stage: the initial spatial distribution was found again underlining the active microbial degradation rates involved and the role of further deposits. These results highlight the rapid response to flood deposits in prodeltaic areas which may act as a suboxic sediment reactor and shorten the relaxation time.

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1 Introduction

River dominated shelves represent a dynamic interface linking land and ocean biogeochemical cycles of relevant element such as Organic Carbon (OC) (Hedges, 1992; Gattuso et al., 1998; McKee et al., 2004). They are productive areas sustained by high inputs of nutrients and terrestrial material (Dagg et al., 2004), characterized by a tight pelagic-benthic coupling and active benthic mineralization rates (Smith and Hollibaugh, 1993). Indeed, over 50% of all organic carbon burial in the ocean takes place in continental margins (Hedges and Keil, 1995). In addition, it is estimated that up to 70% of the 0.15×10^{15} gC of particulate OC annually discharged from rivers to ocean is oxidized in these areas (Hedges et al., 1997; Burdige, 2005; Galy et al., 2007).

River inputs to the coastal ocean are highly variable over time, shifting from flood and high sediment supply to low-river discharge (Wheatcroft and Borgeld, 2000). This variability causes a non-stationary OC deposition in deltas and prodeltas (Bentley and Nittrouer, 2003; McKee et al., 2004). Post-depositional processes such as physical (winnowing) and biological (bioturbation) reworking can also affect the organic matter reaching the sea floor in these environments (Rabouille et al., 2003). OC oxidation in sediments is coupled to the utilization of terminal electron acceptors: with the highest free energy yield, oxygen is first consumed by aerobic bacteria in the sedimentary column (Froelich et al., 1979). Oxygen distribution in sediments also reflects chemical reactions (oxidation of reduced species). Integrating benthic microbial respiration and reoxidation of anoxic reduced compounds, oxygen consumption by marine sediments is thus a good proxy to estimate benthic metabolism and OC mineralization rates and their variability over time and space in river dominated environments (Rabouille et al., 2003; Glud et al., 2000, 2003; Lansard et al., 2003; Cai et al., 1995).

River flood may modify the sediment mineralization of organic matter by introducing large quantities of terrigeneous organic carbon with various reactivities and favour its preservation in shallow coastal environments (Leithold and Hope, 1999). Tesi et al. (2008) showed evidence of major changes in the biogeochemical composition and

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reactivity of sedimentary organic matter in a flood deposit in the Po River prodelta. Furthermore, the retention capacity of flood inputs in estuaries is variable: some estuaries may retain only 20% of the flood inputs in the innershore region (Lisitsyn, 1995; Sommerfield and Nittrouer, 1999), while other larger systems like the Atchafalaya River may act as efficient traps for flood inputs (Allison et al., 2000).

Since the damming of the Nile, the Rhône River is now the most important river of the Mediterranean Sea both in terms of water and particles discharges (Pont et al., 2002; Copin-Montegut, 1993). Its influence over the continental shelf of the Gulf of Lions has been widely documented (Monaco et al., 1999; De Madron et al., 2000, 2003; Sempere et al., 2000). Recently, Lansard et al. (2009) proposed a first snapshot of the oxygen uptake rates in the continental shelf sediments off the Rhône River mouth and observed a specific pattern with high sediment uptakes rates near the outlet with an exponential gradient offshore.

Yet the evolution of this pattern of organic carbon recycling in sediments during the seasons and under flood conditions is completely unknown. Floods may play a major role as it has been shown that floods may account for as high as 80% of the particles input from the Rhône River to the Mediterranean Sea (Antonelli et al., 2008). It has been proposed using a modelling approach that the Rhône River prodelta acts as a deposit centre for flood inputs (Ulses et al., 2008). Consequently, Rhône River flood events are most likely to modify the recycling of organic matter in the river prodelta and alter the filtering capacity of river particulate inputs.

In this paper, we present results from a seasonal survey of the sediments in the Rhône River prodelta and adjacent shelf. The same stations were visited four times between April 2007 and December 2008, including a Rhône River flood period in June 2008. Transient evolution of the spatial pattern of the sediment oxygen uptake in the prodelta was investigated using in situ and laboratory measurements. As proxies of organic matter quality, OC and Chlorophyll-*a* (Chl-*a*) contents in surface sediments also brought insights on the existing links between flood deposit lability, OC sediment degradation and the transitory processes involved between both. We discuss the effect of

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flood inputs and seasonal changes on the prodelta filtering capacity and the dynamics of oxygen and organic carbon in sediments after flood deposition.

2 Material and methods

2.1 Study area

The Gulf of Lions is a large continental shelf located in the NW Mediterranean Sea. The North Western Mediterranean current flows southwestward along the slope and imposes a general cyclonic circulation. The water column is seasonally stratified, but vertical intense mixing events inducing major nutrient export occur during strong regional winds outbursts (Millot, 1990; de Madron et al., 1999). The Gulf of Lions is a microtidal sea and the moderate wave-energy is swell-dominated. The Rhône River has a drainage basin of 97 800 km^2, a mean water flow of 1700 $m^3 s^{-1}$, and an annual particulate organic carbon discharge of $19.2 \pm 6 \times 10^4$ $tC\,y^{-1}$ (Sempere et al., 2000). The Rhône River is thus the main source of freshwater, nutrients and organics for the Gulf of Lions (Sempere et al., 2000; Pont et al., 2002; De Madron et al., 2000). The hydrological regime of the Rhône River shows strong seasonal contrast with a large difference between low ($<500\,m^3 s^{-1}$) and high ($>3000\,m^3 s^{-1}$) water-discharge (Pont et al., 2002). Large amounts of terrestrial muddy sediments accumulate in the wide prodelta off the Rhône river mouth, extending then the shoreline to 60 m depth (Wright and Friedrichs, 2006). Net sedimentation rates in the prodelta are up to 50 $cm\,yr^{-1}$ at the river mouth (Charmasson et al., 1998) and decrease rapidly offshore on the continental shelf, i.e. 0.2–0.6 $cm\,yr^{-1}$ at 20 km (Miralles et al., 2005).

2.2 Field sampling work and sampling procedures

Sediment samples were collected during four cruises in April 2007, September 2007, June 2008 and December 2008 (Fig. 1). In April 2007, 16 stations were sampled off

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the Rhône river mouth in order to get a better estimate of the benthic mineralization rates in the Rhône prodelta. Key stations were then selected along onshore-offshore transects in water from 20 to 98 m depth. During the three other cruises, these selected stations were investigated again (Fig. 1). The June 2008 cruise took place while the Rhône River was experiencing an annual flood with a peak water discharge rate of 4156 $m^3 s^{-1}$. This flood event occurred after massive precipitations over the Durance drainage basin (French Southern Alps), leading to a flood of this Rhône River tributary with massive erosion of river banks leading to a suspended load of up to 3.7 $g l^{-1}$ (Fig. 2).

At each station in situ microelectrode measurements were performed as described in Rabouille et al., 2003: briefly, 3–4 h deployments were performed at the sediment water interface using an autonomous microprofiling unit which records 5 oxygen microprofiles using Clark micro-electrodes and one resistivity microprofile. Sediment samples were collected with a multicorer MUC 8/100 (Oktopus GmbH) that collect simultaneously eight P.C cores (I.D. 9.5 cm) with a preserved sediment-water interface (60 cm height with around 25 cm of overlying water and 35 cm of sediment). For micro-porosity measurements, cores were subsampled with a 50 ml syringe and sliced at increasing depth intervals: 0.2 cm depth resolution for the first cm and 0.5 cm from 1 to 6 cm deep. Porosity φ was determined from the weight loss upon drying at 60°C until complete dryness (~2weeks) of sediment core segments of known weight and volume. Additional sediment cores with undisturbed surface structure were also collected for solid sediment sampling, cores incubation and microprofiling in the laboratory under in situ conditions. Sediments for organic carbon and Chl-*a* analysis were collected and frozen on board ship immediately after sub-sampling within one hour after core collection. For core incubation and laboratory microprofiling, the cores were stored in a pool supplied by cooled sea water recirculation until they were brought to the shore and placed in a refrigerated box at in situ temperature.

Bottom-water was sampled at 2 m above bottom by a Niskin bottle for determination of temperature and dissolved oxygen (Table 1).

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2.3 Organic carbon content analysis

OC contents were analysed using milled, freeze-dried 0–0.5 cm surface sediments. Organic carbon concentrations were measured on homogeneised, precisely weighed subsamples in an automatic CN – analyser LECO 2000, after in cups acidification with 2N HCl (overnight, at 50°C) in order to remove carbonates prior to the analyses of OC (Cauwet et al., 1990). The precision for OC was 2%.

2.4 Pigment analysis

Surface sediments (0–0.5 cm layer) were rapidly thawed and 100 mg were extracted overnight in 5 ml of acetone at 5°C in the dark. Adjustment was made for sediment water content to obtain a final acetone degree of 90%. The fluorescence of the sediment extracts was measured on a LS 55 spectrofluorimeter (Perkin Elmer Inc., USA) according to the method developed by Neveux and Lantoine (1993). Uncertainty on the Chlorophyll-*a* (Chl-*a*) content was lower than 1%. For each station, the analyses were performed on three cores and in triplicates (i.e. 9 independent extracts). Data are expressed as weight per gram dry sediment.

2.5 Grain size measurement

Sediment granulometry was assessed using a Malvern® Mastersizer 2000 laser microgranulometer. Grain size is given as the d(0.5), which corresponds to the median of the size distribution based on the equivalent spherical volume diameters.

2.6 Microelectrode measurements

The 200 μm resolution O_2 and resistivity in situ profiles were obtained by a benthic microprofiler (Unisense®) equipped with 4–5 O_2 microelectrodes and 1 resistivity sensor. The profiling unit was mounted on an autonomous tripodal frame.

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Ex situ measurements of O_2 microprofiles were performed in a thermostated bath maintained at in situ sampling temperature. Up to 15 steady-state O_2 microprofiles (50–100 μm resolution) were completed within 6 h after sampling. Conservation of overlying water oxygenation was achieved by a soft bubbling system.

Dissolved oxygen concentration was measured by oxygen microelectrodes (Unisense®) provided with a built-in reference and an internal guard cathode (Revsbech, 1989). The O_2 microsensors had tip outer diameters of 50–100 μm, a stirring sensitivity of <1%, a 90% response time <10s, and less than 2% per hour current drift. The electrode signals were recorded in the overlying-water before and after each profile to assess the stability of the measurements. We used a linear calibration for the microelectrodes, between the bottom water oxygen content estimated by Winkler titration (Grasshoff et al., 1983) and the anoxic zone of the sediment.

The location of the sediment-water interface relative to the in situ oxygen profiles was determined from O_2 microprofiles. We used the classical method which consists in assigning the interface location to a break in the oxygen concentration gradient. The observed change of slope is due to the increased diffusion coefficient in the sediment compared to the diffusive boundary layer (DBL) (Jorgensen and Revsbech, 1985; Revsbech, 1989; Sweerts et al., 1989). In some profiles, the slope break was not clearly visible: they rather displayed a steady increase of the slope towards a maximum within the first millimeter below the initial concentration decrease. In these cases, we adopted the position of this maximum gradient as the sediment-water interface. Oxygen penetration depth was determined from the O_2 profile and was assigned to the depth where the microelectrode signal reached the zero current.

Resistivity measurements were carried out with an electrode similar to the one described by Andrews and Bennett (1981). Four thin parallel wires were buried in a matrix of epoxy, with only their tips in electrical contact with seawater. The resistivity sensor has a rectangular section of 10×3mm and is edged at the lower end. Recordings were made at 200 μm as for the oxygen but the pertinent resolution is certainly around 1 mm due to the shape of the sensor (Rabouille et al., 2003; Andrews and Bennett, 1981).

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Voltage outputs were calibrated to resistivity with standard KCl solutions, and the resistivity recordings were converted to inverse formation factor values by the formulation of Berner (1980):

$$F^{-1} = R_{bw}/R_z \quad (1)$$

Where R_{bw} is the average resistivity in the bottom water and R_z is the mean resistivity at given depth z.

Then we calculated a porosity profile by converting F^{-1} values using the empirical Archie's relation:

$$F^{-1} = \varphi^{-m} \quad (2)$$

Where φ is the porosity and m is an experimental factor usually ranging from to 2 to 3. m was determined for each station as corresponding to the best least square fit to the measured porosity profile (through an Microsoft Excel® solver routine).

2.7 Sediment diffusive oxygen fluxes calculations

Sediment oxygen consumption rates were estimated from O_2 microprofiles by two ways. Diffusive oxygen uptake (DOU) was calculated from O_2 concentration gradients at the sediment-water interface by using the 1-D Fick's first law of diffusion: $\mathrm{DOU}=F^{-1}D_{0_{O_2}}\left[\frac{dO_2}{dx}\right]_{x=0}$ where F^{-1} is the inverse of the formation factor at the sediment-water interface, $D_{0_{O_2}}$ is the molecular diffusion coefficient of O_2 ($cm^2 s^{-1}$) at in situ temperature, salinity and hydrostatic pressure and $\left[\frac{dO_2}{dx}\right]_{x=0}$ is the oxygen gradient just below the sediment-water interface (estimated from the profiles).

We also used the numerical model PROFILE (Berg et al., 1998), which calculates the consumption rates with depth by adjusting a calculated oxygen profile to the observed one. It allowed us to determine the location of oxygen production and oxygen consumption layers, the extent of these zones, and the resulting fluxes across the

sediment-water interface. The two boundary conditions used for the calculations correspond to the zero oxygen concentration and flux at the bottom of the oxic zone.

2.8 Sediment core incubation and total oxygen uptake measurements

Immediately after retrieval, 3 sediment cores per station were selected with undisturbed interface and placed in a refrigerated box at in situ temperature back to the laboratory. Once sealed, overlying water was kept homogenised by a rotating floating magnet fixed to the upper core cap. Dark incubations started within 6 h after sampling. Every 2–4 h, 50 ml of the overlying water was sampled and replaced with the same volume of filtered bottom water (Denis et al., 2001; Hulth et al., 1997). We determined the oxygen concentration in the overlying water of each core and the filtered bottom water by Winkler titration (Grasshoff et al., 1983). Sampling intervals and incubation duration were adjusted so that oxygen concentration in the overlying water did not decrease by more than 20–30% of the initial concentration. TOU was calculated from concentration change of oxygen in the overlying water with incubation time, after correction had been made for input of replacement water. This approach allowed the determination of TOU with only a small deviation from the ambient bottom water concentrations in the overlying water.

2.9 Statistical calculation

In order to assess statistical differences between in situ vs. ex situ DOU and Oxygen Penetration Depth (OPD), and given our limited data sets (generally $n<20$), we used the non parametric Mann Whitney test using a 95% confidence level. We assumed that the samples considered were different when $p<0.05$. We statistically tested the seasonal difference between in situ DOU for each station, by using the non parametric Kruskal Wallis test ($\alpha=0.05$) when the station had been sampled more than twice, and the Mann Whitney test when it had been sampled only twice.

3 Results

3.1 Porosity: cores measurements and estimation from F^{-1}

At all stations, porosity decreases gradually with depth from 0.85–0.9 for the top 2 mm to a value ranging between 0.62–0.77 at 6 cm depth (Fig. 3). These profiles show relatively high values of porosity consistent with data reported by Reimers et al. (1992).

The porosity derived from F^{-1} factor through the power law $F^{-1}=\varphi^{-m}$ show similar pattern and is in good agreement with the measured values: as displayed in Fig. 3, the calculated profiles (plain curves) matched the measured porosity profiles (dots). Indeed, in average r^2 is 0.9939 ranging between 0.9795 and 0.9997. m values (Table 1) displayed an average of 2.2±0.4. The observed variations were not correlated to the mean diameter (r^2=0.06, n=28).

Most stations show constant porosity profile with time, except station A located at the river outlet. This station also displays a large change in grain size between April 2007 and June 2008, i.e. normal to flood condition (mean ⌀=6.7–37.4 μm; Table 1).

3.2 Surface sediment carbon content

Organic Carbon (OC) content of surficial sediments in the Rhône river prodelta ranged from 0.99% to 1.99% d.w (Fig. 4). Stations away from the river outlet (D, E, F, H, I, J) displayed an homogeneous and stable organic content of 1.03±0.08% (i.e. a Coefficient of variation C.V of only 7.7%). At all cruises except June 08, stations close to the river outlet showed higher content around 1.5–2%, station A being the more enriched: OC content decreased exponentially with distance from station A i.e. from the river outlet (r^2=0.90 and r^2=0.88 in April and September 2007, respectively; Fig. 4). On the contrary, OC content in June 2008 was homogeneous over all the prodelta: all stations ("off-shore" stations as nearshore ones) presented the same low content of 1.04±0.08%.

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3.3 Surface sediment pigment content

Chlorophyll-*a* (Chl-*a*) content of surficial sediments in the Rhône River prodelta are available for April 2007, September 2007 and June 2008 cruises. Chl-*a* contents displayed an exponential decrease with distance from the river mouth (r^2>0.7178, p<0.01) with highest values located in the prodelta (Fig. 5). Chl-*a* sediment contents were significantly lower in June 2008 than the April and September 2007 values pooled together (test: Mann-Whitney, p<0.05). In April and September, Chl-*a* content were around 5.33±3.28 $\mu g g^{-1}$ d.w. near the river outlet (stations A, B) decreasing to low values about 1.73±0.86 $\mu g g^{-1}$ d.w. offshore. In June 2008, however, during the flood event, the pattern was different with values in stations A and B around 2.71±0.68 $\mu g g^{-1}$ d.w. and lower concentration in shelf sediments with an average of 1.08±0.94 $\mu g g^{-1}$ d.w (Fig. 5).

3.4 Sediment oxygen uptake

In April 2007, the microprofiler was deployed at 16 stations, an extension of the area previously covered (Lansard et al., 2009): 8 and 12 of these stations were resampled, respectively in September 2007 and June 2008. Finally in December 2008, only 6 stations close to the Rhône River mouth were sampled because of meteorological conditions. All oxygen profiles showed decreasing O_2 concentrations through a diffusive boundary layer of about 0.2–2.2 mm above the sediment-water interface (Fig. 6). Below, O_2 concentrations decrease rapidly with steep gradients, depending on the station. The oxygen penetration depth (OPD) into the sediment ranges from 1.6±0.3mm in front of the Rhône River mouth to 12.7±1.7mm about 30 km south-westward (Table 2). There was no statistical difference between in situ and ex situ OPD (p>0.05). Generally OPD increased with distance from the Rhône River mouth. Apart from the June 2008 cruise corresponding to a river flood event, all OPD on the SW transect showed linear increase with distance from station A, i.e. near the river mouth (r^2>0.883). Near the Rhône River mouth (stations A, B, K), OPD were statistically different in June 2008

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compared to the other cruises. The other stations did not display any differences in OPD between cruises.

Positive fluxes of O_2 (from the overlying water into the sediment) were measured in all investigated stations. Total Oxygen Uptake rates measured by cores incubation had average values ranging from $\sim 16 \mathrm{mmol} O_2 \mathrm{m}^{-2} \mathrm{d}^{-1}$ close to the river mouth (stations A and B) to $\sim 3 \mathrm{mmol} O_2 \mathrm{m}^{-2} \mathrm{d}^{-1}$ further offshore in the South-East direction. Table 2 displays DOU/TOU ratios for each station. Generally they were not significantly different from unity except for stations far offshore as J and I, which displayed a value around 2 during some cruises, indicating substantial contribution of non-diffusive processes such as bioturbation (Table 2).

The DOU rates were calculated using both Fick's law at the sediment water interface and the PROFILE software taking $D_S = \frac{D_0}{1+3(1-\phi)}$ (data not shown). Differences between DOU from both calculations (PROFILE and interface gradient) did not exceed 20%, thus confirming the reliability of the estimation. The average in situ Diffusive Oxygen Uptake (DOU) rates ranged from approx. $20 \mathrm{mmol} O_2 \mathrm{m}^{-2} \mathrm{d}^{-1}$ near the Rhône river mouth (stations A, B, K) to approx. $4.5 \mathrm{mmol} O_2 \mathrm{m}^{-2}\ \mathrm{d}^{-1}$ at station on the middle shelf (stations I, J, F, U). DOU rates from cores presented the same distribution pattern with high fluxes at the Rhône river outlet and similar lower values as going offshore. Except at stations A, B, and C, there was no statistical difference between in situ and ex situ values ($p>0.05$; Table 3).

Except for station A and K, O_2 fluxes were not statistically different from one cruise to another (Table 4). They displayed the same spatial pattern with intense consumption near the Rhône river mouth and lower DOUs over the shelf (Fig. 7a). This tendency is clearly displayed when plotting the DOU rates as a function of distance to station A for the April 2007 cruise (Fig. 8). Under normal discharge rate conditions, the negative gradient in sediment oxygen uptake rates was generally smoother in the South West direction than along the other transects (S, S–SE and SE).

This general pattern was observed at every cruise except during the flood event in June 2008 (Fig. 7b). In contrast, the DOU rates obtained in June 2008 were much lower

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in the prodelta and homogeneous over the shelf up to a distance of 10 km from the outlet ($p>0.05$; Fig. 7b). As the SW direction seems to be a preferential trend, plotting the South-West transect for all cruises reveals different gradient over time (Fig. 9). The linear regression applied to the data allows the estimation of the DOU gradients over the prodelta which are similar for all cruises except June 2008 corresponding to the flood.

The PROFILE program on station A was used to determine the location of oxygen consumption in June 2008. It appeared that the consumption was low and spread all over the oxic layer, or located at the bottom of the oxygen profile. On average at station A, the maximum consumption rates were 9×10^{-2} mmolO_2 l^{-1} h^{-1} (Fig. 10) compared to 1.1 ± 0.3 mmolO_2 l^{-1} h^{-1} for normal conditions.

4 Discussion

4.1 Comparison of in situ and ex situ diffusive oxygen uptake rates

When comparing in situ and ex situ oxygen fluxes calculated from the profiles using similar calculation methods, stations A, B, and C, located near the river outlet, presented significant differences between the two techniques. Stations located out of the Rhône River mouth, however, displayed similar DOU rates for both techniques (Table 3). For stations A, B and C, ex situ DOU rates were 30–40% lower than the in situ ones.

Several reasons may explain this difference: exact ship positioning in a high DOU gradient environment, natural variability in sediment porosity, spatial heterogeneity of the sediment at the station scale. All these phenomena should, at some point, be averaged over the seasons investigated, and should not provide a consistent difference between the two techniques. The bias introduced for ex situ measurements by the operator by selecting the profile location or fauna exclusion due to the size of cores (Glud et al., 1998) should even provide larger fluxes for ex situ technique in comparison

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to in situ, which contradicts our observations. Identically, systematic bias such as T and P differences can be ruled out as bottom water T was never below 14°C and depth never exceeded 100 m, the most affected stations being located at the shallowest and warmest sites.

The most affected stations are located at the Rhône River mouth, where the DOU are highest. In these sediments, the thickness of the diffusive boundary layer (DBL) linked to the level of turbulence in the water column influences O_2 fluxes at the sediment water interface by shortening the diffusion path length to the thin oxic sediment layer (Berner, 1980; Lorke et al., 2003; Kelly-Gerreyn et al., 2005; Roy et al., 2002; Brand et al., 2009). For instance, Glud et al. (2007) observed that a decreased oxygen availability, as imposed by a thicker DBL, reduced heterotrophic respiration while increasing aerobic reoxidation of reduced compounds and resulted in an overall decrease of sediment oxygen uptake. Similarly, Jorgensen and Revsbech (1985) showed enhanced sediment respiration rates as a consequence for thinner DBL. As stations A and B display in situ OPD around 2–3 mm and shallower (except during the flood), it is likely that DOU rates measured on cores at these sites were underestimated due to difficulty to mimic in situ DBL thickness with laboratory mixing devices.

4.2 Spatial and temporal distribution of benthic mineralization in the Rhône River prodelta

O_2 uptake rates measured out of the June 2008 flood period display a spatial distribution pattern (Fig. 7a) consistent with the one previously described by Lansard et al. (2009). High sediment oxygen consumption were found in a radius of 8 km from the vicinity of the Rhône river mouth with values from 10 to 20 $mmol O_2 m^{-2} d^{-1}$, depending on the sampling time; these rates decreasing offshore to values around 5 (stations F, I, J). The sediment oxygen uptake rates observed at the outlet of the Rhône River are in the range of values reported in the literature. Morse and Rowe (1999) reported DOU rates decreasing from 50 $mmol O_2 m^{-2} d^{-1}$ near the Mississippi River mouth down to 2 $mmol O_2 m^{-2} d^{-1}$ further on the Gulf of Mexico shelf while Alongi (1995) measured

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fluxes ranging from 18–47 mmolO_2 m^{-2} d^{-1} in the Gulf of Papua influenced by river inputs.

In our study, the distribution pattern over the shelf indicates that the decrease of benthic degradation fluxes is slower to the South-West than towards the South or the Southeast (Fig. 8). This feature is linked to the dispersion of the Rhône River inputs (Naudin et al., 1997; Calmet and Fernandez, 1990) the South West being a preferential direction for deposition of the terrestrial material. The Rhône River deposits concentrate at the most coastal station with high sedimentation rates, terrigeneous $\delta^{13}C$ signature, high OC and phytodetritus contents (indicated by Chl-*a* concentrations, Fig. 5). Although terrestrial material is generally supposed to be more refractory than marine inputs (Epping et al., 2002), this South West transect highlights high microbial degradation activity, related both to the amount of material supplied and to its lability as indicated by high Chl-*a*. The results of this paper in agreement with previous literature (Aloisi et al., 1982; De Madron et al., 2000; Radakovitch et al., 1999b; Lansard et al., 2009) indicate that the Rhône River inputs are mainly deposited and processed in a restricted area corresponding to a radius of 8 km off station A.

Our study indicates that under normal discharge rates, spatial pattern of OC oxidation in the prodelta is stable seasonally: a similar distribution of DOU in the sediments was observed in spring, late summer or fall.

Temporal variations of benthic mineralisation in the Rhône River prodelta seem to result directly from extreme deposition events linked to flood conditions (June 2008). This annual flood delivered up to 3.5×10^6 tons of sediment in a 10 days period. This corresponds to $\sim80\times10^3$ tons of C and an average flood deposit of 30 cm, as recorded at a station located at 45 m depth (Fig. 11). Consistently with local hydrodynamics features, the Rhône River material settled near the river mouth (as much as 60 cm deposit at the nearest station) mainly in a south-westward direction (SW: 30–40 cm vs. SE: 13 cm) (Millot, 1990). Ulses et al. (2008) used a model coupling hydrodynamics and sediment transport in the Gulf of Lions for the flood of December 2003 and showed that the riverine material is deposited in the prodelta and mainly in front of the river

mouth (20 cm deposit). This flood is comparable to the June 2008 event: the water discharge rate was higher (up to 9346 $m^3 s^{-1}$) but the total sediment discharge was similar (~4 Mt). Rapid and efficient sedimentation of the riverine material was also observed after the Po River flood in 2000 (Miserocchi et al., 2007). The Rhône River prodelta is thus likely to act as an OC accumulation centre for flood material. This idea is consistent with the high sedimentation rates between 48 to 10 $cm y^{-1}$ observed in the area (Radakovitch et al., 1999a; Charmasson et al., 1998; Miralles et al., 2005) and the spatial distribution Pu isotopes, a tracer of river particles in sediments (Lansard et al., 2007).

The June 2008 flood delivered large quantities of organic matter (OM) that settled down in the prodelta and induced a sudden change in biogeochemical conditions in the sediment. Oxygen fluxes decreased by 20–30% at all stations close to the outlet of the Rhône River (Fig. 7) while deeper oxygen penetration depth were observed a few days after the flood deposit. This is in agreement with a study of the Po River flood in 2000 (Dell'Anno et al., 2008) who observed a decrease of OM degradation rates in coastal sediments from the North Adriatic. Similarly, a drop in benthic community respiration was observed after a flood in south-eastern Australian rivers (Rees et al., 2005) and in the Australian subtropical Brunswick estuary (Eyre et al., 2006). Authors argued that the flood scoured the sediment, leaving a poor carbon content layer to be degraded. In our study, the flood in June 2008 did not erode the sediment as evidenced by the presence of an ochre mud below the flood deposit (Fig. 11). Alternatively, the flood brought a low OC content layer, poor in phytodetritus and labile organic matter which resulted in a decrease of OM mineralization rate. Indeed, surface sediments of stations A, B, K, L, C located near the river mouth presented lower OC contents in June 2008 compared to the "non-flood" cruises (1.1±0.1% vs. 1.5±0.2%) and were principally impoverished in bio-available compounds (4 vs. 7 $mg g^{-1}$ d.w.) and Chl-*a* (3 vs. 10 $\mu g g^{-1}$ d.w.). The Suspended Particulate Matter (SPM) of the Rhône River during the June 2008 flood event had a low OC content (0.8%) with depleted $\Delta^{14}C$ and enriched $\delta^{13}C$ signatures ($\Delta^{14}C = -500‰$, $\delta^{13}C = -25.8‰$), compared to the normal

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hydrological regimes where POC content in the river is 3.5%, with $\Delta^{14}C \sim 100‰$ and $\delta^{13}C \sim -27‰$ signatures (Cathalot et al., 2009). Linked to a Western Alps related flood which eroded river banks and cultivated land, the flood has certainly brought large quantities of soil carbon as evidenced by Tesi et al. (2008) at the Po River outlet in October 2000. The low $\Delta^{14}C$ signal and slightly enriched $\delta^{13}C$ values indicate a mixture of old soil-derived OC, with minor contribution of vascular plants and riverine and estuarine phytoplankton, as indicated by the low Chl-*a* content observed in the flood deposit. Mean diameter of surface sediments at the river outlet (station A and in lower extent station K) dropped from 37.40 to 6 μm shifting from silt to clay like sediments (cf. Table 1) in agreement with the soil origin of the particles. An important part of the organic material from the flood may be associated to clay and thus protected from bacterial degradation (Mayer, 1994; Keil et al., 1994) which could reduce mineralisation of organic matter in the sediments after this type of flood.

Important issues are the dynamics and pathways involved in the relaxation of the sediment system linked to mineralisation. The heavy loaded June 2008 flood obviously generated a transient state in the sediment compared to April and September 2007 distributions. Dell'Anno et al. (2008) noticed that after the immediate decrease consecutive to the deposition of flood material, sediment oxygen uptake rates rose up again, as a consequence of the system relaxation. The return to stationary conditions results from a combination of all biogeochemical processes taking place in the sedimentary column: a new interface is forming, all chemical species are diffusing, marine bacteria are colonizing the new sediment and consuming the organic carbon (Deflandre et al., 2002; Mucci et al., 2003; Sundby, 2006). New sedimentation of river particles can also occur as in December 2008 when a new layer rich in organic carbon was deposited (Fig. 11). Erosion of the 30 cm soft deposit in the prodelta is certainly limited since the deposited layer, sampled 2.7 km south from the Rhône River mouth, remains identical until at least October 2008 (Fig. 11): slight compaction (from 30 cm thickness to ~25 cm) is visible with no significant organic carbon decrease. However, in December only 18 cm of this soft mud from the June 2008 flood remains and a new deposit is

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visible mainly due to further November flood, which brought organic-rich material (6% OC).

Six months after the flood event, oxygen fluxes in the prodelta had increased and reached back their values before the flood. At the same time, the Southwest gradient of oxygen consumption was re-established (Fig. 9). Oxygen consumption in station A sediment during the flood was around 9×10^{-2} mmolO_2 l^{-1} h^{-1} (Fig. 10). Considering a mean oxygen concentration among the sediment in the new deposit of 300 μmol l^{-1}, it would only take 3.3 h for the whole oxygen trapped in porewaters during mud deposition to be consumed, indicating that consumption of oxygen at the observed rates can significantly contribute to the relaxation of the system. Redistribution of reactive chemical species associated with reduction and oxidation participates to the oxygen consumption pattern in the sediment column (Hyacinthe et al., 2001). Deflandre et al. (2002) observed drastic changes in reactive species distribution in a flood deposit: Mn and Fe oxides brought by the new deposit and those previously present were reduced. Although the Fe(II) was mostly trapped at the former sediment interface by precipitation, the reduced Mn migrated towards the new interface where it was re-oxidized by oxygen. A calculation of diffusion timescale as a mechanism of relaxation (i.e. migration through the 30 cm flood deposit) leads to $\tau=\frac{L^2}{2D_s}\approx\frac{30^2}{10^{-5}}\approx1040$ days approximately 2.8 years. In addition to migration, the reduction of the iron and manganese oxides contained within the flood deposit may also be a major controlling factor in the oxygen distribution inside this newly settled sediment. Thus, the re-establishment of oxygen profile in the sediment after the June 2008 flood may imply the building of the redox front inside the deposit, the migration of the former one toward the new water-sediment interface and involve reactive oxidation processes with short kinetics (Hunter et al., 1998).

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5 Conclusions

This paper describes the seasonal variability of organic matter mineralization in sediments from the Rhône River prodelta and Gulf of Lions adjacent shelf using oxygen demand as a proxy.

The results indicate that the observed pattern of decreasing oxygen demand with distance from the river mouth is persistent over seasons under "normal discharge conditions" i.e. out of the flood periods. River organic inputs are concentrated and largely mineralized in a zone located around 8 km from the river outlet. This large mineralization is linked to substantial inputs of reactive terrestrial organic matter indicated by the presence of Chl-*a* at the river outlet.

During major flood deposition (average of 30 cm), the oxygen demand in the prodelta decreases by 20–30%, whereas the shelf is not affected. For the flood encountered in June 2008, a realistic scenario is the deposition of a large quantity of low reactivity material originating from soils in the drainage basin near the outlet of the Rhône River. Transient processes are involved after a flood deposit: bacterial respiration, chemical species migration and reduction and oxidation cycles, deposition of new organic material from the river, which create a rapid relaxation of the oxygen distribution towards its initial state (<6 months). With high porosity and large shear stress values, the flood deposit may act as a suboxic sediment reactor (Aller, 1998) dominated by reactive redox processes. The short kinetics involved make the coastal sediments off the Rhône River mouth acting as a real deposit and degradation centres for flood deposits.

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Table 1. Seasonal variation of Rhône River prodelta bottom water and sediment properties. *m* coefficient from Archie's law used for porosity assessment and mean sediment grain size diameter (μm) are detailed for each station.

Stations	Lat. (° N)	Long. (° N)	Depth (m)	Distance(km)	Cruise	T_{bw} (°C)	$[O_2]_{bw}$ (μM)	*m* coeff	Meandiameter	%Corg in surficial sediment
A	43°18′47″	4°51′4″	24	1.9	Apr-07	14.9	259	2.74	37.40	1.99
					Sep-07	17.7	244	1.99	–	1.40
					Jun-08	16.8	238	2.17	6.74	1.13
					Dec-08	14.8	237	1.97	–	–
B	43°18′14″	4°50′4″	54	3.0	Apr-07	14.6	249	2.42	14.83	1.61
					Sep-07	14.5	214	2.42	–	1.37
					Jun-08	14.0	223	2.45	23.87	1.75
					Dec-08	14.7	234	2.64	–	–
C	43°16′17″	4°46′33″	76	8.6	Apr-07	14.5	243	2.29	11.38	1.25
					Jun-08	14.7	239	1.80	14.51	1.16
					Dec-08	14.7	235	2.40	–	–
D	43°14′54″	4°43′46″	74	13.0	Apr-07	14.3	244	1.43	10.45	1.05
					Sep-07	15	217	1.46	–	0.99
					Jun-08	14.0	226	2.31	12.10	1.00
					Dec-08	14.8	237		–	–
E	43°13′12″	4°41′54″	75	17.0	Apr-07	14.2	245	2.09	9.43	
					Jun-08	15.6	245	2.18	15.02	1.07
F	43°10′1″	4°41′59″	78	21.6	Apr-07	14.2	257	2.55	9.15	1.04
					Jun-08	14.7	242		–	1.03
U	43°5′2″	4°35′58″	90	33.8	Jun-08	13.8	231	2.58	14.27	0.82
G	43°18′30″	4°47′17″	47	5.2	Apr-07	14.8	249	2.33	17.38	–
H	43°15′53″	4°49′10″	86	7.5	Apr-07	14.5	236	2.28	9.99	1.17
					Sep-07	14.9	202	1.35	–	1.00
					Jun-08	14.0	245	2.71	14.15	1.11
I	43°16′0″	4°53′1″	89	7.7	Apr-07	15.1	231	2.56	10.70	1.03
					Jun-08	15.9	238	2.64	16.26	1.12
J	43°16′7″	4°58′6″	86	12.1	Apr-07	14.1	243	2.42	11.59	0.99
					Jun-08	14.0	227	2.36	14.27	1.01
K	43°18′7″	4°51′29″	62	3.3	Apr-07	14.6	249	2.21	17.49	1.79
					Sep-07	18.2	241	2.05	–	1.39
					Jun-08	16.8	240	2.01	11.98	1.02
					Dec-08	14.7	235	2.65	–	–
L	43°18′24″	4°52′59″	62	4.0	Apr-07	14.3	247	2.85	13.56	1.51
					Sep-07	18.0	238	2.03	–	1.26
					Jun-08	16.7	229	3.02	9.10	1.06
					Dec-08	15.0	233	1.95	–	–
M	43°9′59″	4°44′4″	91	20.3	Apr-07	14.1	241	2.42	9.89	–
N	43°17′33″	4°47′59″	67	5.5	Apr-07	14.5	253	1.79	14.01	1.43
					Sep-07	14.5	217	1.75	–	1.20
					Jun-08	16.3	240	2.22	10.65	1.00
O	43°17′0″	4°50′6″	79	5.2	Apr-07	14.4	251	1.94	11.06	1.20
R2	43°14′30″	4°53′4″	98	10.3	Apr-07	14.1	242	2.40	9.55	–

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Table 2. Temporal variation of Oxygen Uptake Rates in the sediments of the Rhône River prodelta (means ±SD). OPD stands for oxygen penetration depth; DOU for Diffusive oxygen uptake and TOU for total oxygen uptake.

Stations	Cruise	n=number of replicated O_2 profiles		OPD (mm)		DOU ($mmolO_2 m^{-2} d^{-1}$)				TOU ($mmolO_2 m^{-2} d^{-1}$)	TOU/DOU
		in situ	ex situ	in situ	ex situ	in situ	C.V (%)	ex situ	C.V (%)		
A	Apr-07	4	5	1.4±0.2	2.0±0.3	21.5±3.9	18%	14.4±2.1	15%	15.6±5.0	1.1±0.5
	Sep-07	5	–	1.7±0.1	–	15.3±1.5	10%	–		–	–
	Jun-08	5	7	5.8±0.8	3.5±0.4	9.2±3.1	34%	9.4±1.6	17%	9.8±1.4	1.0±0.3
	Dec-08	4	8	1.6±0.3	2.6±0.2	16.6±2.9	17%	9.3±1.2	13%	11.9±1.5	1.3±0.3
B	Apr-07	4	6	2.2±0.3	2.5±0.5	15.7±2.1	14%	12.1±2.4	20%	15.9±3.6	1.3±0.4
	Sep-07	5	–	2.1±0.3	–	14.7±5.3	36%	–		–	–
	Jun-08	5	11	3.3±0.6	2.8±0.2	10.6±2.8	26%	9.9±0.7	7%	16.5±1.4	1.7±0.2
	Dec-08	5	10	1.8±0.4	3.1±0.1	17.5±7.6	44%	8.5±1.1	13%	10.8±3.0	1.3±0.4
C	Apr-07	4	7	4.7±1.5	4.2±0.3	10.3±3.2	31%	7.6±1.2	15%	7.8±0.6	1.0±0.2
	Jun-08	5	6	3.4±0.7	3.4±0.7	9.3±3.3	36%	7.2±2.5	35%	10.0±1.3	1.4±0.5
	Dec-08	5	9	5.4±0.8	6.1±0.4	6.8±2.8	40%	5.0±0.3	5%	4.4±0.4	0.9±0.1
D	Apr-07	4	–	6.4±1.3	–	6.3±3.1	49%	–		–	–
	Sep-07	5	–	8.2±1.2	–	4.5±0.3	6%	–		–	–
	Jun-08	5	12	5.5±0.4	4.9±0.7	8.0±3.7	47%	6.0±1.0	17%	6.0±1.0	1.0±0.3
	Dec-08	–	12	–	8.4±1.1	–		4.6±0.9		3.2–1.5	0.7–−0.7
E	Apr-07	4	–	5.2±0.7	–	8.4±1.7	20%	–		–	–
	Jun-08	5	–	4.3±0.8	–	8.5±1.8	21%	–		–	–
F	Apr-07	4	8	9.7±2.1	7.8±1.1	5.3±0.7	12%	5.3±0.7	13%	7.0±2.0	1.3±0.4
	Jun-08	5	12	–	6.9±1.2	–		4.7±1.1	23%	5.6±0.3	1.2±0.3
U	Jun-08	5	–	12.7±1.7	–	4.8±1.7	35%	–		–	–
G	Apr-07	4	–	3.6±0.2	–	9.7±2.2	22%	–		–	–
H	Apr-07	4	–	4.8±0.9	–	7.2±0.9	13%	–		–	–
	Sep-07	5	–	6.5±0.9	–	5.1±2.2	43%	–		–	–
	Jun-08	5	10	3.0±0.6	4.8±0.5	7.6±1.1	15%	6.8±1.4	21%	11.9±6.1	1.8±0.7
I	Apr-07	4	6	6.7±0.3	4.3±0.7	4.6±0.8	18%	6.3±1.1	18%	10.1±0.9	1.6±0.3
	Jun-08	5	9	5.6±2.6	4.7±0.3	8.7±4.9	56%	7.7±1.6	21%	7.7±2.4	1.0±0.5
J	Apr-07	4	3	7.5±2.2	8.7±0.7	7.2±3.3	46%	4.4±0.8	19%	9.6±2.0	2.2±0.4
	Jun-08	5	6	8.3±0.3	7.9±1.4	6.2±2.6	42%	4.9±0.5	10%	4.4±1.0	0.9±0.3
K	Apr-07	4	8	2.6±0.7	2.8±0.3	10.8±2.2	21%	11.0±2.3	21%	10.2±2.2	0.9±0.4
	Sep-07	5	–	3.2±0.6	–	19.9±2.1	10%	–		–	–
	Jun-08	5	7	6.0±1.1	–	8.8±3.9	44%	–		–	–
	Dec-08	5	7	2.2±0.7	3.0±0.2	12.5±5.5	44%	8.6±0.7	8%	6.1±2.8	0.7±0.5
L	Apr-07	3	5	4.9±2.1	3.5±0.3	7.0±3.9	55%	7.2±0.6	8%	11.8±9.8	1.6±0.9
	Sep-07	5	–	3.0±0.8	–	9.9±2.6	26%	–		–	–
	Jun-08	5	–	3.4±0.8	–	11.3±4.5	40%	–		–	–
	Dec-08	5	10	4.0±1.1	4.3±0.4	8.9±6.1	68%	6.0±1.2	20%	2.3±0.2	0.4±0.3
M	Apr-07	4	–	9.4±2.7	–	6.9±3.5	50%	–		–	–
N	Apr-07	4	5	3.3±0.6	3.1±0.4	9.5±1.2	12%	10.1±1.2	12%	11.4±2.6	1.1±0.4
	Sep-07	5	–	4.9±1.1	–	6.6±0.9	14%	–		–	–
	Jun-08	5	–	3.8±0.6	–	9.2±1.9	20%	–		–	–
O	Apr-07	4	–	4.7±0.3	–	8.1±0.9	11%	–		–	–
R2	Apr-07	4	–	7.1±1.8	–	7.0±3.4	49%	–		–	–

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Table 3. Comparison between in situ and ex situ DOU rates Results of non-parametric statistical tests (Mann-Whitney when degrees of freedom=1 and Kruskal Wallis when ≥2). Bold indicate significant differences.

Stations	In situ – ex situ DOU comparison *p*	Degree of freedom
A	**0.0001**	5
B	**0.0001**	5
C	**0.0005**	5
D	0.8961	1
E	–	–
F	0.2567	3
H	>0.05	1
I	**0.0430**	3
J	0.3608	3
K	0.08875*	3
L	0.3600	3
N	0.2780	1

* significant for threshold α=0.1.

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Table 4. Comparison of in situ DOU rates between cruises Results of non-parametric statistical tests (Mann-Whitney when degrees of freedom=1 and Kruskal Wallis when ≥2). Bold indicate significant differences.

Stations	In situ DOU: comparison over cruises p	Degree of freedom
A	**0.0042**	3
B	0.2035	3
C	0.2241	2
D	0.2268	2
E	0.5480	1
F	0.2780	1
H	0.1661	2
I	0.0950	1
J	0.4520	1
K	**0.0420**	3
L	0.1131	3
N	0.06687*	2

* significant for threshold α=0.1.

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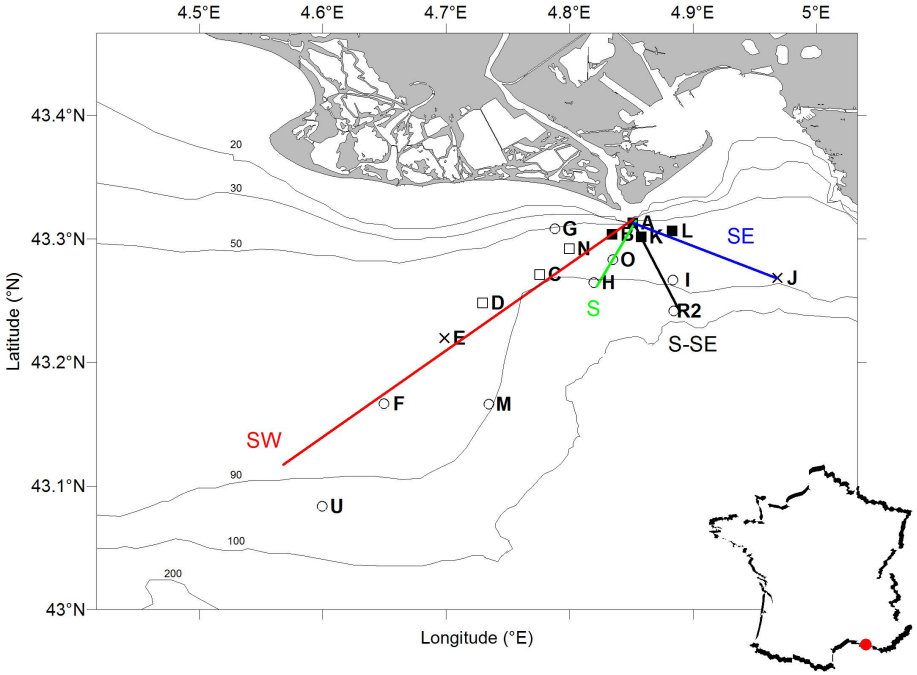

Fig. 1. Map of the Rhône delta indicating the locations of sampling stations. Black squares indicate stations sampled the four cruises. Empty squares indicate stations sampled three times. Black crosses indicate stations sampled twice. Empty circles indicate stations sampled once (April 2007).

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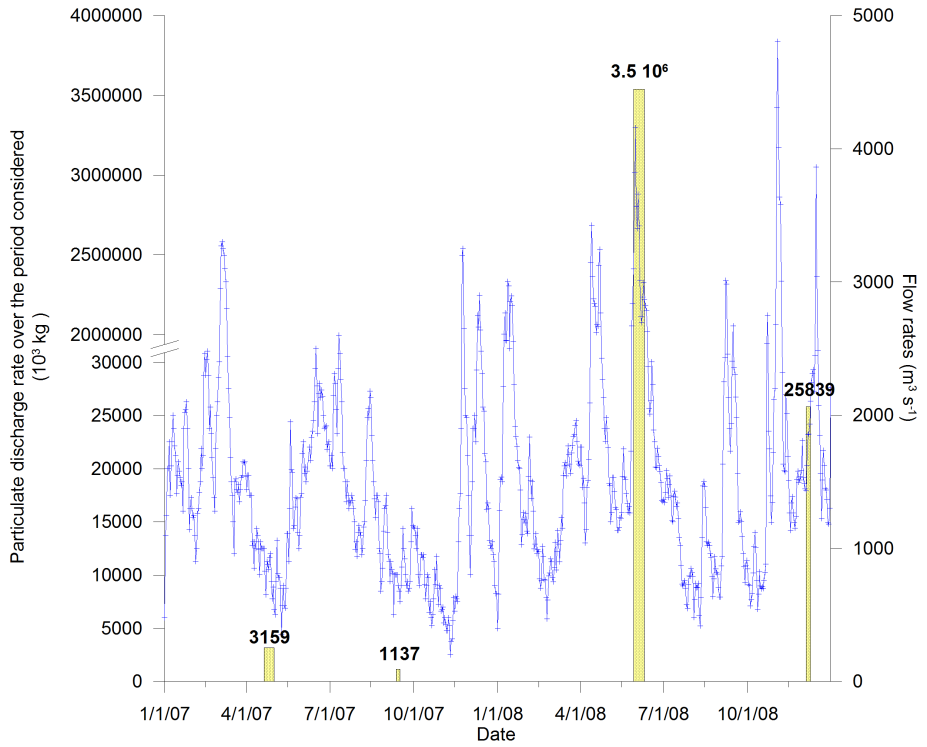

Fig. 2. Mean daily flow and particulate discharge rates of the Rhône River. The integrated SPM amount delivered during the sampling cruises period are indicated in yellow.

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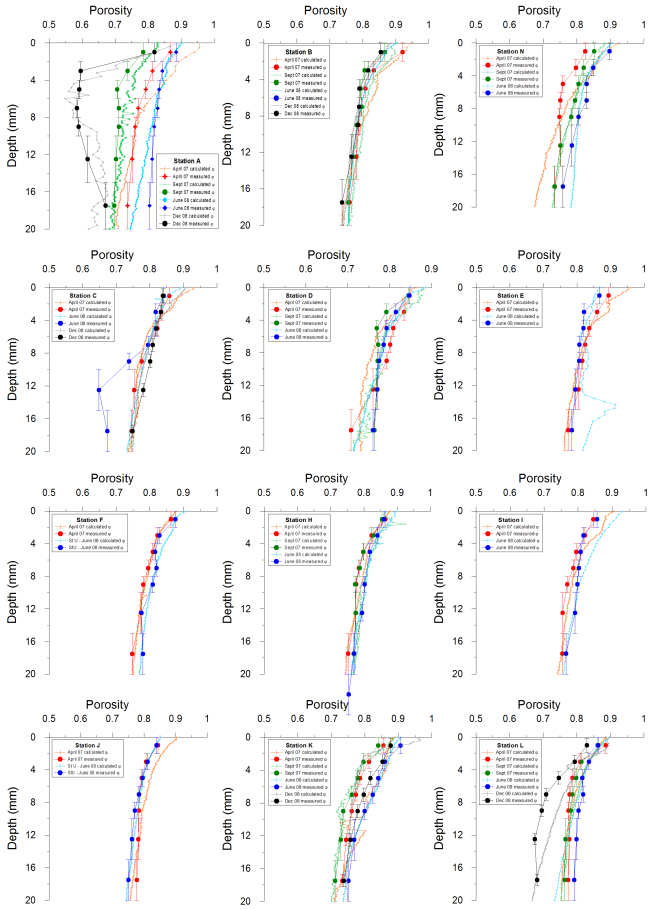

Fig. 3. Porosity profiles for all stations during all cruises. Data points indicate measured values while thin curves represent the calculation based on resistivity measurements and Archie's law (see text for details).

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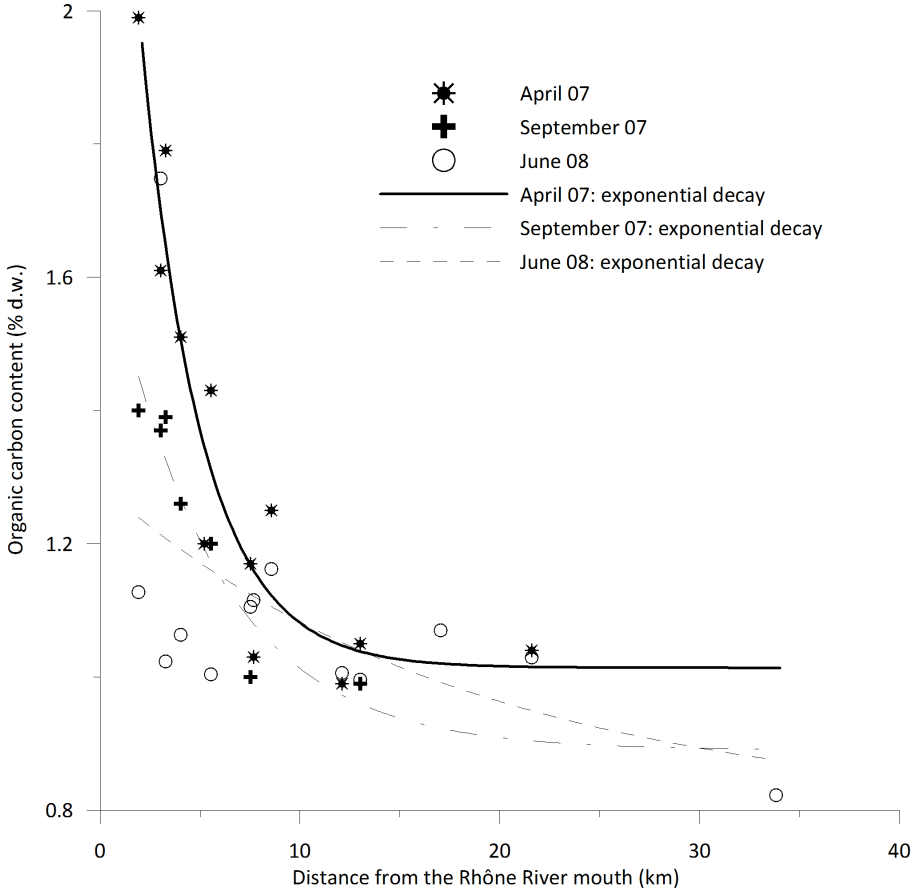

Fig. 4. Organic carbon (OC) content in surficial sediments as a function of distance from the river outlet for April 2007 (black stars), September 2008 (black crosses) and June 2008 cruises (empty circles). Exponential decays of OC with distance in April and September 2007 were significant (r^2=0.90, and r^2=0.88, respectively) but not in June 2008.

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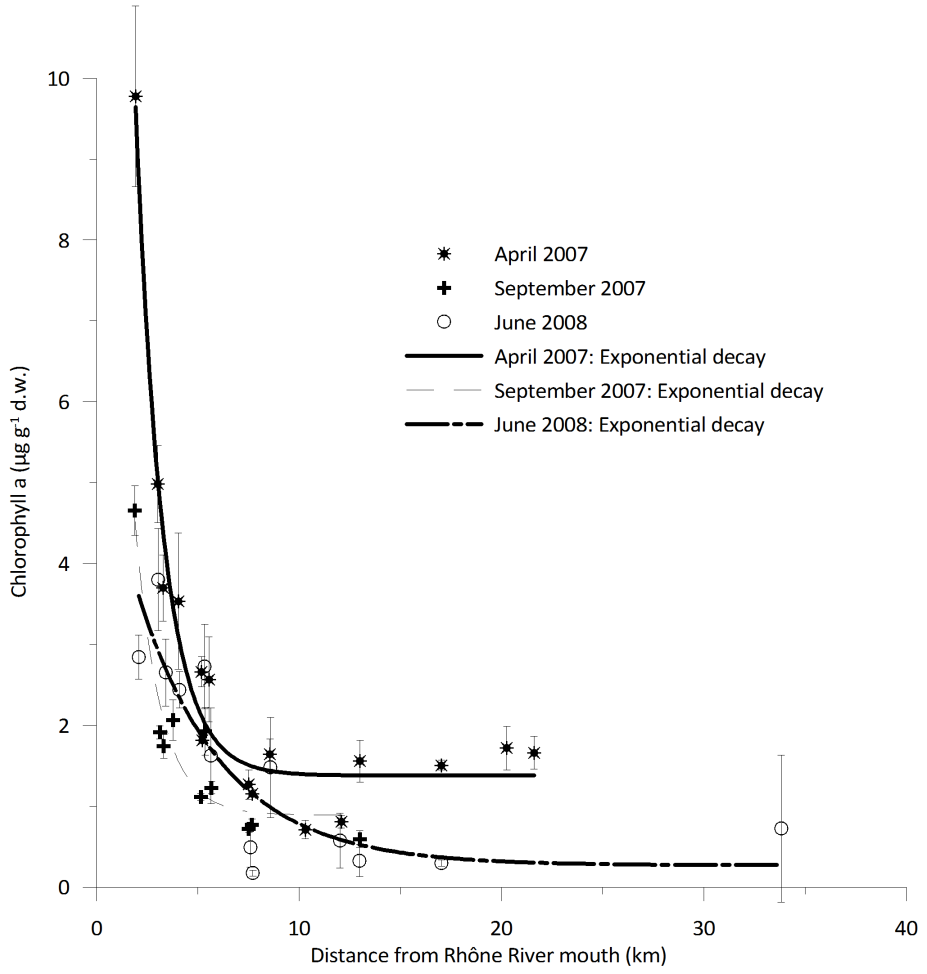

Fig. 5. Surface sediments Chl-*a* contents as a function of distance from the river outlet: black stars – April 2007, black crosses – September 2007 and empty circles – June 2008.

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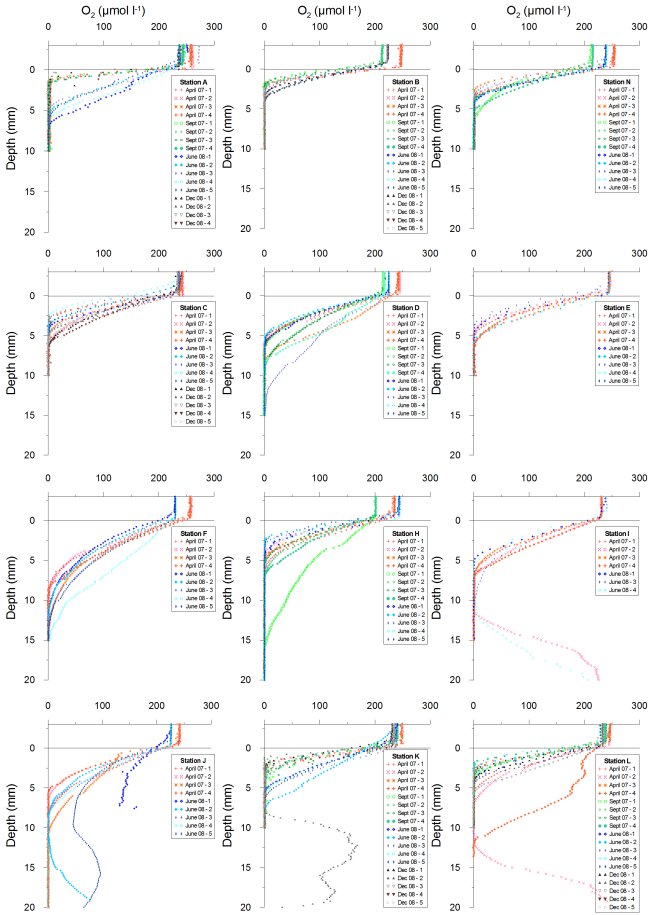

Fig. 6. In situ Oxygen microprofiles in the sediment at all station investigated for April 2007 (red), September 2007 (green), June 2008 (blue) and December 2008 (brown).

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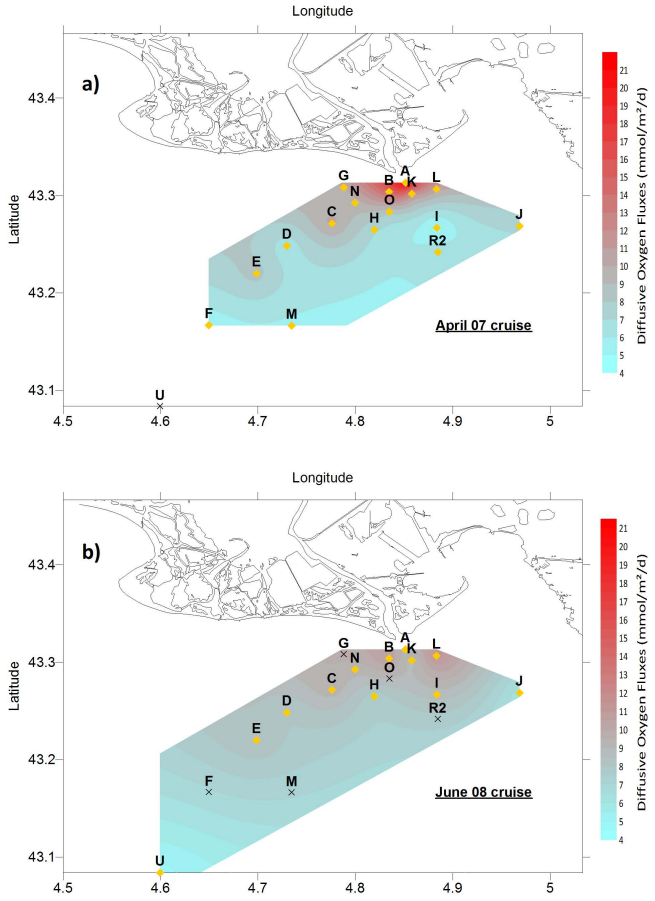

Fig. 7. Spatial distribution of Diffusive Oxygen Uptakes Rates in sediments during April 2007 "normal condition" **(a)** and June 2008 "flood condition" **(b)** × indicate stations which were not sampled during his cruise.

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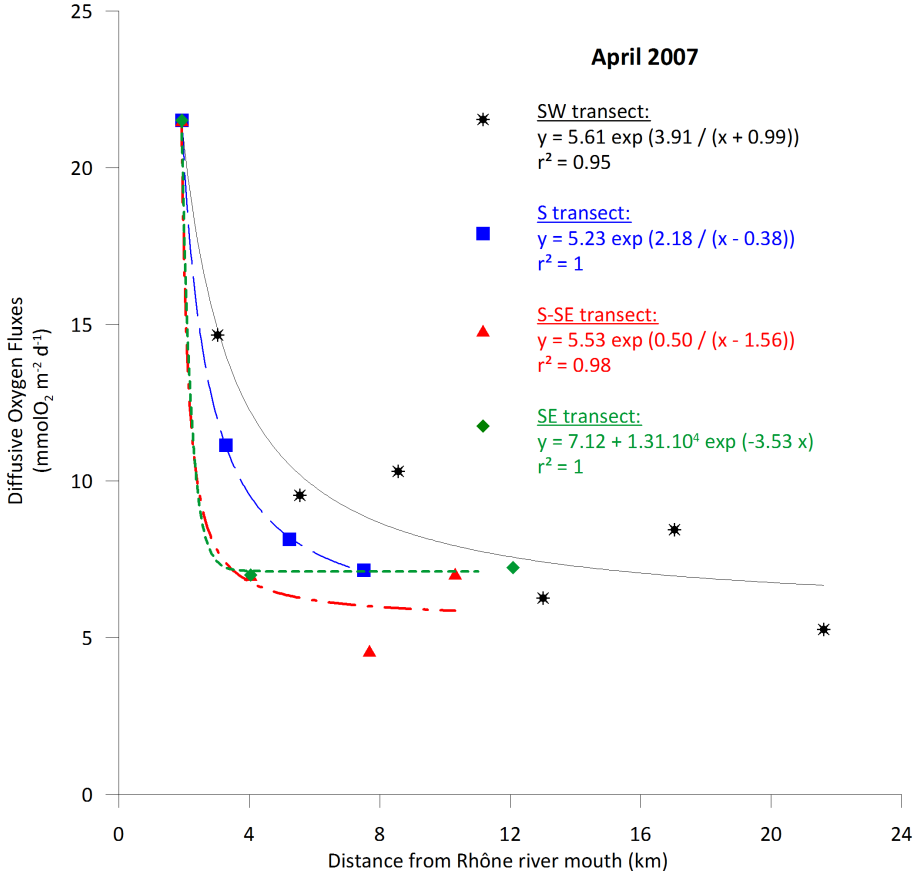

Fig. 8. Decrease of DOU rates with distance from station A in April 2007 for different transects: black crosses – South West SW (stations A, B, N, C, D, E, F, U – black plain line), blue square – South S (stations A, K, O, H – blue dashed line), green diamond – South-South-East S-SE (stations A, L, I, R2 – red dotted-dashed line) and red triangle – South-East SE (stations A, L, J – green dotted line).

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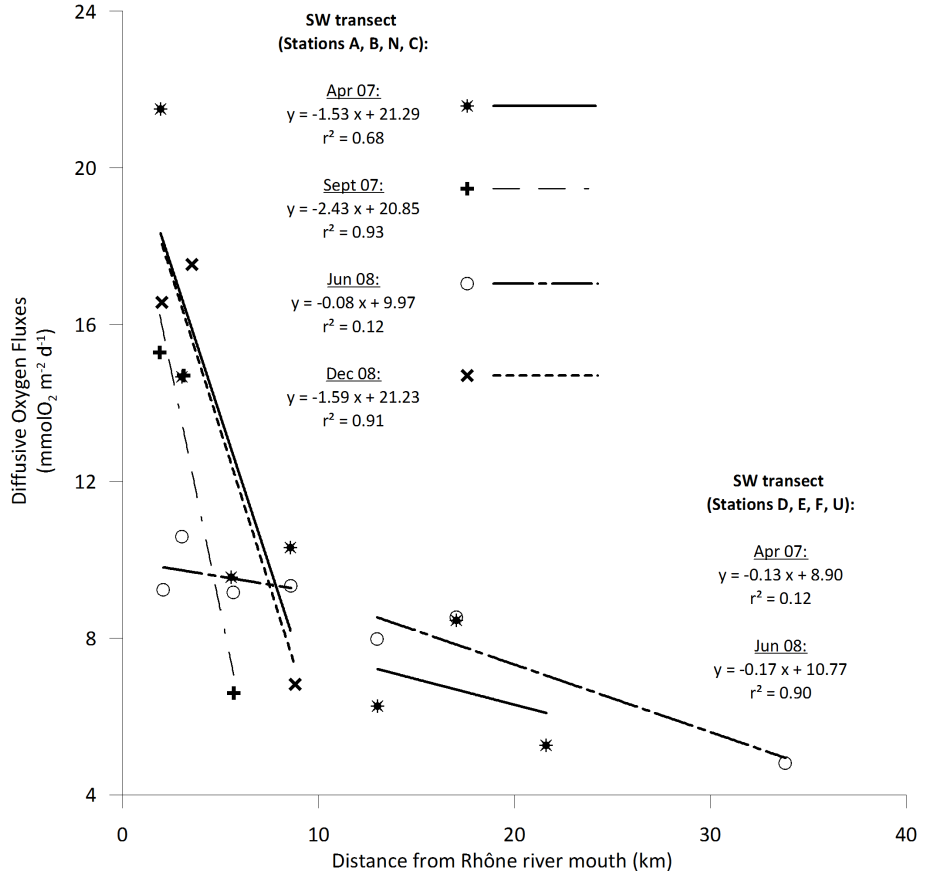

Fig. 9. Seasonal variations of South West DOU gradient. Stations close to the river outlet (A, B, N, C – left part of the chart) were separated from stations offshore (D, E, F, U – right part of the chart).

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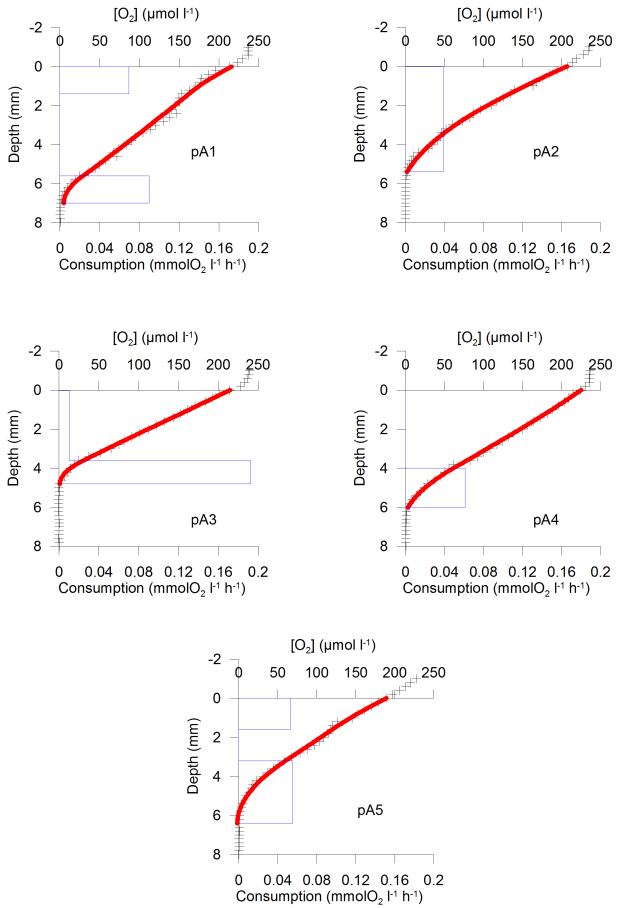

Fig. 10. Consumption pattern in the sediment at station A in June 2008 for different profiles obtained during the same deployment.

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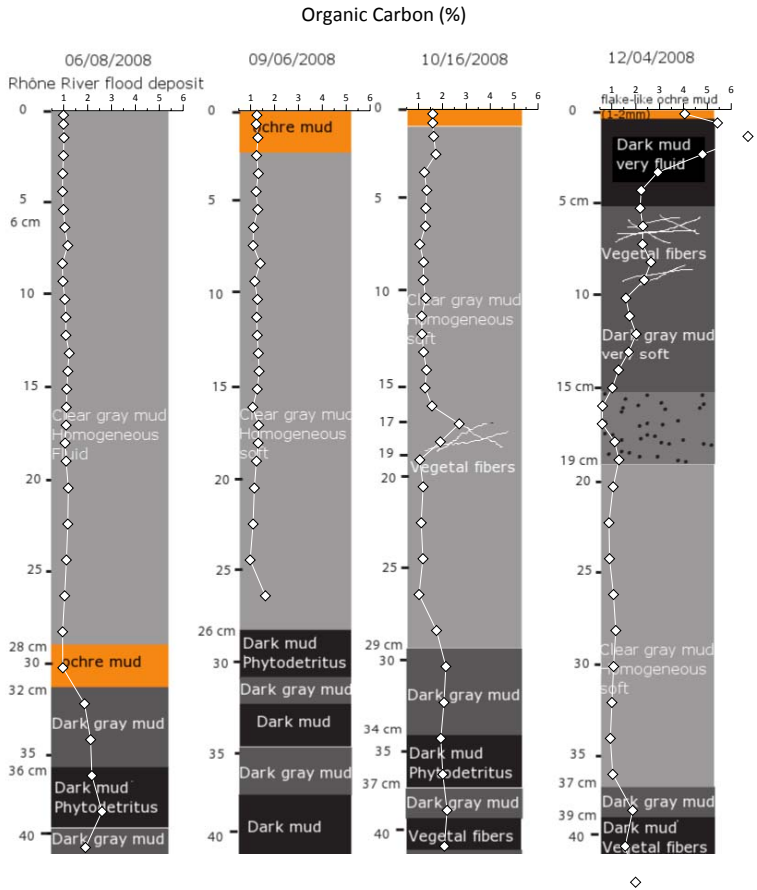

Fig. 11. The evolution of the flood deposit of June 2008 at a depth of 45 m, 2.7 km of the river mouth (visual observations a few months after the flood event).

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