Devenir et impact des apports fluviaux sur les marges continentales : importance biogéochimique et environnementale du recyclage dans les sédiments du prodelta du Rhône

Cécile Cathalot

To cite this version:

Cécile Cathalot. Devenir et impact des apports fluviaux sur les marges continentales : importance biogéochimique et environnementale du recyclage dans les sédiments du prodelta du Rhône. Hydrologie. Université Pierre et Marie Curie - Paris VI, 2008. Français. <NNT : 2009PA066378>. <tel-00813147>

HAL Id: tel-00813147

https://tel.archives-ouvertes.fr/tel-00813147

Submitted on 15 Apr 2013

THESE DE DOCTORAT DE
L'UNIVERSITE PIERRE ET MARIE CURIE

Spécialité

Science de l'Environnement d'Ille de France
(ED 129)

Présentée par

Melle CATHALOT Cécile

Pour obtenir le grade de

DOCTEUR de l'UNIVERSITÉ PIERRE ET MARIE CURIE

Devenir et impact des apports fluviaux sur les marges continentales : importance biogéochimique et environnementale du recyclage dans les sédiments du prodelta du Rhône

soutenue le 8 Décembre 2008

devant le jury composé de :

M. **SALIOT Alain**, Président du Jury

M. **RABOUILLE Christophe**, Directeur de thèse

M. **GRENZ Christian**, Rapporteur
M. **RADAKOVITCH Olivier**, Rapporteur

M. **REGNIER Pierre**, Examinateur
M. **MISEROCCHI Stefano**, Examinateur
M. **SEMPERE Richard**, Examinateur

THESE DE DOCTORAT DE L'UNIVERSITE PIERRE ET MARIE CURIE

Spécialité
Science de l'Environnement d'Ille de France (ED 129)

Présentée par
Melle CATHALOT Cécile

Pour obtenir le grade de
DOCTEUR de l'UNIVERSITÉ PIERRE ET MARIE CURIE

Devenir et impact des apports fluviaux sur les marges continentales : importance biogéochimique et environnementale du recyclage dans les sédiments du prodelta du Rhône

soutenue le 8 Décembre 2008, devant le jury composé de :

M. SALIOT Alain, Président du Jury

M. RABOUILLE Christophe, Directeur de thèse

M. GRENZ Christian, Rapporteur
M. RADAKOVITCH Olivier, Rapporteur

M. REGNIER Pierre, Examinateur
M. MISEROCCHI Stefano, Examinateur
M. SEMPERE Richard, Examinateur

REMERCIEMENTS

Mes premiers remerciements vont à Christophe Rabouille qui a supervisé ce travail de thèse. Bien au-delà de l'encadrement scientifique et pédagogique de qualité qu'il m'a apporté, je tiens à le remercier pour son soutien permanent, sa disponibilité et son écoute chaleureuse qui m'ont permis de mener à bien ce travail de thèse mais également de m'épanouir intellectuellement et personnellement et de construire un bout de la personne que je suis aujourd'hui. Merci pour ces discussions et débat de tout ordre partagés au retour de cantine ou de mission (quand je ne dormais pas dans la voiture! Si.. si.. il doit bien y en avoir…).Merci pour ta gentillesse, ton ouverture et ton amitié qui m'ont porté pendant les moments, agréables et plus difficiles, que j'ai traversé pendant ces trois ans. L'avenir est imprévisible mais j'espère que d'autres occasions de poursuivre cette aventure professionnelle et humaine se présenteront.

Je ne peux continuer ces remerciements sans penser à Bruno Bombled, qui m'a offert son amitié et son soutien pendant ces trois années et demie passées au LSCE. En plus de qualités professionnelles remarquables, ces qualités humaines ont largement contribué à la qualité et l'aboutissement de ce travail. Merci Bruno pour tout : pour la « forme de poire » pendant les missions, pour le bar de chez Bruno, pour les échanges politiques animés, pour l'épaule amicale et les conseils échangés. Merci, simplement, pour « avoir été là ».

Je souhaite remercier chaleureusement les différents membres de mon jury qui ont accepté de rapporter et d'examiner ce travail : M. Olivier Radakovitch du Centre Européen de Recherche et d'Enseignement des Géosciences de l'Environnement (Rapporteur), M. Grenz Christian au Centre d'Océanologie de Marseille et l'Universidad Autonoma Metropolitana de Mexico (rapporteur), Pr. Alain Saliot du laboratoire d'Océanologie et du Climat : Expérimentations et Analyses Numériques de l'UPMC (président du jury), M. Pierre Regnier de l'Université d'Utrecht (examinateur), M. Stefano Miserocchi de l'Instituto di Scienze Marine (examinateur) et M. Richard Sempéré du Centre d'Océanologie de Marseille. Un merci tout particulier aux rapporteurs : je sais le travail que cela représente et le temps que cela nécessite, hors de nos jours, en recherche comme ailleurs, le temps est précieux (au sens propre et figuré). Olivier, tu m'as déjà beaucoup aidé dans le cadre de Chaccra, je te remercie d'avoir pris cette responsabilité là en plus.

Je tiens à remercier Xavier Durrieu de Madron (CEntre de Formation et de Recherche sur l'Environnement Marin), Eric Viollier (Laboratoire de Géochimie des Eaux, Université Paris VII), Christine Hatté (Laboratoire de Sciences du Climat et de l'Environnement) et Sophie Ayrault (Laboratoire de Sciences du Climat et de l'Environnement) pour avoir suivi mes travaux dans le cadre de mes comités de thèse, et m'avoir conseillée et guidée par leur remarques judicieuses et pertinentes.

Je remercie mes collaborateurs de projet Chaccra, partenaires de mission et/ou co-auteurs qui ont rendu possible ce travail en apportant chacun une pierre à l'édifice, que ce soit par leur travail scientifique ou leur bonne humeur. Ainsi dans le désordre et de manière non exhaustive, un grand merci à Roselyne Buscail, Fabien Joux, Bruno Deflandre, Philippe Kerhervé, Audrey Pruski, Jean-Jacques Naudin, Eric Viollier, les marins du Thétys… Lucie Pastor, bien plus qu'une partenaire de travail, une amie que je remercie pour les « séances modélo » qui se finissent en discussions jusqu'au bout de la nuittttttt…

Ce travail de thèse n'aurait pu être réalisé sans l'accueil chaleureux au sein du Laboratoire de Sciences du Climat et de l'Environnement et de l'équipe Transferts Continents Océans. Merci à vous pour votre gentillesse et vos conseils et les réunions d'équipes souvent longues mais très agréables, surtout lorsqu'elles se finissent sur un pot... Un merci particulier à Nadine et Evelyne pour leur aide et compétence dans les analyses 14C.

Un grand merci également à Karline Soetaert du Netherlands Institute of Ecology qui m'a accueillie et initiée avec gentillesse et efficacité à la modélisation diagénétique.

Je souhaite remercier mes collègues et amis : Claire, Cindy, Sandra, Aline, Abel, Eline, Hélène, Nico et Fabien… Merci à vous. Juste d'avoir été là, d'être vous et d'avoir partagé avec moi cette expérience de vie qu'est la thèse. Une dédicace et un merci tout particulier à Claire : et oui avec une semaine d'intervalle nos bébés respectifs ont vu le jour… Cette thèse est un petit peu pour toi baby Anatole ;)

Merci à mes amis et à ma famille: vous avez su m'épauler et me soutenir pendant cette expérience. Cette thèse se termine complètement différemment de ce qui était prévu et grâce à vous j'ai pu tirer le meilleur de mes multiples rebondissements personnels et m'accrocher. Dans ce contexte merci à Vivien et Ralf qui bien que nos chemins soient désormais distincts m'ont apporté des joies et des bonheurs précieux.

Max, you definitely arrived unexpectedly in my life but played a great role in the final accomplishment of the PhD work, I would never thank you enough for this. Thank for your light and keep shining…

TABLE DES MATIERES

LISTE DES FIGURES

LISTE DES TABLEAUX

CHAPITRE 6. SYNTHESE ET CONCLUSION : ASSESSING PARTICULATE ORGANIC CARBON BUDGETS IN THE RHONE RIVER DELTA UNDER DIFFERENT HYDROLOGICAL CONDITIONS 168

CHAPITRE 1. INTRODUCTION ET SYNTHÈSE BIBLIOGRAPHIQUE

CHAPITRE 1. INTRODUCTION ET SYNTHESE BIBLIOGRAPHIQUE

La question environnementale et les problématiques de développement durable occupent une place prépondérante dans le paysage politique, économique et social actuel: synonymes de progrès ou de contraintes supplémentaires, médiatisées à l'extrême, constituant désormais un argument politique et électoral de poids, elles sont au cœur des décisions gouvernementales. En effet, l'accroissement démographique mondial débuté à partir du XIXème siècle consécutif à la forte croissance économique qui a suivi la révolution industrielle, a soulevé, dès les années 70 et les premiers chocs pétroliers, la question de l'exploitation des ressources naturelles, de la modification de l'environnement par les activités humaines, et des rétroactions potentielles sur ces dernières. Après la publication en 1972 du livre The limits of growth (Meadows *et al.*, 1972), les différentes Conférences des Nations Unies sur l'Environnement et le Développement, la mise en place du protocole de Kyoto et la création du Groupe d'Experts Intergouvernemental sur l'évolution du climat (GIEC), traduisent la prise de conscience à l'échelle mondiale. Le prix Nobel de la paix 2007 attribué conjointement à Al Gore et aux GIEC met en évidence les perturbations écologiques résultant de l'activité anthropique et la nécessité d'une collaboration et d'une concertation internationale dépassant le simple cadre de la recherche scientifique. La création de programmes mondiaux tels que l'International Geosphere-Biosphere program et le World Climate Research program ont permis la mise en place à l'échelle mondiale d'une recherche scientifique mondiale coordonnée et d'avancées considérables sur le changement climatique, tant au niveau des perturbations environnementales qui y sont liées que des mécanismes clés qui le contrôlent.

Le dioxyde de carbone étant le plus important gaz à effet de serre d'origine anthropique, l'augmentation de sa concentration atmosphérique, observée depuis 50 ans et résultant de l'utilisation des combustibles fossiles et des changements de l'affectation des terres, a significativement contribué à l'accroissement du forçage radiatif terrestre. La forte solubilité du CO_2 associée et la pompe biologique font de l'océan le puits de carbone naturel le plus important (Raven and Falkowski, 1999; Siegenthaler and Sarmiento, 1993). La compréhension fine du cycle biogéochimique du carbone et des éléments qui y sont associés en milieu océanique est donc un enjeu scientifique majeur, supporté par de nombreux programmes internationaux tels que le Global Carbon Project ou l'International Ocean Carbon Coordination Project.

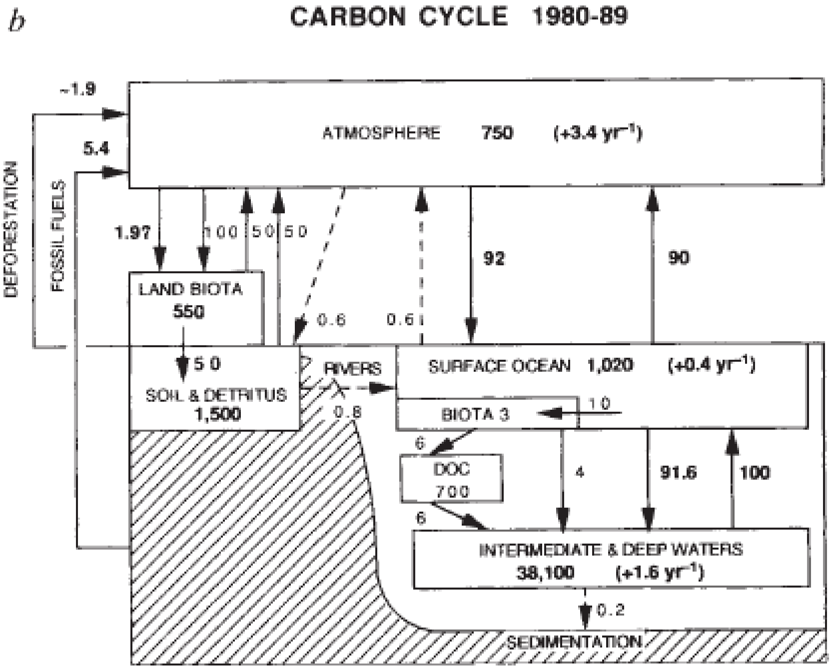

Figure 1. Cycle global du carbone et flux, en GtC et GtC a^{-1} (from Siegenthaler and Sarmiento, 1993)

1.1 LES ZONES COTIERES : DES ENVIRONNEMENTS AU CŒUR D'ENJEUX MULTIPLES

Dans ce contexte, l'océan côtier constitue un environnement critique : interfaces entre les continents, l'atmosphère et l'océan, les zones côtières sont au carrefour d'enjeux socio-économique et écologiques multiples. Les zones côtières sont des espaces riches qui fournissent plus de 50% des ressources naturelles et supportent des activités variées (pêche, exploitation pétrolière et minérale, tourisme). En raison du lien étroit existant entre disponibilité des ressources et développement démographique, quasiment la moitié de la population mondiale actuelle vit à moins de 200 km des côtes, et une augmentation de 35% sur la bande étroite des 100 km littoral est prévue pour 2025 : environ 2.75 milliards de personnes sont et seront donc soumis aux effets de l'eutrophisation, de l'hypoxie côtière (malaïgues), de la contamination, de la surpêche et aux effets renforcés du changement climatique dans l'océan côtier, notamment l'élévation du niveau des mers. Les écosystèmes côtiers sont donc le siège de pressions anthropiques diverses susceptible d'en altérer le fonctionnement et notamment d'en déséquilibrer le cycle du carbone très actif.

En effet, les marges continentales, qui ne représentent que 8% de la surface océanique mondiale, jouent un rôle majeur dans les cycles biogéochimiques mondiaux et notamment celui du carbone (Borges, 2005; Gattuso *et al.*, 1998). Caractérisé par un couplage pélagique-benthique étroit du fait des faibles profondeurs mises en jeu, les océans côtiers constituent une zone d'accumulation préférentielle avec 80 % de l'enfouissement mondial du Carbone Organique (Corg) ayant lieu dans les marges continentales (Hedges and Keil, 1995; Smith and Hollibaugh, 1993). En effet, les rivières, résurgences sous-terraines et upwellings apportent d'importantes quantité de nutriments qui sont le support d'une très forte productivité des océans côtiers : ces derniers représentent environ 25% de la production primaire océanographique mondiale (Smith and Hollibaugh, 1993). En plus des sels nutritifs (NO_3^-, PO_4^{3-}), les fleuves exportent du matériel terrigène vers l'océan issus de l'érosion et du lessivage des continents (Dagg *et al.*, 2004) : environ 1 GtC y^{-1} de carbone sont exportés dont environ 0.4 GtC se trouve sous forme organique, particulaire ou dissoute (Hedges *et al.*, 1997) représentant ~1% de la production primaire continentale. En termes quantitatifs, les apports de matière organique particulaire (MOP) délivrés par les rivières sont suffisants pour subvenir à eux seuls à la totalité du CO enfoui dans les sédiments marins (Hedges and Keil, 1995). On estime d'ailleurs que moins de 5% des sédiments fluviaux délivrés dans l'océan côtier atteignent l'océan profond (Meade, 1996). Une étude récente a montré par exemple que l'accumulation de carbone organique dans le Golfe du Bengale qui résulte des apports du système fluvial du Gange-Brahmapoutre représente autour de 10-20 % du carbone organique terrestre enfoui dans la totalité des sédiments marins (Galy *et al.*, 2007). De même, à l'échelle européenne, bien que les plateaux continentaux soient globalement des puits de CO_2 atmosphérique, les zones estuariennes au contraire constituent des sources de CO_2 atmosphérique (Borges *et al.*, 2006). Ainsi, les zones marges continentales influencées par les rivières, encore appelées River-dominated Ocean Margins (RiOMar) joue un rôle particulier et apparaissent comme des zones primordiales pour la compréhension du cycle du carbone global.

1.2 CARACTERISTIQUES DE LA MATIERE ORGANIQUE PARTICULAIRE DES OCEANS COTIERS

Issus principalement de l'érosion et du lessivage des sols et des roches continentales, et dans une moindre mesure de la production autochtone, le Corg allochtone exporté par les rivières consiste en un mélange hétérogène et complexe de matériel détritique (kérogène), de matière organique des sols (substances humiques, issue de la dégradation des plantes vasculaires) et de tissus végétaux supérieurs (Hedges *et al.*, 1997; Raymond and Bauer, 2001a; Tesi *et al.*, 2007b). La composition de ce matériel fluvial lui confère une signature toute particulière, distincte de la MOP marine. En effet, les plantes vasculaires, presque exclusivement terrestres, ont développé des stratégies évolutives physiologiques et structurales permettant notamment aux tissus photosynthétiques de rechercher la lumière et aux tissus hétérotrophes racinaires d'échanger eau et sels nutritifs avec le sol. Les composés de lignine, hémicellulose mais aussi résines, cires et cutines constituent ainsi quelques-unes des bio-macro-molécules structurales spécifiques aux plantes vasculaires (Hedges and Oades, 1997). La détection de ces composés dans des sédiments ou des particules en suspension (Goni and Montgomery, 2000) est d'ailleurs utilisée fréquemment comme traceur qualitatif de l'export du matériel fluvial dans l'océan (Buscail *et al.*, 1995; Goni *et al.*, 2003; Tesi *et al.*, 2007a). La contribution des végétaux supérieurs dans le matériel fluvial se traduit également par un rapport C/N élevé (20 – 500) distinct de celui des cellules planctoniques ou bactériennes (4 -10) (Goni *et al.*, 2006; Goni *et al.*, 2003; Hedges *et al.*, 1986a), ce dernier étant aussi utilisé comme indicateur de l'origine potentielle de la matière organique (Buscail *et al.*, 1995; Harmelin-Vivien *et al.*, 2008; Lansard *et al.*, 2005).

Une autre caractéristique essentielle de la matière organique terrigène est sa faible teneur en isotope ^{13}C par rapport au ^{12}C. En effet, dans l'atmosphère, les molécules $^{13}CO_2$ coexistent avec les molécules $^{12}CO_2$, à hauteur d'environ 1,1 % du total du CO_2. Les végétaux utilisent les deux types de carbone lors de la photosynthèse, mais on observe un fractionnement isotopique, en faveur du ^{12}C. Cette discrimination est faible et on la mesure en unités δ^{13}C qui représentent la différence du rapport $^{13}C/^{12}C$ avec un standard (e.g. Pee Dee Belemnite), exprimé en ‰. La plupart des plantes terrestres, notamment toutes les essences forestières, arbres compris, fixent le carbone via le cycle de Calvin-Benson en C3 et ont des valeurs de δ^{13}C autour de -25 à -29 ‰, alors que le phytoplancton marin présentent des signatures isotopiques comprises entre -19 ‰ et - 22 ‰ (Fry and Sherr, 1984). Le phytoplancton d'eau douce présente un signal encore plus appauvri entre -30 ‰ et -40 ‰ (Forsberg *et al.*, 1993; Palmer *et al.*, 2001; Rau, 1978). De plus, on observe de légères différences, liées au type de photosynthèse. Les plantes vasculaires à cycle en C4 (essentiellement des Graminées et Cypéracées tropicales de milieux ouverts telles que maïs, canne à sucre, bambous et herbacées) absorbent plus de ^{13}C que les plantes en C3 : elles ont donc une signature isotopique moins appauvrie avec des valeurs en $\delta^{13}C$ entre -10 ‰ et -14 ‰ (France-Lanord and Derry, 1994; Fry and Sherr, 1984; Smith and Epstein, 1971) plus enrichie que celle du phytoplancton marin. La signature isotopique stable du Corg des sédiments des marges continentales influencées par les rivières est donc un outil puissant pour la discrimination des sources de matière organique dans ces environnements et l'export des particules fluviales (Boldrin *et al.*, 2005; Faganeli *et al.*, 1994; Hedges *et al.*, 1986a; Tesi *et al.*, 2007a; Tesi *et al.*, 2007b).

La teneur en radiocarbone est également un bon indicateur de la nature terrestre ou marine de la MOP. En effet, les essais nucléaires dans les années 1950 ont injecté d'importantes quantités de ^{14}C dans l'atmosphère, et augmenté le rapport $^{14}C/^{12}C$ atmosphérique. Les activités atmosphériques sont généralement exprimées comme la différence d'activité en per mille (‰) avec le standard moderne, corrigée du fractionnement isotopique (normalisé) puis de la valeur de l'atmosphère en 1950 et de l'année d'échantillonnage (Mook and van der Plicht, 1999). Les activités atmosphériques dans les années 1960 étaient deux fois plus élevées que les valeurs naturelles « pré-bombes » et ont depuis décru de manière continue : le radiocarbone des bombes a progressivement été échangé avec les autres réservoirs du cycle du carbone. Le radiocarbone des bombes se retrouve notamment intégré dans le pool de carbone inorganique dissous (DIC) des eaux océaniques de surface, qui présentent donc un $\Delta^{14}C$ entre 50 et 150 ‰. Les différentes signatures du DIC marin et du CO_2 atmosphérique est directement incorporé par le processus de photosynthèse, et le phytoplancton marin et la MOP marine, produits dans les eaux de surface présentent en général des valeurs enrichies entre -45 et +110 ‰ (Wang *et al.*, 1998; Williams *et al.*, 1992). A l'échelle mondiale, les MOP fluviales présentent donc des signatures $\Delta^{14}C$ diverses très variables entre -980 to +75‰ (Nagao *et al.*, 2005; Raymond and Bauer, 2001a). En effet, la signature radioisotopique de la matière organique des particules en suspension fluviales est dépendante du système considéré : elle intègre les processus d'érosion des roches continentales (âgées et très appauvries en $\Delta^{14}C$), du ruissellement sur le bassin versant (matière des sols constituée de débris récents et anciens de matière organique, présentant donc une signature $\Delta^{14}C$ mixte) et de la production autochtone locale (Goni *et al.*, 2006). Néanmoins, à l'échelle régionale, le signal $\Delta^{14}C$ d'une rivière est très discriminant (Hedges *et al.*, 1986b; Raymond and Bauer, 2001a) et fournit des informations uniques sur les sources, les âges et les temps de résidence de la MOP (Druffel *et al.*, 2005; Goni *et al.*, 2006; Goni *et al.*, 1997; Raymond and Bauer, 2001b). Les mesures par spectrométrie de masse par accélération (AMS) des valeurs de $\Delta^{14}C$ sont donc des traceurs efficaces des dynamiques du CO dans les systèmes fluviaux et les marges continentales (Druffel *et al.*, 2005; Galy *et al.*, 2007; Hedges *et al.*, 1986a; Megens *et al.*, 2001; Raymond and Bauer, 2001b).

La MOP apportée par les fleuves sur les marges continentales a donc une composition et des signatures isotopiques particulières qui contrastent avec celle du matériel marin avec lequel il est dilué. Au niveau des marges et durant l'export vers l'océan, ce mélange de matériel marin-terrigène subit différents processus qui altèrent sa composition et déterminent son devenir et sa disponibilité pour les cycles biogéochimiques de l'océan ouvert.

1.3 DEVENIR DE LA MATIERE ORGANIQUE PARTICULAIRE DANS LES OCEANS COTIERS

1.3.1 Minéralisation du CO dans la colonne d'eau

Le stock de matière organique particulaire issu de la production primaire de la couche euphotique et des apports continentaux est pour partie directement minéralisé dans la colonne d'eau par les microorganismes hétérotrophes (Azam *et al*, 1983). En effet, les bactéries hétérotrophes (Bactéries et Archées) joue un rôle dominant dans la dégradation de la matière organique, notamment grâce à la boucle microbienne : la remise à disposition de sels nutritifs dans le milieu sert de support à la production primaire appelée alors production régénérée (cf. Figure 2).

Bien que basée majoritairement sur le carbone organique dissous (COD), les bactéries attachées aux particules présentent une très forte activité d'hydrolyse enzymatique qui joue un rôle important dans la solubilisation du POC (Smith *et al.*, 1992) et donc dans le cycle du

COD et de sa dégradation future notamment par les bactéries libres du milieu (Cho and Azam, 1988). En effet, dans les milieux côtiers et estuariens, les agrégats constituent des micro-habitats majeurs et les bactéries attachées aux particules contribuent très majoritairement à l'activité bactérienne (production de biomasse et dégradation de la matière organique) via cette importante activité enzymatique extracellulaire (Crump *et al.*, 1998; Vallières *et al.*, 2008). La dégradation de la matière organique dans la colonne d'eau est gouvernée par plusieurs facteurs intrinsèques et extrinsèques qui limite son efficacité dans les milieux aquatiques (Del Giorgio and Davis, 2003). Les facteurs extrinsèques sont ceux qui régulent le métabolisme bactérien, comme la température, la disponibilités des nutriments inorganiques, et les interactions trophiques qui peuvent générer du stress tels que les pressions de broutage par exemple (Alonso-Saez *et al.*, 2008; Gaudy *et al.*, 2003). Les facteurs intrinsèques incluent les caractéristiques chimiques de la matière organique affectant sa biodisponibilité et sont fonction de son origine et de son état de dégradation.

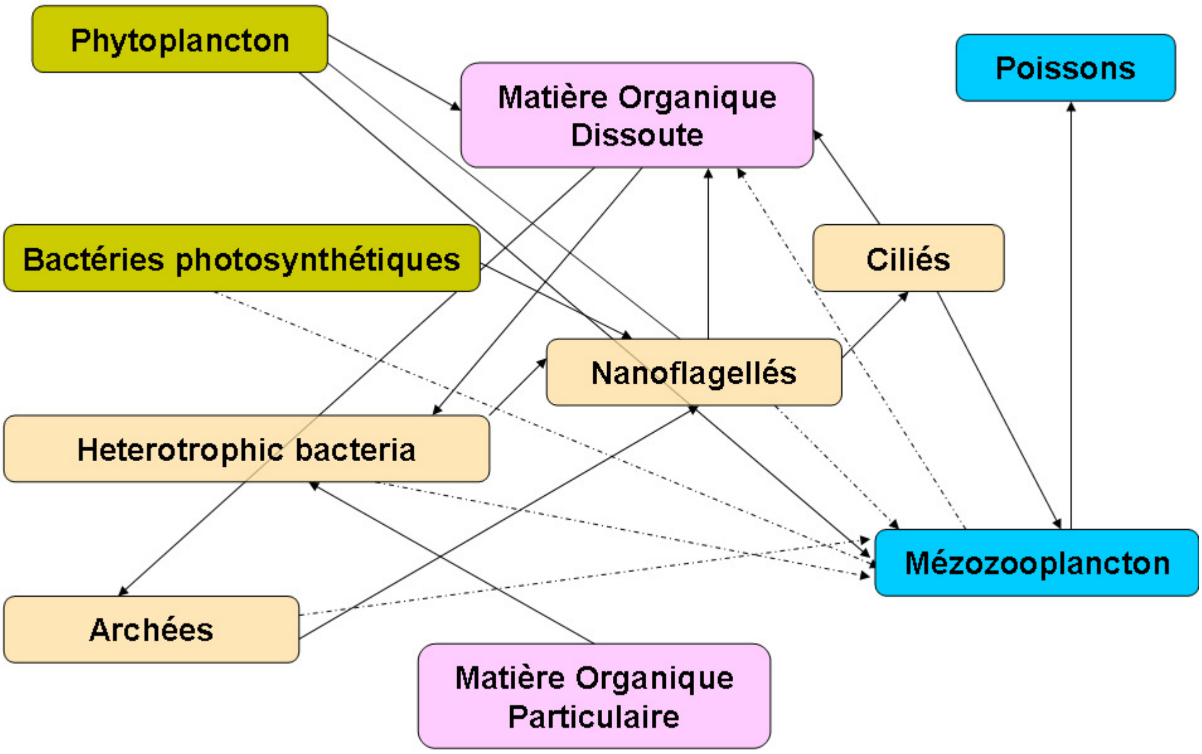

Figure 2. Diagramme simplifié du réseau trophique océanique démontrant l'importance de la boucle microbienne. Les flux de carbone et d'énergie dominant sont représentés par des lignes continues ; les flux moindre sont représentés par des tirets. Autres que le mezozooplancton, les et les poissons (boîtes bleues), les autres boîtes représentent les organismes qui font partie de la boucle microbienne (vert = photosynthétique et jaune = hétérotrophes). Adapté de (Pomeroy *et al.*, 2007).

1.3.2 L'enfouissement du CO dans les sédiments côtiers

Du fait des apports très important de matériel fluvial délivré et des faibles profondeurs d'eau mises en jeu, seule une partie est reminéralisée dans la colonne d'eau et une grande quantité de matière organique se dépose sur le fond. La conséquence directe de ces dépôts de matière organique est que les sédiments des zones côtières représentent 80% de l'enfouissement du CO mondial (Berner, 1989; Hedges and Keil, 1995). Galy *et al* (2007) ont par exemple montré que le Golfe du Bengale enfouissait environ 70 à 85% du carbone organique délivré par le système hydrologique Gange-Brahmapoutre, ce qui correspondrait à quasiment 10-20% du carbone organique terrestre séquestré dans les sédiments océaniques. Plus généralement, les environnements deltaïques sont des zones d'enfouissement majeures : elles séquestrent à elles-seules environ 50% du CO enfoui dans les sédiments marins (Blair *et al.*, 2004; Burdige, 2005). Les écosystèmes deltaïques constituent de véritables réacteurs benthiques conjuguant dégradation et préservation de la matière organique terrigène supposée réfractaire (Aller, 1998; Aller *et al.*, 2004; Buscail *et al.*, 1995). En effet, en plus de cette accumulation préférentielle, les sédiments côtiers sont aussi le siège d'une dégradation active de la matière organique : on estime que jusqu'à 70% des 0.2 10^{15} gC de POC délivrés annuellement des rivières à l'océan y sont oxydés (Burdige, 2005; Galy *et al.*, 2007; Hedges *et al.*, 1997; Meybeck, 1982).

1.3.3 Minéralisation benthique du CO

L'activité de minéralisation benthique dans les milieux côtiers dépend d'abord de l'intensité des apports de CO à l'interface eau-sédiment et donc à la fois des apports fluviaux et de la dynamique de leur export, de la productivité des eaux de surface et de la profondeur. En effet, la matière organique se déposant est, comme vu précédemment, un mélange complexe de matériel biogénique et lithogénique avec des constituants variés (protéines, lipides, polysaccharides, dérivés de lignine…) dont la réactivité change au cours des processus de dégradation dans la colonne sédimentaire (Berner, 1980). Ces dépôts sédimentaires sont instables thermodynamiquement et subissent des changements chimiques rapides : leur composition, leur comportement, leur distribution spatiale et leur devenir dépendent essentiellement de l'origine des dépôts (nature des constituants) et des conditions environnementales dans lesquelles ils évoluent.

La décomposition de la matière organique constitue une chaîne de réactions biogéochimiques majeure dans les dépôts sédimentaires : elle influence notamment les propriétés redox de l'environnement, le recyclage des nutriments biologiques essentiels (N, P) et détermine la qualité et la quantité du matériel finalement stocké (Mc Kee *et al*, 2004, Heip *et al*, 1995).

La minéralisation de la matière organique, que l'on peut schématiser par la stoechiométrie de Redfield $(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$, est basée sur l'utilisation, par des organismes hétérotrophes, de l'énergie stockée dans des composés carbonés réduits. Elle constitue en une séquence de réactions biogéochimiques médiées d'oxydo-réductions : le carbone de la matière organique est oxydé en CO_2, produit ultime de la réaction. Les microorganismes utilisent de manière séquentielle les accepteurs terminaux d'électrons: la séquence est fonction de la quantité d'énergie libre, de la disponibilité de l'oxydant, de la cinétique et de la physiologie des bactéries mises en jeu. En effet, les microorganismes utilisent préférentiellement les oxydants ayant l'enthalpie d'énergie libre la plus grande pour subvenir à leurs besoins physiologiques (croissance, reproduction etc.). La conséquence de ces contraintes thermodynamiques et physiologiques est la stratification verticale de la colonne sédimentaire en différentes zones de réactions redox (Berner, 1980; Froelich *et al.*, 1979)

Les accepteurs d'électrons naturellement présents dans les sédiments superficiels sont l'oxygène, les nitrates, les nitrites, les oxydes de manganèse et de fer, les sulfates, le dioxyde de carbone et les composés organiques oxydés. (v. Figure 3). Typiquement, on distingue la succession verticale des trois environnements suivants:

- Milieux oxiques ou aérobiques, en sub-surface, où l'oxygène dissous est réduit. A l'interface eau-sédiment, l'oxygène pénètre dans la colonne sédimentaire par diffusion des eaux de fond ou par bio-irrigation des organismes benthiques (Forster *et al.*, 1999). Dans cette zone superficielle, l'oxygène est le premier oxydant à être utilisé.
- Milieux suboxiques, plus en profondeur, où nitrates et nitrites sont réduits (dénitrification aérobie et anaérobie) ainsi que les oxydes de fer et manganèse. Lorsque l'oxygène devient insuffisant, les nitrates provenant de la réoxidation du NH4+ dans la zone oxique sont réduits par des bactéries dites dénitrifiantes (Bonin *et al.*, 1998; Pakulski *et al.*, 2000). Les oxydes métalliques sont ensuite utilisés comme oxydant, car moins disponibles (Canfield *et al.*, 1993).

- Milieux anoxiques ou anaérobiques, plus profondément encore, où la réduction des sulfates et la méthanogénèse ont lieu. Les sulfures formés lors de la sulfato-réduction ont la propriétés de piéger de nombreux métaux, et la formation de pyrite par association avec le fer réduit issus de la minéralisation est fréquente (Aller *et al.*, 2004; Joachimski *et al.*, 2001).

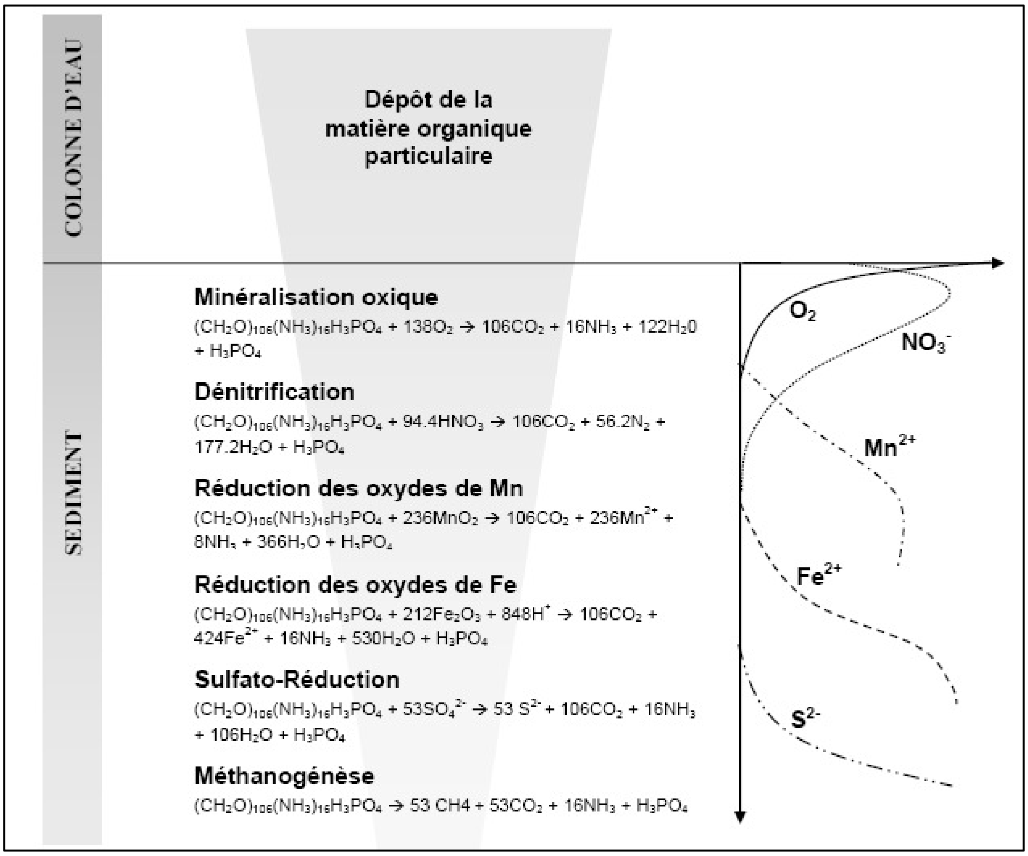

Figure 3. Les principales voies de minéralisation de la matière organique dans les sédiments marins (Froelich *et al.*, 1979)en assumant les ratios stœchiométriques de Redfield *et al*, 1963. A droite : une distribution schématique des espèces dissoutes dans la colonne sédimentaire montrant l'utilisation préférentielle de l'oxygène suivi des nitrates, des oxydes métalliques puis des sulfures.

1.3.4 Importance de l'oxygène dans la minéralisation benthique du CO

Lors de la diagenèse précoce, au sein de la séquence d'oxydoréduction de dégradation de la matière organique, l'oxygène est l'accepteur d'électron le plus favorable énergétiquement, ce qui en fait un acteur majeur de la transformation et du devenir de la matière organique. Par ailleurs, l'oxygène est également réutilisé par l'oxydation des produits réduits issus de la minéralisation anoxique qui diffusent vers la zone oxique. La consommation totale en oxygène des sédiments est donc une approximation de la minéralisation oxique et anoxique de la matière organique. L'étude des flux d'oxygène à l'interface eau/sédiment est alors un bon moyen pour appréhender les conditions de dégradation de la matière organique, l'état trophique du milieu et l'activité de la faune benthique (Rabouille *et al*, 2003, Revsbech *et al*, 1980, Canfield *et al*, 1993 ; Heip *et al*, 1995). La demande diffusive en oxygène des sédiments est d'ailleurs couramment utilisée pour appréhender l'activité de minéralisation benthique dans les sédiments influencés par les rivières (Morse and Rowe, 1999; Alongi, 1995;Cai *et al.*, 1995; Dedieu *et al.*, 2007; Denis and Grenz, 2003; Denis *et al.*, 2001; Epping and Helder, 1997; Glud *et al.*, 1994).

Néanmoins, ces flux intègrent différents processus qui peuvent influer sur le bilan et l'estimation du carbone dégradé dans les sédiments. Ainsi, la fixation des espèces réduites (co-précipitations des sulfures et du fer sous forme de FeS ou FeS_2), leur libération dans la colonne d'eau (dégazage de méthane) et les mécanismes de remaniement sédimentaire peuvent modifier la séquence diagénétique classique. Ainsi, les facteurs contrôlant la demande benthique en oxygène sont multiples : l'oxygénation de l'eau de fond et la température (Cai et Reimers, 1995 ; Thamdrup *et al.*, 1998), le flux de matière organique déposé à la surface du sédiment, sa quantité et réactivité (Canfield *et al.*, 1993; Archer et Devol, 1992 ; Holstein et Wirtz, 2009), les processus de bioturbation et l'hydrodynamisme local pouvant modifier la couche limite diffusive benthique (Diffusive Boundary Layer, DBL) ou générer de la resuspension qui affecte le temps d'exposition de la matière organique à l'oxygène (Arzayus et Canuel, 2005 ; Damste *et al*, 2002 ; Hartnett *et al*, 1998 ; Aller et Aller, 2004 ; Tengberg *et al*, 2003).

La quantification et l'importance des différents chemins réactionnels, notamment l'utilisation de l'oxygène dans la dégradation du CO dans les sédiments, ainsi que les facteurs de contrôle mis en jeu passent par l'utilisation de modèles diagénétiques numériques. Intégrant les processus principaux telles que les réactions diagénétiques, le transport diffusif et advectif, ils permettent d'étudier l'évolution spatiale et temporelle de la concentration en matière organique (Berner, 1980; Boudreau, 1997). Ils sont ainsi des outils puissants pour l'établissement de bilans de carbone, l'importance de chaque processus, l'évaluation des constantes de temps mises en œuvre et les prédictions éventuelles sur l'évolution du système après changements des conditions environnementales (Epping *et al.*, 2002; Soetaert *et al.*, 1996).

Les apports fluviaux vers l'océan côtier sont très variables dans le temps, alternant entre des périodes d'étiage, de crues, de fortes charge particulaire (Wheatcroft and Borgeld, 2000). Cette variabilité des apports génère un dépôt non stationnaire de CO dans les deltas et prodelta (Bentley and Nittrouer, 2003; McKee *et al.*, 2004). Ainsi, au vu des processus décrits précédemment, il est clair que les phénomènes de crues peuvent modifier la minéralisation de la matière organique dans les sédiments deltaïques et favoriser sa préservation dans les environnements côtiers peu profonds (Leithold and Hope, 1999) : un apport massif de CO d'origine terrigène avec un spectre de réactivités variées peut entrainer des changements de compositions biogéochimiques et de dégradabilité de la matière organique dans les sédiments (Tesi *et al.*, 2008). De plus, la capacité de rétention des apports de crues dans les écosystèmes cötiers est variable et dépend du système considéré, certains constituant un filtre très efficace (Lisitsyn, 1995; Sommerfield et Nittrouer, 1999; Allison *et al.*, 2000).

1.4 CADRE DE L'ETUDE

Le présent travail est centré sur les sources et le devenir du CO dans le prodelta du Rhône. Directement influencé par les apports du Rhône et soumis à la circulation générale, cette zone occupe une place et un rôle particulier au sein du Golfe du Lion.

1.4.1 Le Rhône

D'une longueur de 812 km et avec un bassin versant d'une surface de 97 800 km², le Rhône est le premier fleuve du bassin méditerranéen. En effet, depuis le barrage du Nil, il est la source la plus importante en termes d'eau douce et de débit solide (Copin-Montegut, 1993; Pont *et al.*, 2002). Son influence sur le plateau continental a été très largement documentée (De Madron *et al.*, 2000; de Madron *et al.*, 2003; Monaco *et al.*, 1999; Sempere *et al.*, 2000).

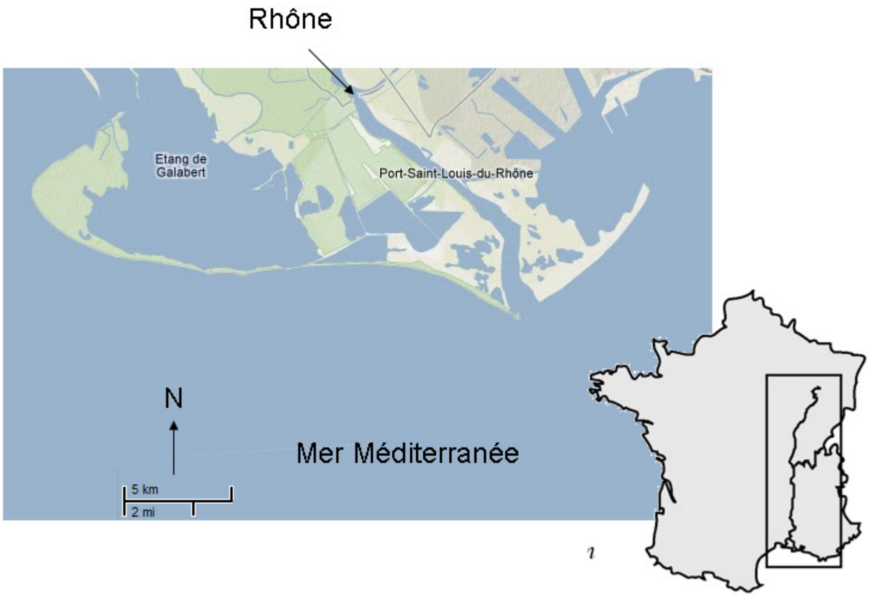

Figure 4. Site d'étude (prodelta du Rhône).

Le régime hydrologique du Rhône est marqué par une très forte variabilité saisonnière et interannuelle. Avec un débit moyen annuel de 1700 $m^3 s^{-1}$, le Rhône présentent des débits très contrastés où des périodes de crue en automne et début de l'hiver pouvant atteindre plus de 10 000 $m^3 s^{-1}$ succèdent à des étiages estivaux sévères inférieurs à 500 $m^3 s^{-1}$ (Pont *et al.*, 2002). Les crues annuelles sont caractérisées par un débit liquide autour de 3000 $m^3 s^{-1}$.

Le bassin versant du Rhône représente plus de 80% des apports solides terrigènes du Golfe du Lion (Monaco *et al*, 1990). La variabilité observée des débits liquides se reflète également dans la dynamique saisonnière des débits solides : globalement de l'ordre de 2 à 8 Mt a^{-1}, ils peuvent atteindre 26.5 Mt a^{-1} (Pont *et al.*, 2002 ; Antonelli, 2002). De plus, le Rhône délivre annuellement 19.2 ± 6 10^4 tC/an sous forme POC (Sempere *et al.*, 2000) : le Rhône est à l'origine de la majeure partie des apports de carbone organique (dissous et particulaire) sur le plateau continental du Golfe du Lion (Cauwet *et al*, 1990). De plus, le flux de nutriments exportés par le Rhône supporte au moins 50% de la production primaire du plateau (Cruzado et Velasquez, 1990).

Il est estimé que 80% environ du matériel Rhodanien est stocké à proximité de son embouchure, dans son prodelta, et que la majorité de ces exports particulaires se fait sous forme pulsée correspondent à des périodes de crues ou des tempêtes marines (Ulses *et al.*, 2008 ; Roussiez *et al.*, 2006 ; Cauwet *et al.*, 1990; Lansard *et al.*, 2007; Miralles *et al.*, 2005).

1.4.2 Brève description du prodelta du Rhône

Réceptacle direct des apports particulaires du Rhône, le prodelta assure la liaison avec le plateau continental. Les réactions de floculation et d'agrégations liées aux changements de conditions chimiques du milieu (salinité, pH) entrainent une sédimentation massive à l'embouchure. Cette accumulation de matériel sédimentaire participe à l'élaboration du prisme sédimentaire épicontinental et la mise en place de trois domaines sédimentaires :

- Le domaine proximal caractérisé par une faible pente jusqu'à 3% et la présence de sables littoraux et pré-littoraux.
- Le domaine du prodelta caractérisé par une pente importante qui s'étend jusqu'à 60m de profondeur et des sédiments de types vases silteuses (Wright and Friedrichs, 2006). Les taux de sédimentations dans cette zone varient rapidement : très élevés à l'embouchure, de l'ordre de 50 cm a^{-1}, ils décroissent rapidement avec la profondeur (Charmasson *et al.*, 1998). Ainsi, dans ce travail de thèse, le prodelta désignera la zone centrée autour du prodelta présentant des taux de sédimentation supérieurs à 1 cm a^{-1}.
- Le domaine distal, situé en dessous de 60 m de profondeur, et présentant des taux de sédimentation plus faible d'environ 0.2–0.6 cm a^{-1} (Miralles *et al.*, 2005).

Les très forts taux de sédimentation observés dans le prodelta associé à la dynamique d'export des apports du Rhône soulignent l'importance de cette zone dans le devenir du carbone organique particulaire fluvial, notamment en terme d'enfouissement.

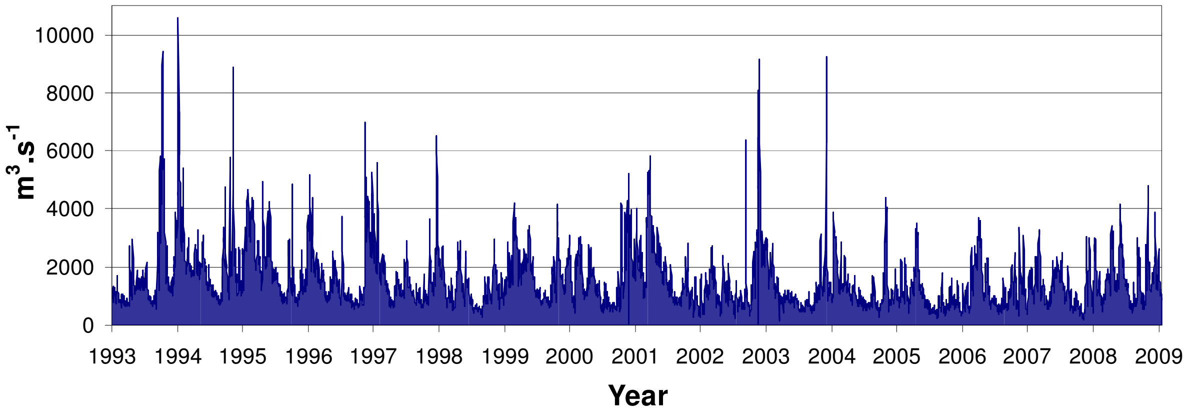

Figure 5. Débits moyens journaliers du Rhône mesurés à Beaucaire entre 1993 et 2009 par la compagnie nationale du Rhône.

1.4.3 Circulation générale du Golfe du Lion

Situé en Méditerranée Nord Occidentale, le Golfe du Lion est le plus important plateau continental de la Méditerranée. D'une superficie de 6700 km², il s'étend au maximum sur 70 km de la côte vers le large et a une profondeur maximale de 120m (Figure 6).

Sur environ 40 km de large, le courant Nord ou Liguro-Provençal longe le talus continental à une vitesse moyenne de 30 cm s^{-1} et impose une circulation géostrophique générale sur le plateau de type cyclonique.

La circulation générale du Golfe du Lion est également forcée par un régime de vents contrasté, qui lui confère une très forte variabilité spatiotemporelle. Les vents de terre, Mistral (secteur Nord) et Tramontane (secteur Nord-Ouest) soufflent environ 35% du temps et peuvent induire en hiver upwelling et formations d'eaux denses (de Madron *et al.*, 1999; Millot, 1990). Les vents marins, plus chauds et humides, de secteurs Sud et Est, représentent environ 25% et peuvent générer de violentes tempêtes en direction de la côte. En été, l'absence temporaire de vent peut favoriser la stratification de la colonne d'eau et la mise en place d'une thermocline. Cette dernière est fréquemment mélangée par des coups de vents qui empêchent une stratification de longue durée (Rabouille *et al.*, 2008).

Le plateau continental du Golfe du Lion est caractérisé par un régime hydrodynamique d'énergie modérée dominé par les houles. Les houles de tempêtes induites par les vents marins, et les plongées d'eaux denses induisent de l'érosion et des phénomènes de resuspension du matériel sédimentaire du plateau (Millot, 1990 ; Bourrin *et al*, 2008 ; Ulses *et al*, 2008).

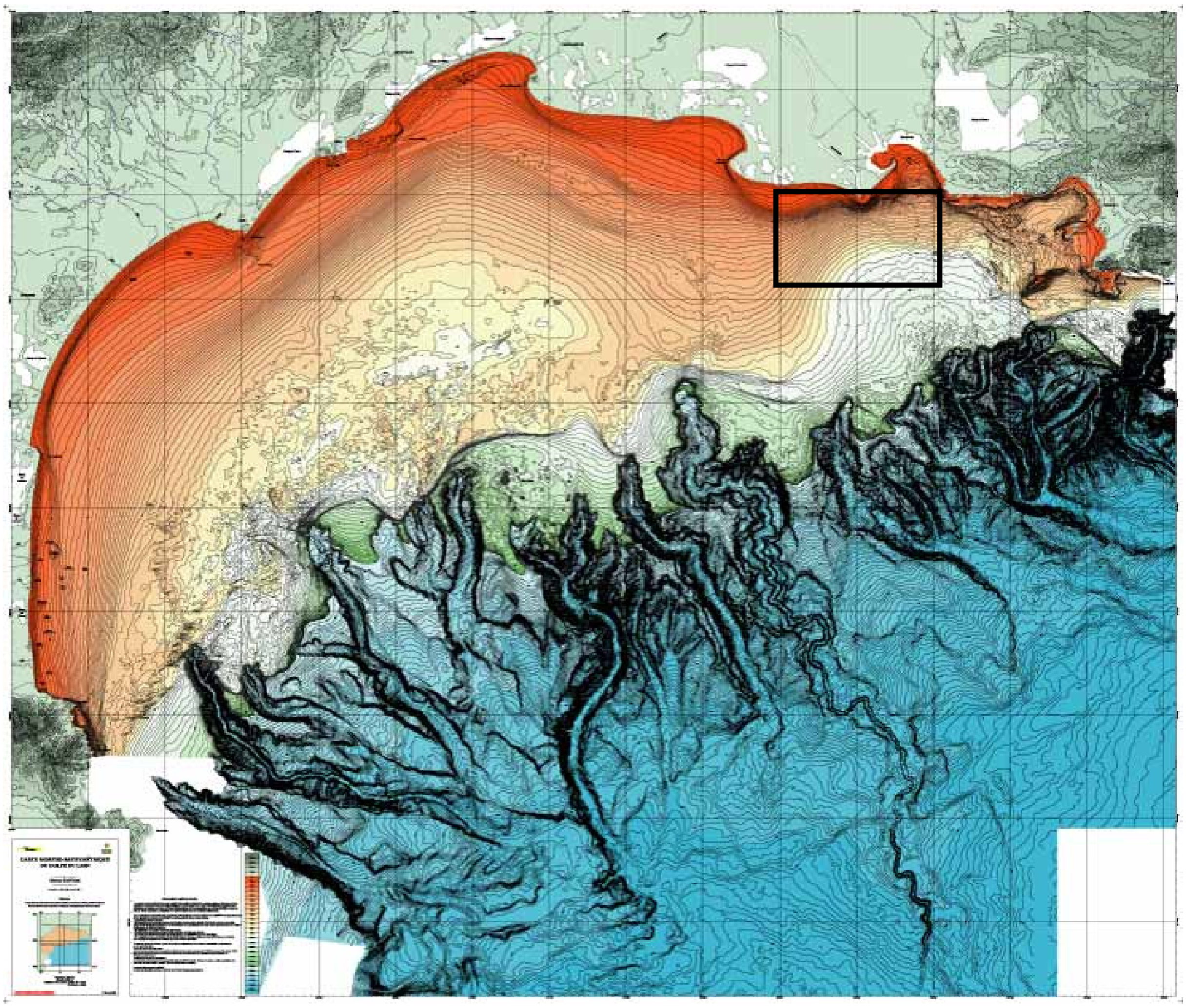

Figure 6. Carte bathymétrique du Golfe du Lion (Ifremer, http://wwz.ifremer.fr/drogm/cartographie/mediterranee/golfe_du_lion/edition). La zone entourée en noir est la zone étudiée.

Dans ce contexte particulier, ce travail s'est intéressé au devenir du carbone organique particulaire du Rhône sur la marge continentale du Golfe du Lion, et plus particulièrement dans la zone du prodelta. En effet, DeMadron *et al*, 2000 ont démontré l'importance de cette zone dans un bilan en carbone réalisé à l'échelle du Golfe du Lion, et ont notamment souligné la nécessité de mieux contraindre les différents termes du budget et leur variabilité. L'étude de la dispersion des particules organiques fluviales, la quantification et la qualification des processus de dégradation mis en jeu ainsi que leur dynamique spatio-temporelle afin d'établir un bilan précis dans la zone du prodelta sont autant d'objectifs qui ont motivés ce travail de thèse.

Ainsi, dans un premier chapitre, nous nous sommes attachés à caractériser la dynamique spatio-temporelle de la dégradation benthique de la matière organique. Le devenir des apports de crue et la relaxation du système sédimentaire a été investiguée grâce au suivi temporel de la consommation en oxygène des sédiments du prodelta.

Dans les chapitres 2 et 3, la caractérisation isotopique ($\delta^{13}C$ et $\Delta^{14}C$) des sédiments et des particules du Rhône a permis de caractériser la dispersion des apports Rhôdaniens et l'origine de la matière organique des sédiments prodeltaïques. Parallèlement, la dégradation de ces particules au sein même de la colonne d'eau a été quantifiée.

Dans un quatrième chapitre, la détermination des différents voies de minéralisation benthique (oxique, anoxique et dénitrification) et de leur proportions respectives a été réalisée grâce à l'utilisation d'un modèle numérique biogéochimique, OMEXDIA, développé par (Soetaert *et al.*, 1996).

Un bilan en carbone à l'échelle du prodelta résultant de l'intégration de tous ces résultats est proposé.

1.5 REFERENCES

Aller, R.C., 1998. Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. Marine Chemistry 61 (3-4), 143-155.

Aller, J.Y., Aller, R.C., 2004. Physical disturbance creates bacterial dominance of benthic biological communities in tropical deltaic environments of the Gulf of Papua. Continental Shelf Research 24 (19), 2395–2416.

Aller, R.C., Hannides, A., Heilbrun, C., Panzeca, C., 2004. Coupling of early diagenetic processes and sedimentary dynamics in tropical shelf environments: the Gulf of Papua deltaic complex. Continental Shelf Research 24 (19), 2455-2486.

Allison, M.A., Kineke, G.C., Gordon, E.S., Goni, M.A., 2000. Development and reworking of a seasonal flood deposit on the inner continental shelf off the Atchafalaya River. Continental Shelf Research 20 (16), 2267-2294.

Alongi, D.M., 1995. Decomposition and recycling of organic matter in muds of the Gulf of Papua, Northern Coral Sea. Continental Shelf Research 15 (11-12), 1319-1337.

Alonso-Saez, L., Vazquez-Dominguez, E., Cardelus, C., Pinhassi, J., Sala, M.M., Lekunberri, I., Balague, V., Vila-Costa, M., Unrein, F., Massana, R., Simo, R., Gasol, J.M., 2008. Factors controlling the year-round variability in carbon flux through bacteria in a coastal marine system. Ecosystems 11 (3), 397-409.

Antonelli, C., 2002. Flux sédimentaires et morphogénèse récente dans le chenal du Rhône aval. Thèse de doctorat, Université Aix-Marseille I, 279p.

Archer, D., Devol, A., 1992. Benthic oxygen fluxes on the Washington shelf and slope: a comparison of in situ microelectrode and chamber flux measurements. Limnology and Oceanography 37, 614-629.

Arzayus, K.M., Canuel, E.A, 2004. Organic matter degradation in sediments of the York River estuary: Effects of biological vs. physical mixing. Geochimica et Cosmochimica Acta 69, n°2, 455-463.

Azam, T., Fenchel, T., Field, J.G., Gray, J.S., Meyer-Reil, L.A., Thingstad, F., 1983. The Ecological Role of Water-Column Microbes in the Sea. Marine Ecology Progress Series 10, 257-263.

Bentley, S.J., Nittrouer, C.A., 2003. Emplacement, modification, and preservation of event strata on a flood-dominated continental shelf: Eel shelf, Northern California. Continental Shelf Research 23 (16), 1465-1493.

Berner, R.A., 1980. Early Diagenesis: A theoretical approach. Princeton University Press, Princeton.

Berner, R.A., 1989. Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over phanerozoic time. Global and Planetary Change 75 (1-2), 97-122.

Blair, N.E., Leithold, E.L., Aller, R.C., 2004. From bedrock to burial: the evolution of particulate organic carbon across coupled watershed-continental margin systems. Marine Chemistry 92 (1-4), 141-156.

Boldrin, A., Langone, L., Miserocchi, S., Turchetto, M., Acri, F., 2005. Po River plume on the Adriatic continental shelf: Dispersion and sedimentation of dissolved and suspended matter during different river discharge rates. Marine Geology 222-223, 135-158.

Bonin, P., Omnes, P., Chalamet, A., 1998. Simultaneous occurrence of denitrification and nitrate ammonification in sediments of the French Mediterranean Coast. Hydrobiologia 389 (1-3), 169-182.

Borges, A.V., 2005. Do we have enough pieces of the jigsaw to integrate CO2 fluxes in the coastal ocean? Estuaries 28 (1), 3-27.

Borges, A.V., Schiettecatte, L.S., Abril, G., Delille, B., Gazeau, E., 2006. Carbon dioxide in European coastal waters. Estuarine Coastal and Shelf Science 70 (3), 375-387.

Boudreau, B., 1997. Diagenetic models and their implementation: modelling transport and reactions in aquatic sediments. Springer.

Bourrin F., Durrieu de Madron, X.D., Heussner, S., Estournel, C., 2008. Impact of winter dense water formation on shelf sediment erosion (evidence from the Gulf of Lions, NW Mediterranean). Continental Shelf Research 28 (15), 1984– 1999

Burdige, D.J., 2005. Burial of terrestrial organic matter in marine sediments: A re-assessment. Global Biogeochemical Cycles 19 (4).

Buscail, R., Pocklington, R., Germain, C., 1995. Seasonal Variability Of The Organic-Matter In A Sedimentary Coastal Environment - Sources, Degradation And Accumulation (Continental-Shelf Of The Gulf-Of-Lions, Northwestern Mediterranean-Sea). Continental Shelf Research 15 (7), 843-869.

Cai, W.J., Reimers, C.E., Shaw, T., 1995. Microelectrode studies of organic carbon degradation and calcite dissolution at a California continental rise site. Geochimica Et Cosmochimica Acta 59 (3), 497-511.

Canfield, D.E., Jorgensen, B.B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N.B., Thamdrup, B., Hansen, J.W., Nielsen, L.P., Hall, P.O.J., 1993. Pathways Of Organic-Carbon Oxidation In 3 Continental-Margin Sediments. Marine Geology 113 (1-2), 27-40.

Cauwet, G., Gadel, F., de Souza Sierra, M.M., Donard, O., Ewald, M., 1990. Contribution of the Rhône River to organic carbon inputs to the northwestern Mediterranean Sea. Continental Shelf Research 10 (9-11), 1025-1037.

Charmasson, S., Bouisset, P., Radakovitch, O., Pruchon, A.S., Arnaud, M., 1998. Long-core profiles of Cs-137, Cs-134, Co-60 and Pb-210 in sediment near the Rhone River (Northwestern Mediterranean Sea). Estuaries 21 (3), 367-378.

Cho, B.C., Azam, F., 1988. Major role of bacteria in biogeochemical fluxes in the ocean's interior. Nature 332 (6163), 441-443.

Copin-Montegut, C., 1993. Alkalinity and carbon budgets in the Mediterranean Sea. Global Biogeochemical Cycles 7 (4), 915-925.

Crump, B.C., Baross, J.A., Simenstad, C.A., 1998. Dominance of particle-attached bacteria in the Columbia River estuary, USA. Aquatic Microbial Ecology 14 (1), 7-18.

Cruzado, A., Velasquez, Z.R., 1990. Nutrients and phytoplankton in the Gulf of Lions, Northwestern Mediterranean. Continental Shelf Research 10 (9-11), 931-942.

Dagg, M., Benner, R., Lohrenz, S., Lawrence, D., 2004. Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: plume processes. Continental Shelf Research 24 (7-8), 833-858.

Damste, J.S.S., Rijpstra W.I.C., Reichart, G.J., 2002. The influence of oxic degradation on the sedimentary biomarker record II. Evidence from Arabian Sea sediments. Geochimica et Cosmochimica Acta 66 (15), 2737-2754.

De Madron, X.D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J.C., Radakovitch, O., Giresse, P., Buscail, R., Kerherve, P., 2000. Particulate matter and organic carbon budgets for the Gulf of Lions (NW Mediterranean). Oceanologica Acta 23 (6), 717-730.

De Madron, X.D., Denis, L., Diaz, F., Garcia, N., Guieu, C., Grenz, C., Loye-Pilot, M.D., Ludwig, W., Moutin, T., Raimbault, P., Ridame, C., 2003. Nutrients and carbon budgets for the Gulf of Lion during the Moogli cruises. Oceanologica Acta 26 (4), 421-433.

De Madron, X.D., Radakovitch, O., Heussner, S., Loye-Pilot, M.D., Monaco, A., 1999. Role of the climatological and current variability on shelf-slope exchanges of particulate matter: Evidence from the Rhone continental margin (NW Mediterranean). Deep-Sea Research Part I-Oceanographic Research Papers 46 (9), 1513-1538.

Dedieu, K., Rabouille, C., Thouzeau, G., Jean, F., Chauvaud, L., Clavier, J., Mesnage, V., Ogier, S., 2007. Benthic O-2 distribution and dynamics in a Mediterranean lagoon (Thau, France): An in situ microelectrode study. Estuarine Coastal and Shelf Science 72 (3), 393-405.

Del Giorgio, P.A., Davis, J., 2003. Patterns in dissolved organic matter lability and consumption across aquatic ecosystems. In: Findlay, S.E.G., Sinsabaugh, R.L. (Eds.), Aquatic Ecosystems: Interactivity of Dissolved Organic Matter. Aquatic Ecology Academic Press, San Diego.

Denis, L., Grenz, C., 2003. Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean). Oceanologica Acta 26 (4), 373-389.

Denis, L., Grenz, C., Alliot, E., Rodier, M., 2001. Temporal variability in dissolved inorganic nitrogen fluxes at the sediment-water interface and related annual budget on a continental shelf (NW Mediterranean). Oceanologica Acta 24 (1), 85-97.

Druffel, E.R.M., Bauer, J.E., Griffin, S., 2005. Input of particulate organic and dissolved inorganic carbon from the Amazon to the Atlantic Ocean. Geochem. Geophys. Geosyst. 6.

Epping, E., van der Zee, C., Soetaert, K., Helder, W., 2002. On the oxidation and burial of organic carbon in sediments of the Iberian margin and Nazare Canyon (NE Atlantic). Progress in Oceanography 52 (2-4), 399-431.

Epping, E.H.G., Helder, W., 1997. Oxygen budgets calculated from in situ oxygen microprofiles for Northern Adriatic sediments. Continental Shelf Research 17 (14), 1737-1764.

Faganeli, J., Pezdic, J., Ogorelec, B., Misic, M., Najdek, M., 1994. The origin of sedimentary organic matter in the Adriatic. Continental Shelf Research 14 (4), 365-384.

Forsberg, B.R., Araujolima, C., Martinelli, L.A., Victoria, R.L., Bonassi, J.A., 1993. Autotrophic carbon sources for fish of the Central Amazon. Ecology 74 (3), 643-652.

Forster, S., Glud, R.N., Gundersen, J.K., Huettel, M., 1999. In situ study of bromide tracer and oxygen flux in coastal sediments. Estuarine Coastal and Shelf Science 49 (6), 813-827.

France-Lanord, C., Derry, L.A., 1994. [delta]13C of organic carbon in the Bengal Fan: Source evolution and transport of C3 and C4 plant carbon to marine sediments. Geochimica Et Cosmochimica Acta 58 (21), 4809-4814.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., Maynard, V., 1979. Early Oxidation Of Organic-Matter In Pelagic Sediments Of The Eastern Equatorial Atlantic - Suboxic Diagenesis. Geochimica Et Cosmochimica Acta 43 (7), 1075-1090.

Fry, B., Sherr, E.B., 1984. $\delta^{13}C$ measurements as indicators of carbon flow in marine and fresh-water ecosystems. Contributions in Marine Science 27 (SEP), 13-47.

Galy, V., France-Lanord, C., Beyssac, O., Faure, P., Kudrass, H., Palhol, F., 2007. Efficient organic carbon burial in the Bengal fan sustained by the Himalayan erosional system. Nature 450 (7168), 407-U406.

Gattuso, J.P., Frankignoulle, M., Wollast, R., 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. Annual Review of Ecology and Systematics 29, 405-434.

Gaudy, R., Youssara, F., Diaz, F., Raimbault, P., 2003. Biomass, metabolism and nutrition of zooplankton in the Gulf of Lions (NW Mediterranean). Oceanologica Acta 26 (4), 357-372.

Glud, R.N., Gundersen, J.K., Jorgensen, B.B., Revsbech, N.P., Schulz, H.D., 1994. Diffusive and Total Oxygen-Uptake of deep-sea sediments in the Eastern South-Atlantic ocean - *in situ* and laboratory measurements. Deep-Sea Research Part I-Oceanographic Research Papers 41 (11-12), 1767-1788.

Goni, M.A., Monacci, N., Gisewhite, R., Ogston, A., Crockett, J., Nittrouer, C., 2006. Distribution and sources of particulate organic matter in the water column and sediments of the Fly River Delta, Gulf of Papua (Papua New Guinea). Estuarine Coastal and Shelf Science 69 (1-2), 225-245.

Goni, M.A., Montgomery, S., 2000. Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples. Analytical Chemistry 72 (14), 3116-3121.

Goni, M.A., Ruttenberg, K.C., Eglinton, T.I., 1997. Source and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. Nature 389 (6648), 275-278.

Goni, M.A., Teixeira, M.J., Perkey, D.W., 2003. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). Estuarine Coastal and Shelf Science 57 (5-6), 1023-1048.

Harmelin-Vivien, M., Loizeau, V., Mellon, C., Beker, B., Arlhac, D., Bodiguel, X., Ferraton, F., Hermand, R., Philippon, X., Salen-Picard, C., 2008. Comparison of C and N stable isotope ratios between surface particulate organic matter and microphytoplankton in the Gulf of Lions (NW Mediterranean). Continental Shelf Research 28 (15), 1911-1919.

Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391 (6667), 572-574.

Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., Santos, U.D., 1986a. Compositions and fluxes of particulate organic material in the Amazon River. Limnology and Oceanography 31 (4), 717-738.

Hedges, J.I., Ertel, J.R., Quay, P.D., Grootes, P.M., Richey, J.E., Devol, A.H., Farwell, G.W., Schmidt, F.W., Salati, E., 1986b. Organic ^{14}C in the Amazon River system. Science 231 (4742), 1129-1131.

Hedges, J.I., Keil, R.G., 1995. Sedimentary Organic-Matter Preservation - An Assessment And Speculative Synthesis. Marine Chemistry 49 (2-3), 81-115.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27 (5-6), 195-212.

Hedges, J.I., Oades, J.M., 1997. Comparative organic geochemistries of soils and marine sediments. Organic Geochemistry 27 (7-8), 319-361.

Heip, C.H.R., Goosen, N.K., Herman, P.M.J., Kromkamp, J., Middelburg, J.J., Soetaert, K., 1995. Production and consumption of biological particles in temperate tidal estuaries. Oceanography and Marine Biology, Annual Review 33 (1995), 1–149.

Holstein, J.M., Wirtz, K.W., 2009. Sensitivity analysis of nitrogen and carbon cycling in marine sediments. Estuarine and Coastal Shelf Science 82, 632–644.

Joachimski, M.M., Ostertag-Henning, C., Pancost, R.D., Strauss, H., Freeman, K.H., Littke, R., Damste, J.S.S., Racki, G., 2001. Water column anoxia, enhanced productivity and concomitant changes in delta C-13 and delta S-34 across the Frasnian-Famennian boundary (Kowala Holy Cross Mountains/Poland). Chemical Geology 175 (1-2), 109-131.

Lansard, B., Charmasson, S., Gasco, C., Anton, M.P., Grenz, C., Arnaud, M., 2007. Spatial and temporal variations of plutonium isotopes (Pu-238 and Pu-239,Pu-240) in sediments off the Rhone River mouth (NW Mediterranean). Science of the Total Environment 376 (1-3), 215-227.

Lansard, B., Rabouille, C., Denis, L., Grenz, C., 2005. In situ oxygen uptake rates by coastal sediments under the influence of the Rhone River (NW Mediterranean Sea). Symposium on Coastal Ecosystem Responses to Changing Nutrient Inputs from Large Temperate and Sub-Tropical Rivers. Pergamon-Elsevier Science Ltd, Fujian, PEOPLES R CHINA, pp. 1501-1510.

Leithold, E.L., Hope, R.S., 1999. Deposition and modification of a flood layer on the northern California shelf: lessons from and about the fate of terrestrial particulate organic carbon. Marine Geology 154 (1-4), 183-195.

Lisitsyn, A.P., 1995. The marginal filter of the ocean. Oceanology 34 (5), 671-682.

McKee, B.A., Aller, R.C., Allison, M.A., Bianchi, T.S., Kineke, G.C., 2004. Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: benthic boundary layer and seabed processes. Continental Shelf Research 24 (7-8), 899-926.

Meade, R.H., 1996. River-sediment inputs to major deltas. In: Milliman, J.D., Haq, B.U. (Eds.), Sea-Level Rise and Coastal Subsidence: Causes, Consequences and Strategies. Kluwer Academic Publishers, pp. 63-85.

Meadows, D.H., Meadows, D.L., Randers, J., Behrens, W.W., 1972. The Limits to growth. A report for the Club of Rome's project on the predicament for mankind. . Universe Books, New York.

Megens, L., van der Plicht, J., de Leeuw, J.W., 2001. Temporal variations in C-13 and C-14 concentrations in particulate organic matter from the southern North Sea. Geochimica Et Cosmochimica Acta 65 (17), 2899-2911.

Meybeck, M., 1982. Carbon, Nitrogen and Phosphorus transport by world rivers. American Journal of Science 282 (4), 401-450.

Millot, C., 1990. The Gulf Of Lions Hydrodynamics. Continental Shelf Research 10 (9-11), 885-894.

Miralles, J., Radakovitch, O., Aloisi, J.C., 2005. Pb-210 sedimentation rates from the Northwestern Mediterranean margin. Marine Geology 216 (3), 155-167.

Monaco, A., Courp, T., Heussner, S., Carbonne, J., Fowler, S.W., Deniaux, B., 1990. Seasonality and composition of particulate fluxes during ECOMARGE I, western Gulf of Lions. Continental Shelf Research 10 (9-11), 959-987.

Monaco, A., de Madron, X.D., Radakovitch, O., Heussner, S., Carbonne, J., 1999. Origin and variability of downward biogeochemical fluxes on the Rhone continental margin (NW Mediterranean). Deep-Sea Research Part I-Oceanographic Research Papers 46 (9), 1483-1511.

Mook, W.G., van der Plicht, J., 1999. Reporting C-14 activities and concentrations. Radiocarbon 41 (3), 227-239.

Morse, J.W., Rowe, G.T., 1999. Benthic biogeochemistry beneath the Mississippi River plume. Estuaries 22 (2A), 206-214.

Nagao, S., Usui, T., Yamamoto, M., Minagawa, M., Iwatsuki, T., Noda, A., 2005. Combined use of delta C-14 and delta C-13 values to trace transportation and deposition processes of terrestrial particulate organic matter in coastal marine environments. Chemical Geology 218 (1-2), 63-72.

Pakulski, J.D., Benner, R., Whitledge, T., Amon, R., Eadie, B., Cifuentes, L., Ammerman, J., Stockwell, D., 2000. Microbial metabolism and nutrient cycling in the Mississippi and Atchafalaya River plumes. Estuarine Coastal and Shelf Science 50 (2), 173-184.

Palmer, S.M., Hope, D., Billett, M.F., Dawson, J.J.C., Bryant, C.L., 2001. Sources of organic and inorganic carbon in a headwater stream: Evidence from carbon isotope studies. Biogeochemistry 52 (3), 321-338.

Pomeroy, L.R., Williams, P.J.I., Azam, F., Hobbie, J.E., 2007. The Microbial Loop. Oceanography 20 (2), 28-33.

Pont, D., Simonnet, J.P., Walter, A.V., 2002. Medium-term changes in suspended sediment delivery to the ocean: Consequences of catchment heterogeneity and river management (Rhone River, France). Estuarine Coastal and Shelf Science 54 (1), 1-18.

Rabouille, C., Denis, L., Dedieu, K., Storac, G., Lansard, B., Grenz C., 2003. Oxygen demand in coastal marine sediments: comparing in situ microelectrodes and laboratory core incubations. Journal of Experimental Marine Biology and Ecology 285–286, 49– 69

Rabouille, C., Conley, D.J., Dai, M.H., Cai, W.J., Chen, C.T.A., Lansard, B., Green, R., Yin, K., Harrison, P.J., Dagg, M., McKee, B., 2008. Comparison of hypoxia among four river-dominated ocean margins: The Changjiang (Yangtze), Mississippi, Pearl, and Rhone rivers. Continental Shelf Research 28 (12), 1527-1537.

Rau, G., 1978. C-13 DEPLETION IN A SUBALPINE LAKE - CARBON FLOW IMPLICATIONS. Science 201 (4359), 901-902.

Raven, J.A., Falkowski, P.G., 1999. Oceanic sinks for atmospheric CO2. Plant Cell and Environment 22 (6), 741-755.

Raymond, P.A., Bauer, J.E., 2001a. Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. Nature 409 (6819), 497-500.

Raymond, P.A., Bauer, J.E., 2001b. Use of C-14 and C-13 natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis. Organic Geochemistry 32 (4), 469-485.

Revsbech, N.P., Jørgensen, B.B., Blackburn, T.H., 1980. Oxygen in the sea bottom measured with a microelectrode. Science 207, 1355-1356.

Roussiez, V., Ludwig, W., Monaco, A., Probst, J. L., Bouloubassi, I., Buscail, R., and Saragoni, G.: Sources and sinks of sediment-bound contaminants in the gulf of lions (nw mediterranean sea): A multi-tracer approach, Cont. Shelf Res., 26, 1843-1857, 2006.

Sempere, R., Charriere, B., Van Wambeke, F., Cauwet, G., 2000. Carbon inputs of the Rhone River to the Mediterranean Sea: Biogeochemical implications. Global Biogeochemical Cycles 14 (2), 669-681.

Siegenthaler, U., Sarmiento, J.L., 1993. Atmospheric carbon-dioxide and the ocean. Nature 365 (6442), 119-125.

Smith, B.N., Epstein, S., 1971. 2 Categories of 13C/12C ratios for higher plants. Plant Physiology 47 (3), 380-&.

Smith, D.C., Simon, M., Alldredge, A.L., Azam, F., 1992. Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature 359 (6391), 139-142.

Smith, S.V., Hollibaugh, J.T., 1993. Coastal Metabolism And The Oceanic Organic-Carbon Balance. Reviews Of Geophysics 31 (1), 75-89.

Soetaert, K., Herman, P.M.J., Middelburg, J.J., 1996. A model of early diagenetic processes from the shelf to abyssal depths. Geochimica Et Cosmochimica Acta 60 (6), 1019-1040.

Sommerfield, C.K., Nittrouer, C.A., 1999. Modern accumulation rates and a sediment budget for the Eel shelf: a flood-dominated depositional environment. Marine Geology 154 (1-4), 227-241.

Tengberg, A., Almroth, E., Hall, P., 2003. Resuspension and its effects on organic carbon recycling and nutrient exchange in coastal sediments: in situ measurements using new experimental technology. Journal of Experimental Marine Biology and Ecology 285– 286, 119–142.

Tesi, T., Langone, L., Goni, M.A., Miserocchi, S., Bertasi, F., 2008. Changes in the composition of organic matter from prodeltaic sediments after a large flood event (Po River, Italy). Geochimica Et Cosmochimica Acta 72 (8), 2100-2114.

Tesi, T., Miserocchi, S., Goni, M.A., Langone, L., 2007a. Source, transport and fate of terrestrial organic carbon on the western Mediterranean Sea, Gulf of Lions, France. Marine Chemistry 105 (1-2), 101-117.

Tesi, T., Miserocchi, S., Goni, M.A., Langone, L., Boldrin, A., Turchetto, M., 2007b. Organic matter origin and distribution in suspended particulate materials and surficial sediments from the western Adriatic Sea (Italy). Estuarine Coastal and Shelf Science 73 (3-4), 431-446.

Thamdrup; B., Hansen, J.W., Jörgensen, B.B., 1998. Temperature dependence of aerobic respiration in a coastal sediment. FEMS Microbiology Ecology 25, 189-200.

Ulses, C., Estournel, C., de Madron, X. D., and Palanques, A.: Suspended sediment transport in the gulf of lions (nw mediterranean): Impact of extreme storms and floods, Cont. Shelf Res., 28, 2048-2070, 10.1016/j.csr.2008.01.015, 2008.

Vallières, C., Retamal, L., Ramlal, P., Osburn, C.L., Vincent, W.F., 2008. Bacterial production and microbial food web structure in a large arctic river and the coastal Arctic Ocean. Journal of Marine Systems 74 (3-4), 756-773.

Wang, X.C., Druffel, E.R.M., Griffin, S., Lee, C., Kashgarian, M., 1998. Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern Pacific Ocean. Geochimica Et Cosmochimica Acta 62 (8), 1365-1378.

Wheatcroft, R.A., Borgeld, J.C., 2000. Oceanic flood deposits on the northern California shelf: large-scale distribution and small-scale physical properties. Continental Shelf Research 20 (16), 2163-2190.

Williams, P.M., Robertson, K.J., Soutar, A., Griffin, S.M., Druffel, E.R.M., 1992. Isotopic Signatures (C-14, C-13, N-15) As Tracers Of Sources And Cycling Of Soluble And Particulate Organic-Matter In The Santa-Monica Basin, California. Progress in Oceanography 30 (1-4), 253-290.

Wright, L.D., Friedrichs, C.T., 2006. Gravity-driven sediment transport on continental shelves: A status report. Continental Shelf Research 26 (17-18), 2092-2107.

CHAPITRE 2. SEASONAL DYNAMICS OF CARBON RECYCLING IN COASTAL SEDIMENTS INFLUENCED BY RIVERS: ASSESSING THE IMPACT OF FLOOD INPUTS IN THE RHÔNE RIVER PRODELTA.

CHAPITRE 2. SEASONAL DYNAMICS OF CARBON RECYCLING IN COASTAL SEDIMENTS INFLUENCED BY RIVERS: ASSESSING THE IMPACT OF FLOOD INPUTS IN THE RHÔNE RIVER PRODELTA.

C. Cathalot [1], C. Rabouille[1], L. Pastor[2], B. Deflandre[2, 3], E. Viollier[2], R. Buscail[4], C. Treignier[1], A. Pruski[5]

[1]{Laboratoire des Sciences du climat et de l'Environnement, Gif-sur-Yvette, France}
[2]{Laboratoire de Geochimie des Eaux, IPGP & Université Paris Diderot, Paris, France}
[3]{Laboratoire Environnements et Paléoenvironnements Océaniques, Université Bordeaux 1, France}
[4]{Centre de Formation et de Recherche sur l'Environnement Marin, Perpignan, France}
[5]{Laboratoire d'Océanographie Biologique de Banyuls, Banyuls-sur-mer, France}
Correspondence to: C. Cathalot (cecile.cathalot@lsce.ipsl.fr)

Keywords: Sediment oxygen uptake rates, carbon recycling, Rhône River, Flood deposit, coastal sediments

Submitted to: Biogeosciences

2.1 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 Uptake (DOU) rates did not show any significant differences except for shallowest organic rich stations, underlining both the need for accurate ship positioning and the importance of the Diffusive Boundary Layer in the assessment of benthic fluxes in these hydrodynamically active and shallow coastal areas.

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) rates achieved 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 30cm 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.

2.2 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.*, 2003;Glud *et al.*, 2000;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 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;De Madron *et al.*, 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 (Chla) 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 flood inputs and seasonal changes on the prodelta filtering capacity and the dynamics of oxygen and organic carbon in sediments after flood deposition.

2.3 MATERIAL AND METHODS

2.3.1 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 km², a mean water flow of 1700 m^3 s^{-1}, and an annual particulate organic carbon discharge of 19.2 ± 6 10^4 tC/an (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 60m depth (Wright and Friedrichs, 2006). Net sedimentation rates in the prodelta are up to 50cm 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 20km (Miralles *et al.*, 2005).

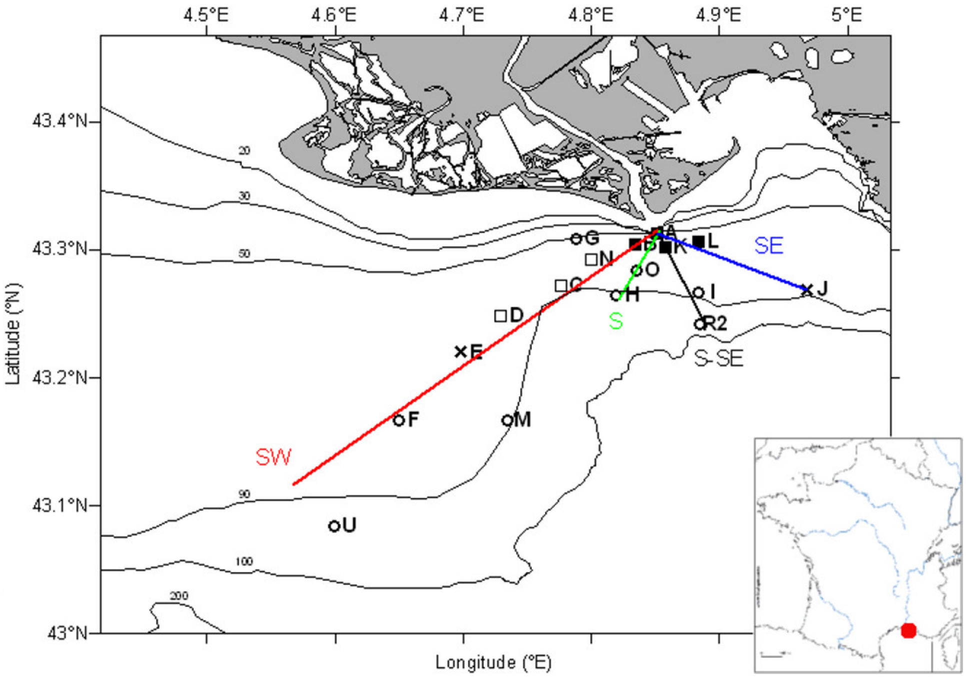

Figure 1. Map of the Rhône delta indicating the locations of sampling stations. Black squares indicate stations sampled the four cruises. Empty squares indicate stations sampled three times. Black crosses indicate stations sampled twice. Empty circles indicate stations sampled once (April 2007).

2.3.2 Field sampling work and sampling procedures

Sediment samples were collected during four cruises in April 2007, September 2007, June 2008 and December 2008 (Figure 1). In April 2007, 16 stations were sampled off 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 (Figure 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} (Figure 2).

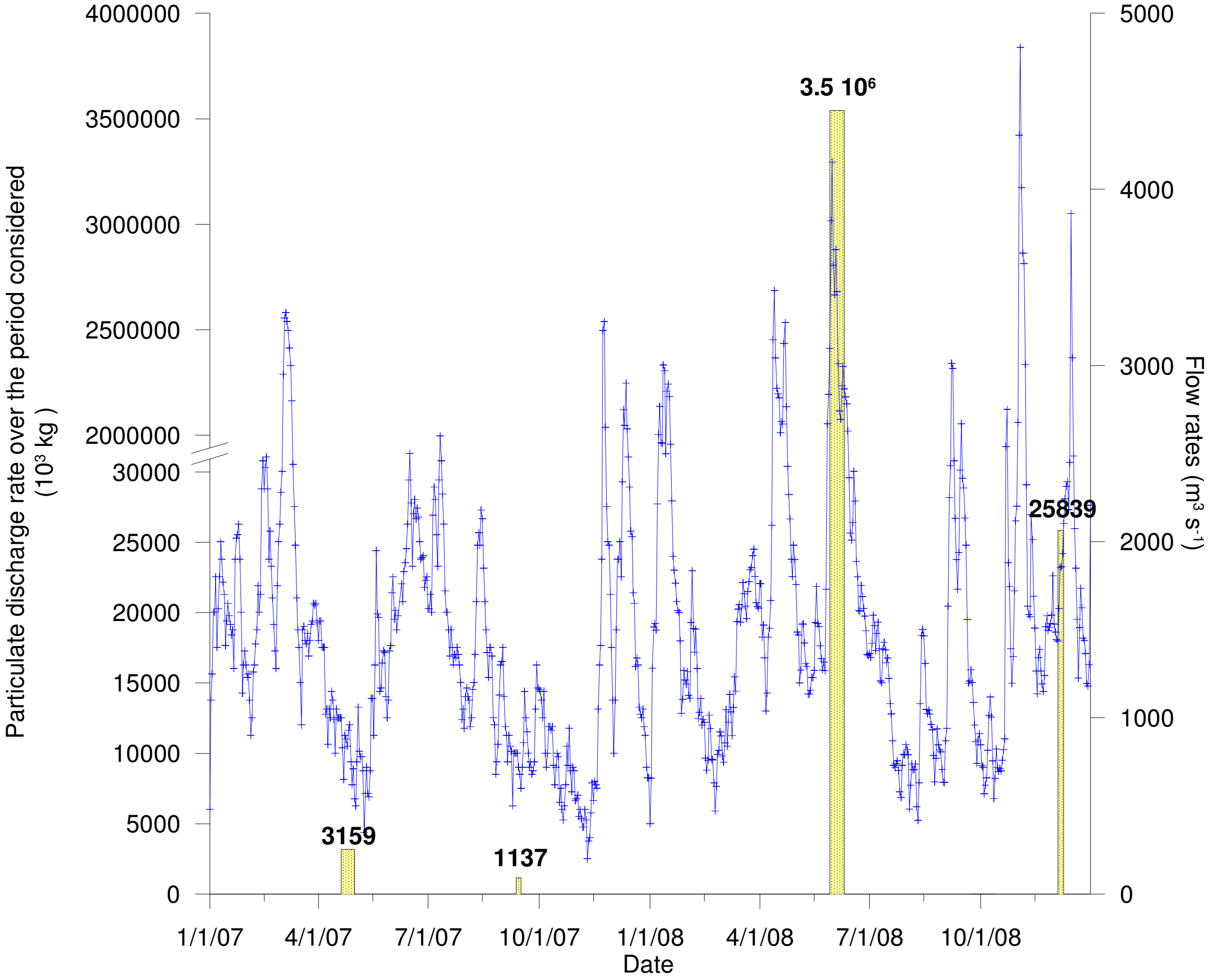

Figure 2. Mean daily flow and particulate discharge rates of the Rhône River. The integrated SPM amount delivered during the sampling cruises period are indicated in yellow.

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 50ml 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 (~ 2 weeks) 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 meters above bottom by a Niskin bottle for determination of temperature and dissolved oxygen (Table 1).

2.3.3 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%.

2.3.4 Pigment analysis

Surface sediments (0-0.5cm 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 (Chla) 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.

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	Tbw (°C)	$[O_2]$bw (µM)	*m* coeff	Mean diameter (µm)	%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	-

2.3.5 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.

2.3.6 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.

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 (50-100µm 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 <10 s, 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 x 3 mm 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). 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):

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

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:

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

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).

2.3.7 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 (cm² 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.

2.3.8 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 hours, 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.

2.3.9 Statistical calculation

In order to assess statistical differences between in situ vs. ex situ DOU and 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.

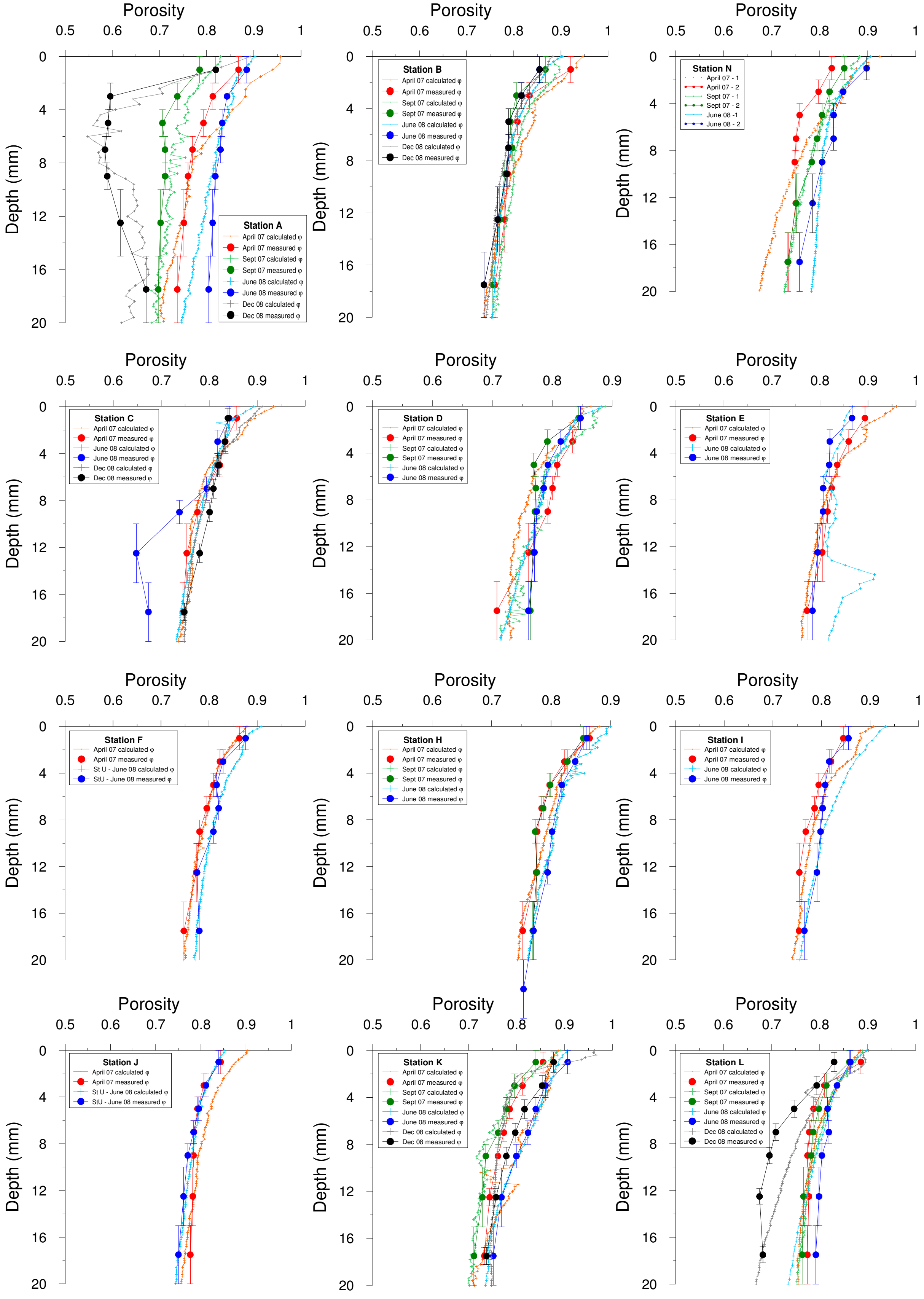

Figure 3. Porosity profiles for all stations during all cruises. Data points indicate measured values while thin curves represent the calculation based on resistivity measurements and Archie's law (see text for details).

2.4 RESULTS

2.4.1 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 (Figure 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 Figure 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).

2.4.2 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 (Figure 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; Figure 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 %.

2.4.3 Surface sediment pigment content

Chlorophyll a (Chla) content of surficial sediments in the Rhône River prodelta are available for April 2007, September 2007 and June 2008 cruises. Chla contents displayed an exponential decrease with distance from the river mouth ($r^2 > 0.7178$, $p < 0.01$) with ighest values located in the prodelta (Figure 5). Chla 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, Chla content were around 5.33 ± 3.28 µg g^{-1} d.w. near the river outlet (stations A, B) decreasing to low values about 1.73 ± 0.86 µg 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 µg g^{-1} d.w. and lower concentration in shelf sediments with an average of 1.08 ± 0.94 µg g^{-1} d.w (Figure 5).

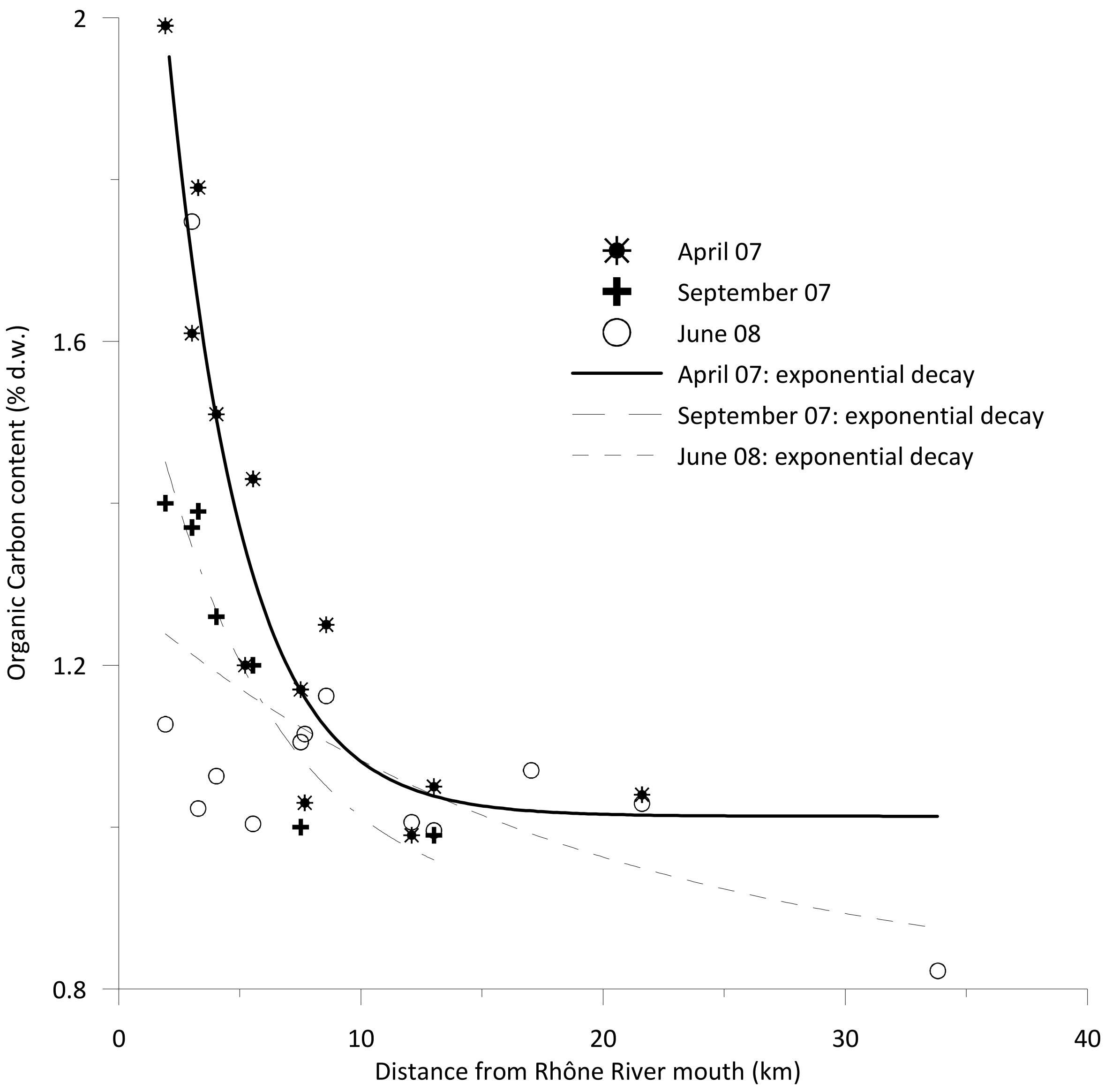

Figure 4. Organic carbon (OC) content in surficial sediments as a function of distance from the river outlet for April 07 (black stars ✷), September 07 (black crosses ✚) and June 08 cruises (empty circles ○). Exponential decays of OC with distance in April and September 2007 were significant ($r^2 = 0.90$, and $r^2 = 0.88$ respectively) but not in June 08.

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%	-		-	-

2.4.4 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 (Figure 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 ± 0.3 mm in front of the Rhône River mouth to 12.7 ± 1.7 mm 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 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 ~16 $\text{mmolO}_2\ \text{m}^{-2}\ \text{d}^{-1}$ close to the river mouth (stations A and B) to ~3 $\text{mmolO}_2\ \text{m}^{-2}\ \text{d}^{-1}$ 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 $\text{mmolO}_2\ \text{m}^{-2}\ \text{d}^{-1}$ near the Rhône river mouth (stations A, B, K) to approx. 4.5 $\text{mmolO}_2\ \text{m}^{-2}\ \text{d}^{-1}$ 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).

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

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 (Figure 7a). This tendency is clearly displayed when plotting the DOU rates as a function of distance to station A for the April 2007 cruise (Figure 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 (Figure 7b). In contrast, the DOU rates obtained in June 2008 were much lower in the prodelta and homogeneous over the shelf up to a distance of 10 km from the outlet ($p > 0.05$; Figure 7b). As the SW direction seems to be a preferential trend, plotting the South-West transect for all cruises reveals different gradient over time (Figure 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 $9\ 10^{-2}$ mmol O_2 L^{-1} h^{-1} (Figure 10) compared to 1.1 ± 0.3 mmol O_2 L^{-1} h^{-1} for normal conditions.

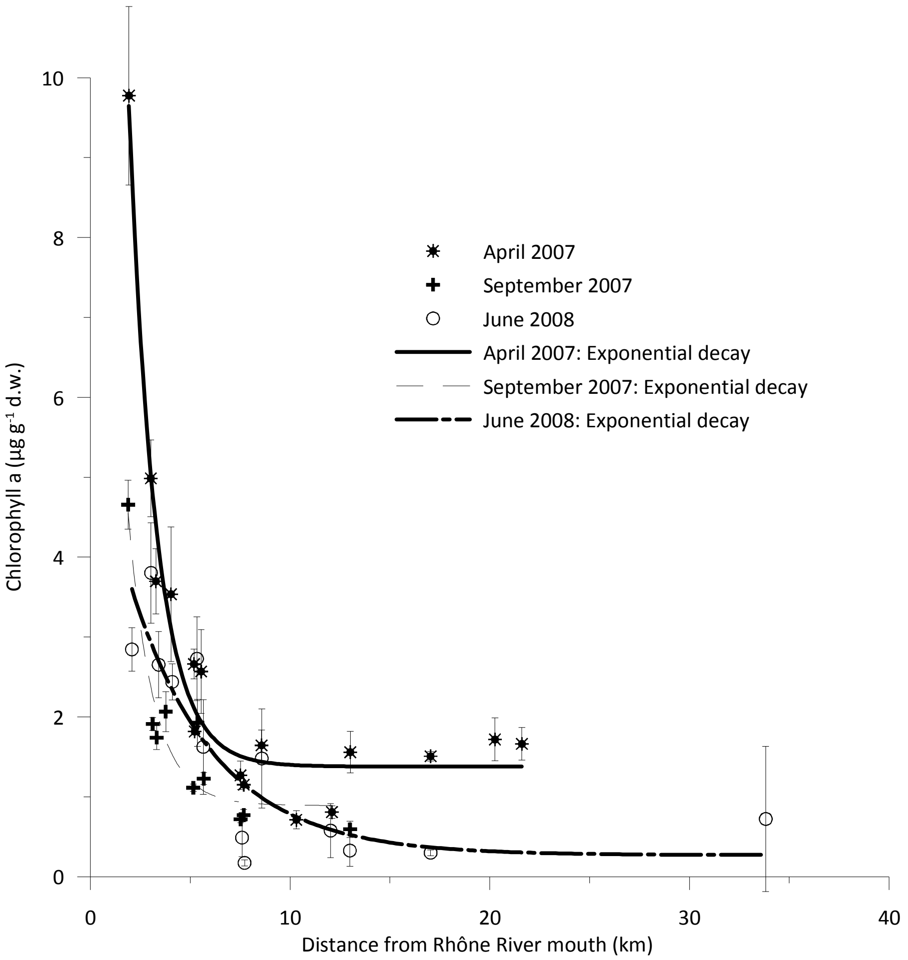

Figure 5. Surface sediments Chla contents as a function of distance from the river outlet: ✱April 07, ✚September 07 and ○ June 08.

2.5 DISCUSSION

2.5.1 Formation factor F and porosity relationship

In our study, we were able to derive the formation factor F and compare it to high resolution porosity measurements according to equation $F = \phi^{-m}$ (1). A coefficient *a* can be added but, consistently with theory, it is usually close to unity and therefore set to 1 (Boudreau, 1996; Iversen and Jorgensen, 1993; Maerki *et al.*, 2004). On the contrary, there is a large discrepancy in *m* values reported in literature. Several authors (Andrews and Bennett, 1981; Glud *et al.*, 1995; Reimers *et al.*, 1992; Ullman and Aller, 1982) have reported *m* values close or superior to 3 for marine muddy sediments or sediments with porosities higher than 0.7, just like ours. In this study, we found *m* values around 2 (average: 2.24) with ~20% values below 2 and only a single one reaching 3. This range of exponents corresponds to the lower end of *m* values reported for sand and sandstones. However, they are consistent with recent results for sediments from the North Atlantic (Sauter *et al.*, 2001) and a high porosity fresh water lake (Maerki *et al.*, 2004). Additional factors than porosity may influence resistivity measurements and thus induce changes in *m* values: grain size, salinity, particle shape, packing of the sediment, calcite fraction (Maerki *et al.*, 2004).

A direct consequence of *m* estimation relies on the DOU rates calculation. Many authors derivate O_2 sediment fluxes from the first Fick's law or use the PROFILE software (Berg *et al.*, 1998) expressing the sediment diffusion coefficient Ds by one of the following equations:

- $D_S = D_0\phi$ (2) or $D_S = D_0\phi^2$ (3) Archie's law with *m* = 2 or 3 (Ullman and Aller, 1982)
- $D_S = \frac{D_0}{1+3(1-\phi)}$ (4) (Iversen and Jorgensen, 1993)

(Cai *et al.*, 1995; Dedieu *et al.*, 2007; Denis and Grenz, 2003; Denis *et al.*, 2001; Epping and Helder, 1997; Glud *et al.*, 1994)

In our case, calculating DOU from Fick's law with m set to 3 instead of its real value leads to a DOU lower by 8% in average ($r^2 = 0.9671$). The best concordance was achieved between DOU $_{Ds(m)}$ (i.e. calculated with the actual m) and DOU calculated with D_s from eq. (4) (DOU $_{Ds(m)}$ = 0.9857 DOU $_{Ds\ eq.\ (4)}$ + 0.2957; $r^2 = 0.9795$). Therefore, we recommend using eq. (4) to assess D_s in order to avoid any misestimation of fluxes and achieve good agreement between Fick and PROFILE values. In order to avoid any bias, both in situ and ex situ DOU rates were calculated from the Fick's first law taking Ds as eq. (4).

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

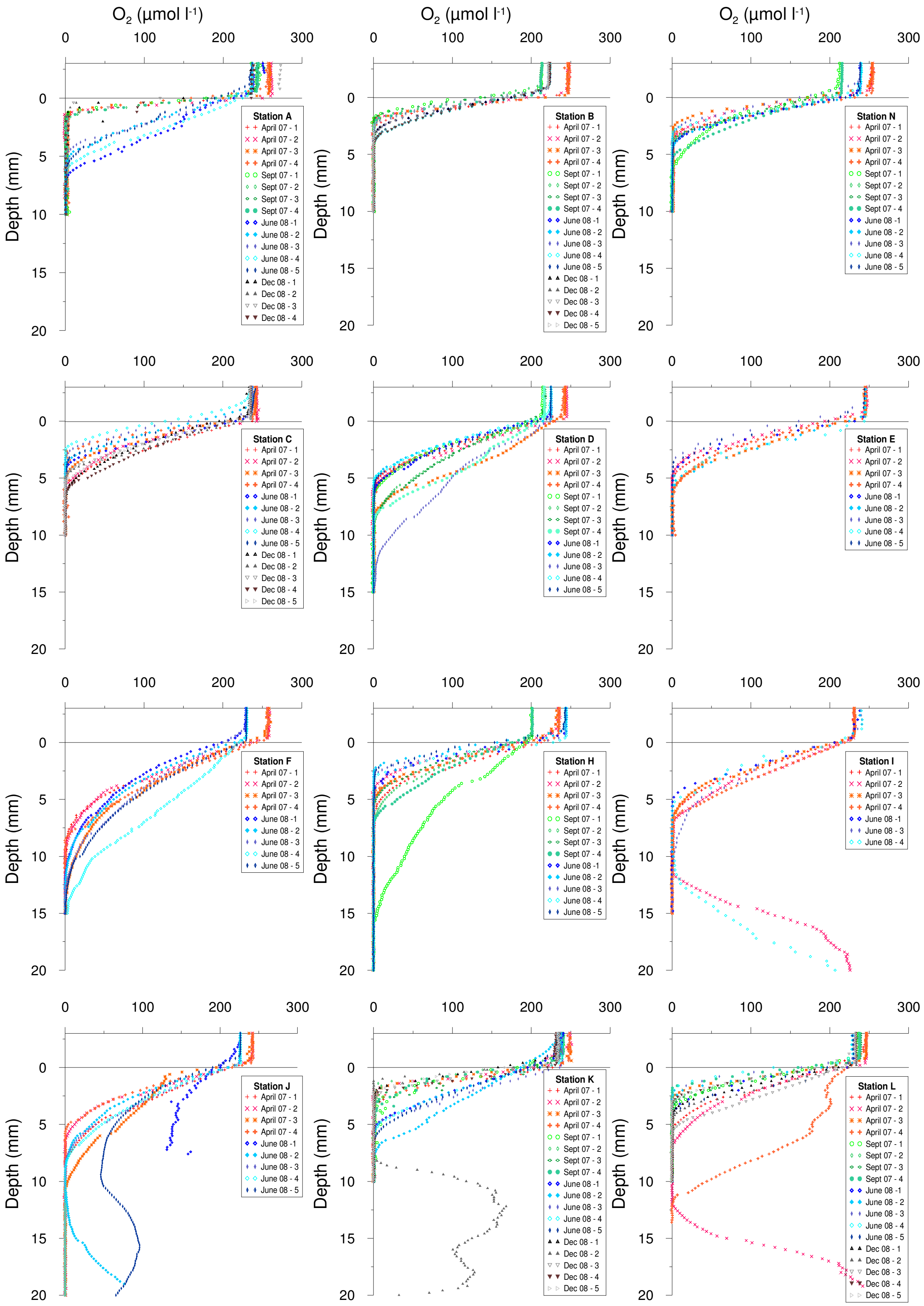

Figure 6. In situ Oxygen microprofiles in the sediment at all station investigated for April 2007 (red), September 2007 (green), June 2008 (Blue) and December 2008 (brown).

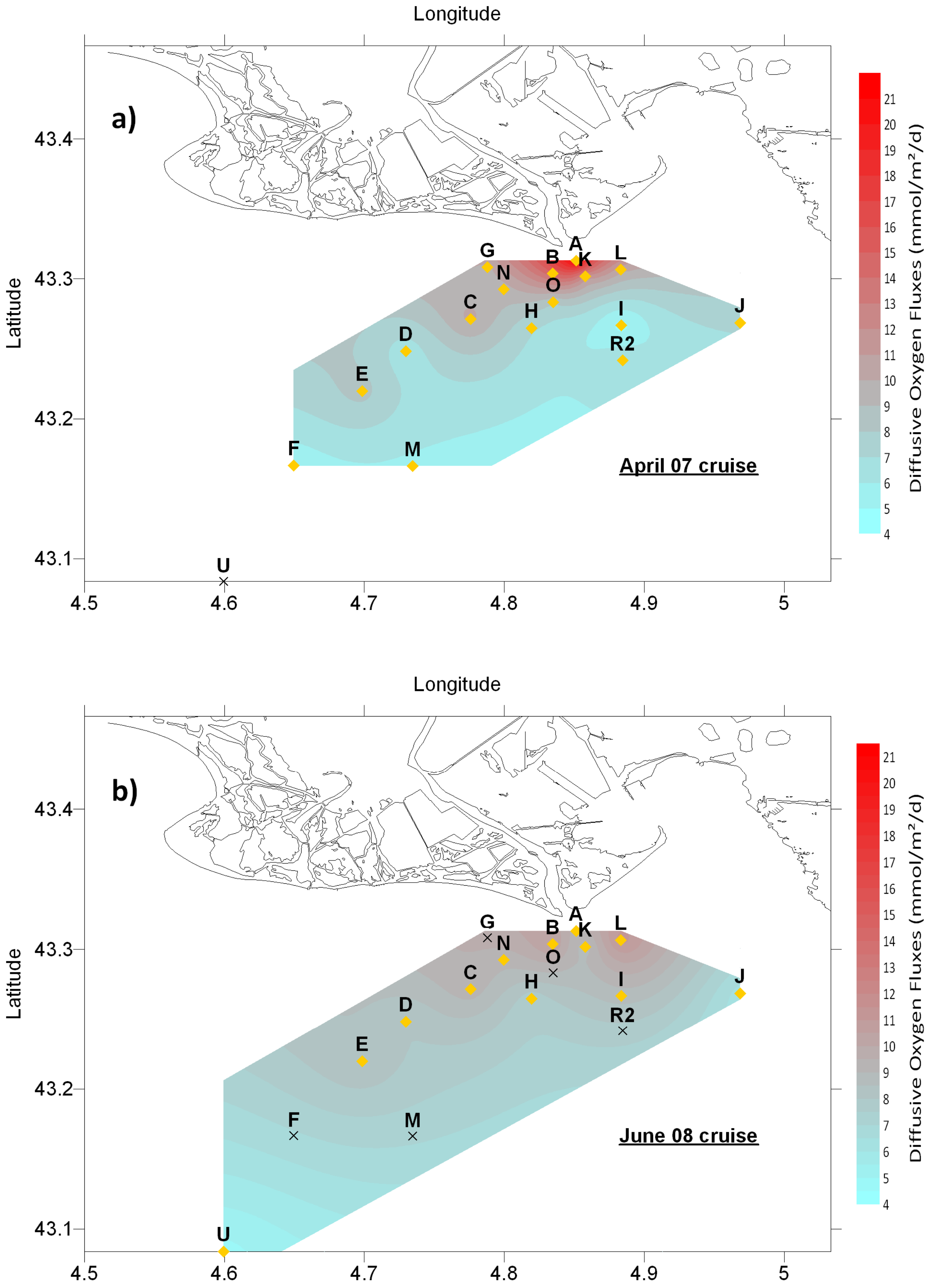

Figure 7. Spatial distribution of Diffusive Oxygen Uptakes Rates in sediments during Apr-07 “normal condition” (a) and June-08 “flood condition”(b). × indicate stations which were not sampled during his cruise.

2.5.2 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 Rhone 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 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 meters, the most affected stations being located at the shallowest and warmest sites.

The most affected stations are located at the Rhone 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.

2.5.3 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 (Figure 7a) consistent with the one previously described by Lansard *et al.* (2009). High sediment oxygen consumption were found in a radius of 8km from the vicinity of the Rhône river mouth with values from 10 to 20 mmolO_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 mmolO_2 m^{-2} d^{-1} near the Mississippi River mouth down to 2 mmolO_2 m^{-2} d^{-1} further on the Gulf of Mexico shelf while Alongi (1995) measured fluxes ranging from 18 – 47 mmolO_2 m^{-2} d^{-1} in the Gulf of Papua influenced by river inputs.

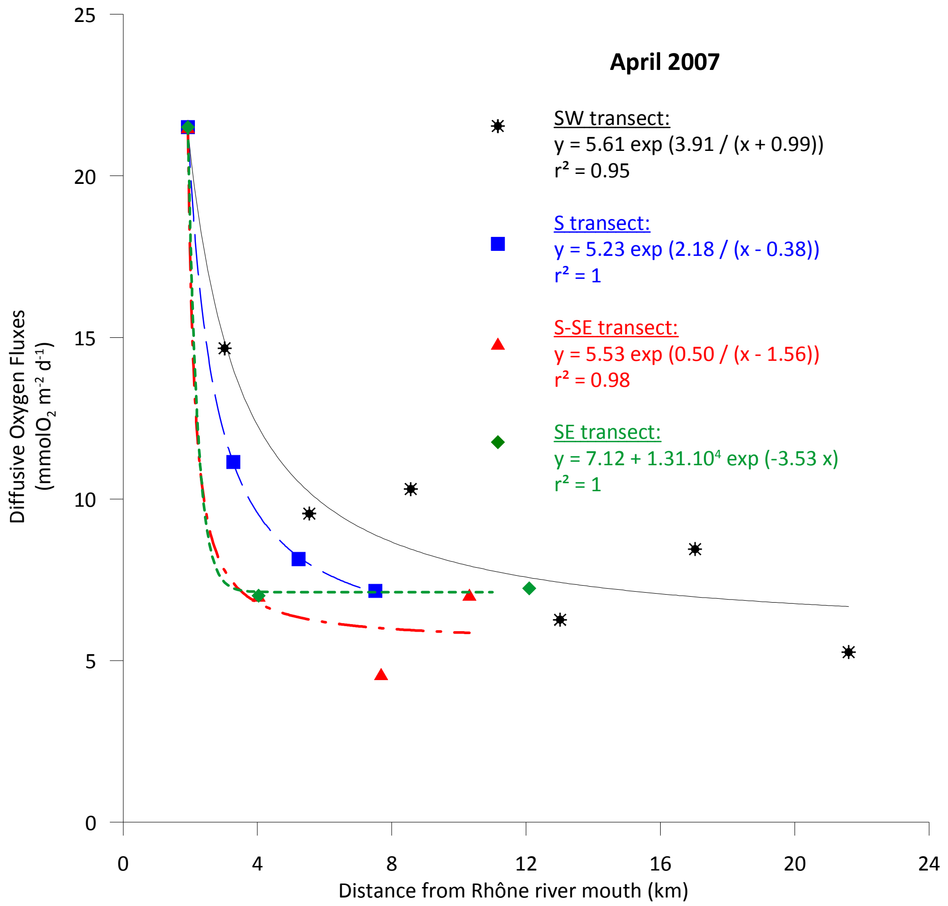

Figure 8. Decrease of DOU rates with distance from station A in April 2007 for different transects: ✱ South West SW (stations A, B, N, C, D, E, F, U - black plain line), ■ South S (stations A, K, O, H – blue dashed line), ◆ South-South-East S-SE (stations A, L, I, R2 – red dotted-dashed line) and ▲ South-East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

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 (Figure 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 δ^{13}C signature, high OC and phytodetritus contents (indicated by Chla concentrations, Figure 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 Chla. 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 ~80 10^3 tons of C and an average flood deposit of 30 cm, as recorded at a station located at 45 meters depth (Figure 11). Consistently with local hydrodynamics features, the Rhône River material settled near the river mouth (as much as 60cm 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 cm y^{-1} 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).

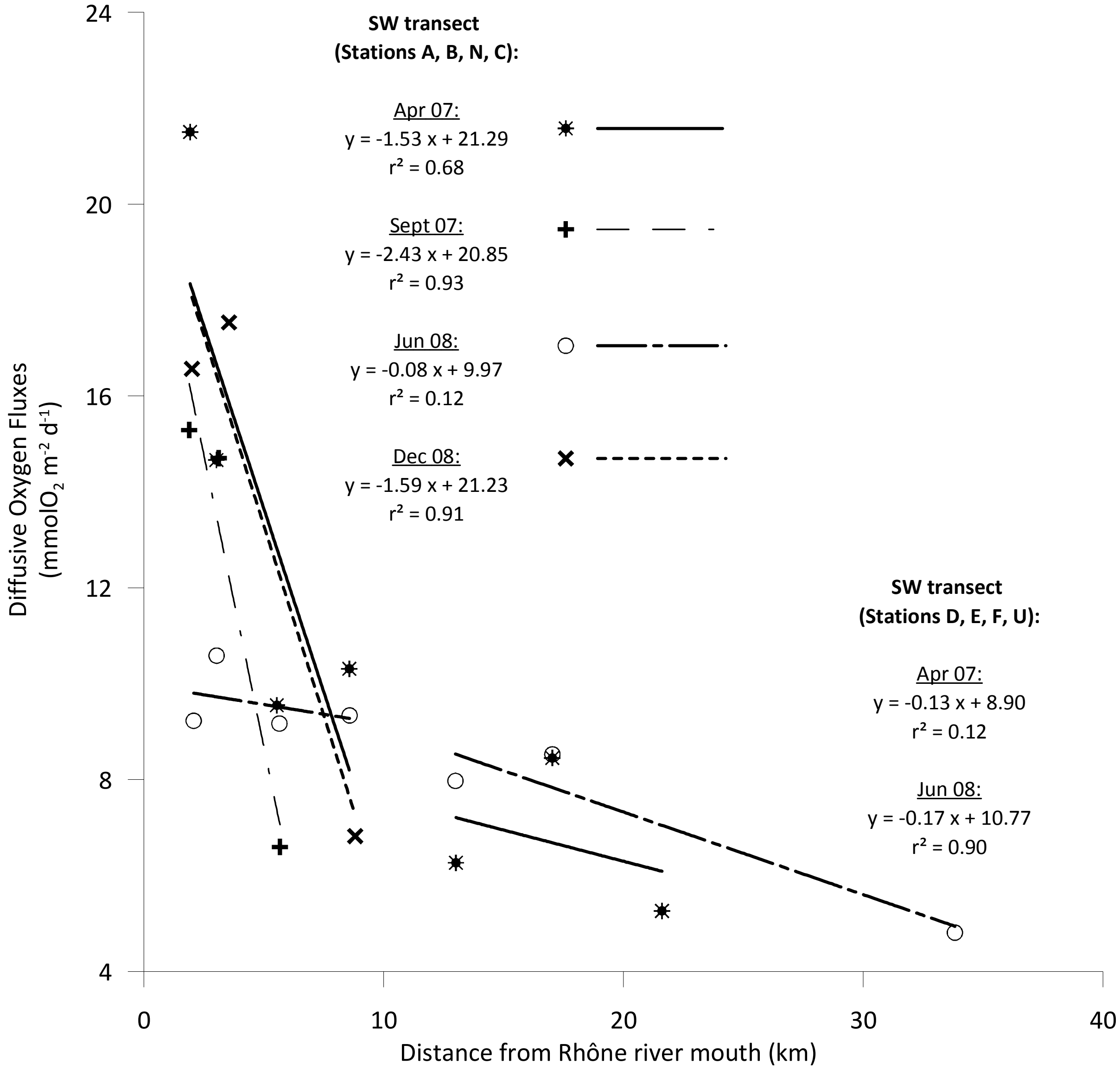

Figure 9. Seasonal variations of South West DOU gradient. Stations close to the river outlet (A, B, N, C – left part of the chart) were separated from stations offshore (D, E, F, U – right part of the chart).

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 (Figure 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 (Figure 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 Chla (3 vs. 10 µg 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 ‰), compare to the normal hydrological regimes where POC content in the river is 3.5%, with $\Delta^{14}C$ ~ 100 ‰ and $\delta^{13}C$ ~ -27 ‰ signatures (Cathalot *et al*, Chapitre 3). 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 Chla 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 µm 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 (Figure 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 (Figure 11): slight compaction (from 30 cm thickness to ~25cm) 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 visible mainly due to further November flood, which brought organic-rich material (6%).

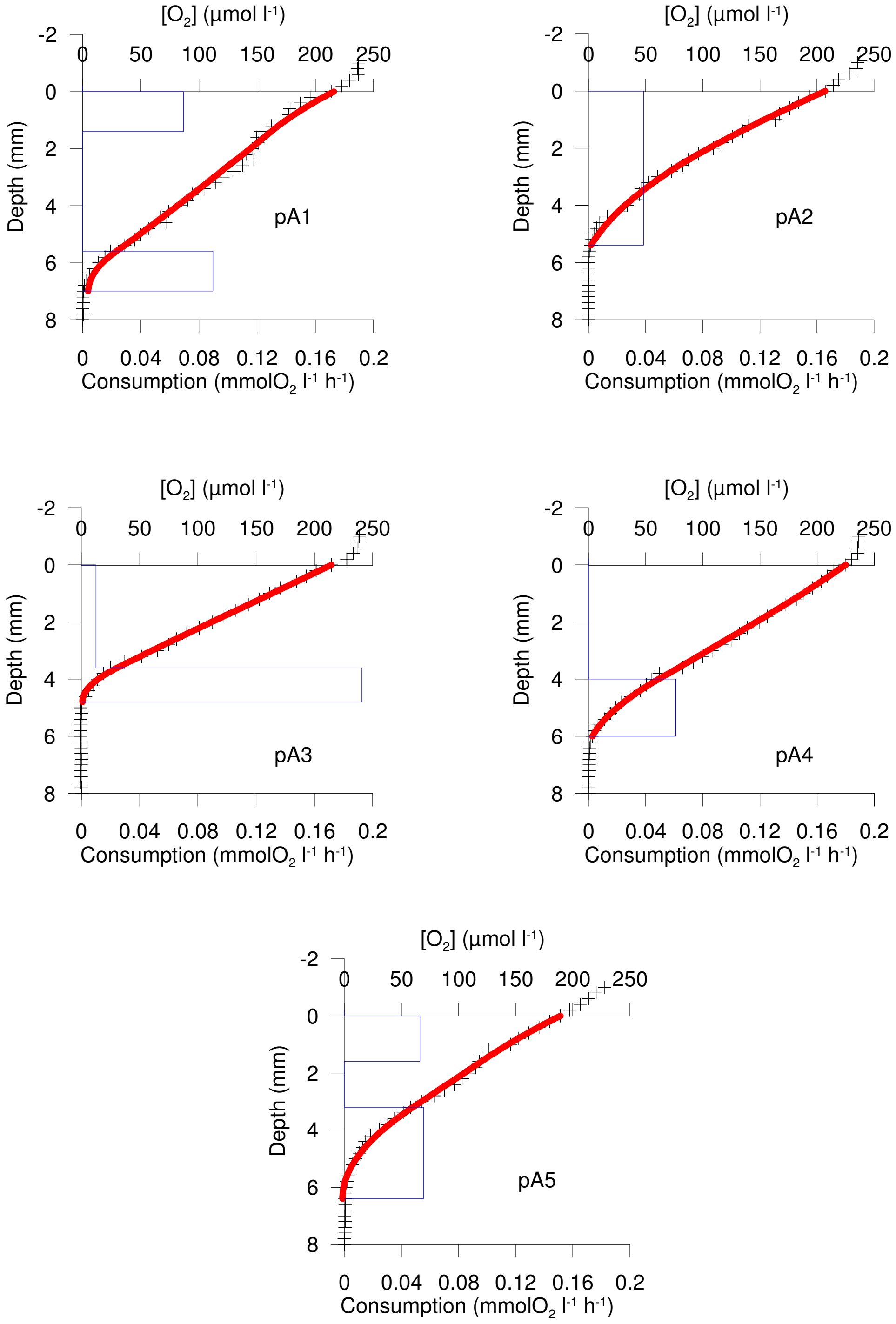

Figure 10. Consumption pattern in the sediment at station A in June 2008 for different profiles obtained during the same deployment.

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 (Figure 9). Oxygen consumption in station A sediment during the flood was around 9 10^{-2} mmol O_2 L^{-1} h^{-1} (Figure 10). Considering a mean oxygen concentration among the sediment in the new deposit of 300 µmol L^{-1}, it would only take 3.3 hours 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 $\tau = \frac{L^2}{2\,D_s} \approx \frac{30^2}{10^{-5}} \approx 1040\ \text{days}$ 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).

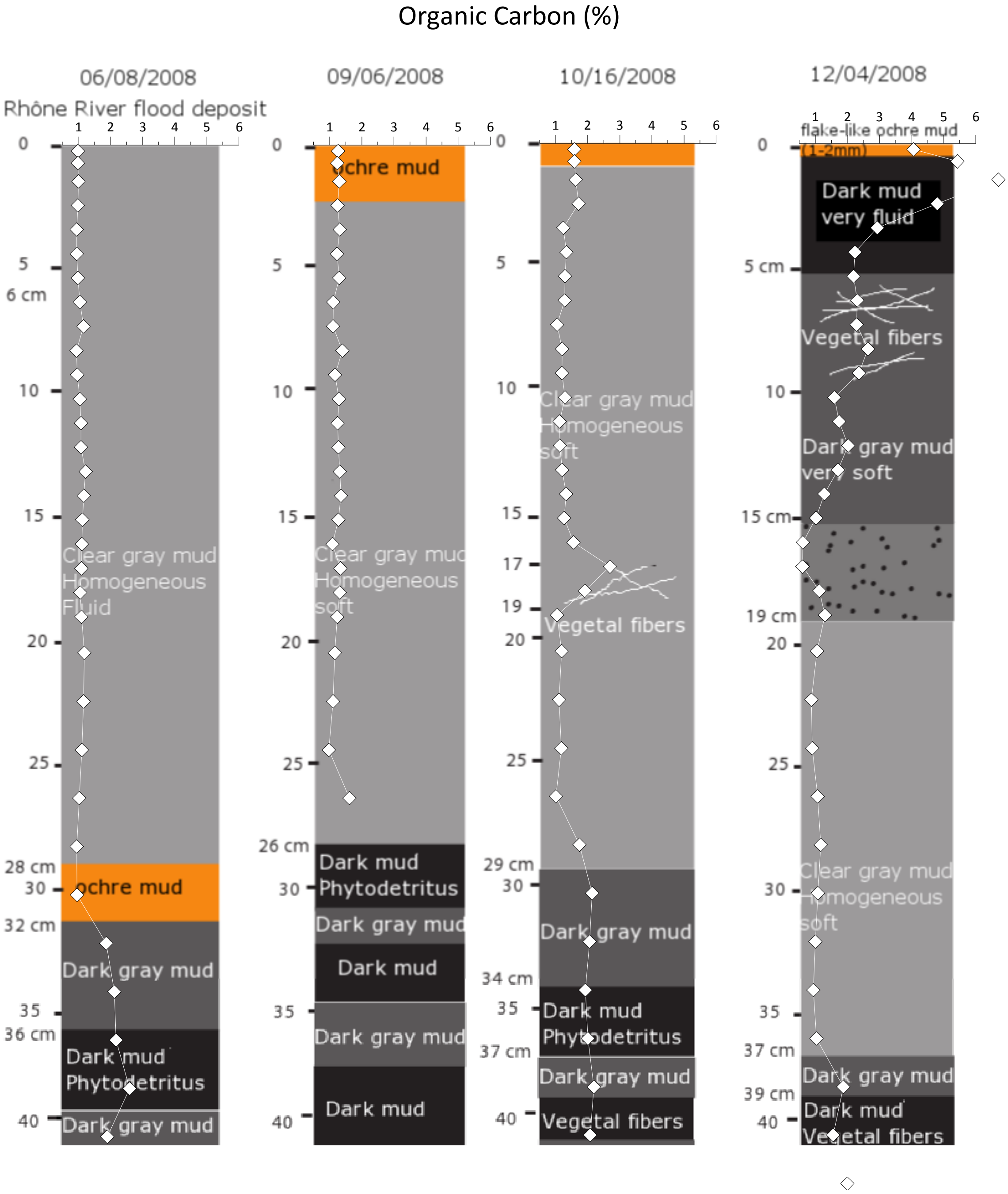

Figure 11. The evolution of the flood deposit of June 2008 at a depth of 45 meters, 2.7 km of the river mouth (visual observations a few months after the flood event).

2.6 CONCLUSION

This paper describes the seasonal variability of organic matter mineralization in sediments from the Rhone 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 8km from the river outlet. This large mineralization is linked to substantial inputs of reactive terrestrial organic matter indicated by the presence of Chla at the river outlet.

During major flood deposition (average of 30cm), 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.

2.7 ACKNOWLEDGEMENTS

We thank the captains and crews of the R.V. Tethys II for their help in sea work during the four sea expeditions of this project. We would like to thank B. Bombled, B. Lansard, M. Desmalades, K. Escoubeyrou, G. Vetion, and B. Rivière for their work and technical support during the cruises and their help during laboratory analyses. F.Lantoine provided expertise in pigment analysis.

This work was funded by the French national ANR program CHACCRA (contract number ANR-VULN-06-001-01), the French INSU-EC2CO program RiOMar.fr, and the CEA.

2.8 REFERENCES

Aller, R. C.: Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors, Mar. Chem., 61, 143-155, 1998.

Allison, M. A., Kineke, G. C., Gordon, E. S., and Goni, M. A.: Development and reworking of a seasonal flood deposit on the inner continental shelf off the atchafalaya river, Cont. Shelf Res., 20, 2267-2294, 2000.

Aloisi, J. C., Cambon, J. P., Carbonne, J., Cauwet, G., Millot, C., Monaco, A., and Pauc, H.: Origin and role of the bottom nepheloid layer in the tranfer of particles into the marine environment - application to the gulf of lions, Oceanol. Acta, 5, 481-491, 1982.

Alongi, D. M.: Decomposition and recycling of organic matter in muds of the gulf of papua, northern coral sea, Cont. Shelf Res., 15, 1319-1337, 1995.

Andrews, D., and Bennett, A.: Measurements of diffusivity near the sediment-water interface with a fine-scale resistivity probe, Geochim. Cosmochim. Acta, 45, 2169-2175, 1981.

Antonelli, C., Eyrolle, F., Rolland, B., Provansal, M., and Sabatier, F.: Suspended sediment and cs-137 fluxes during the exceptional december 2003 flood in the rhone river, southeast france, Geomorphology, 95, 350-360, 10.1016/j.geomorph.2007.06.007, 2008.

Bentley, S. J., and Nittrouer, C. A.: Emplacement, modification, and preservation of event strata on a flood-dominated continental shelf: Eel shelf, northern california, Cont. Shelf Res., 23, 1465-1493, 10.1016/j.csr.2003.08.005, 2003.

Berg, P., Risgaard-Petersen, N., and Rysgaard, S.: Interpretation of measured concentration profiles in sediment pore water, Limnol. Oceanogr., 43, 1500-1510, 1998.

Berner, R. A.: Early diagenesis: A theoretical approach., Princeton series in geochemistry, edited by: Princeton, N. J., Princeton University Press, Princeton, 241 pp., 1980.

Boudreau, B.P.: The diffusive tortuosity of fine-grained unlithified sediments, Geochim. Cosmochim. Acta, 60 (16), 3139-3142, 1996.

Brand, A., Dinkel, C., and Wehrli, B.: Influence of the diffusive boundary layer on solute dynamics in the sediments of a seiche-driven lake: A model study, J. Geophys. Res.-Biogeosci., 114, 12, G0101010.1029/2008jg000755, 2009.

Burdige, D. J.: Burial of terrestrial organic matter in marine sediments: A re-assessment, Glob. Biogeochem. Cycle, 19, 2005.

Cai, W. J., Reimers, C. E., and Shaw, T.: Microelectrode studies of organic carbon degradation and calcite dissolution at a california continental rise site, Geochim. Cosmochim. Acta, 59, 497-511, 1995.

Calmet, D., and Fernandez, J.-M.: Caesium distribution in northwest mediterranean seawater, suspended particles and sediments, Cont. Shelf Res., 10, 895-913, 1990.

Cauwet, G., Gadel, F., de Souza Sierra, M. M., Donard, O., and Ewald, M.: Contribution of the rhône river to organic carbon inputs to the northwestern mediterranean sea, Cont. Shelf Res., 10, 1025-1037, 1990.

Charmasson, S., Bouisset, P., Radakovitch, O., Pruchon, A. S., and Arnaud, M.: Long-core profiles of cs-137, cs-134, co-60 and pb-210 in sediment near the rhone river (northwestern mediterranean sea), Estuaries, 21, 367-378, 1998.

Copin-Montegut, C.: Alkalinity and carbon budgets in the mediterranean sea, Glob. Biogeochem. Cycle, 7, 915-925, 1993.

Dagg, M., Benner, R., Lohrenz, S., and Lawrence, D.: Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: Plume processes, Cont. Shelf Res., 24, 833-858, 2004.

Dedieu, K., Rabouille, C.,Thouzeau, G., Jean, F., Chauvaud, L., Clavier, J., Mesnage, V, Ogier, S.: Benthic O2 distribution and dynamics in a Mediterranean lagoon (Thau, France): An in situ microelectrode study, Estuar. Coast. Shelf Sci. 72, 393-405, 2007.

de Madron, X. D., Radakovitch, O., Heussner, S., Loye-Pilot, M. D., and Monaco, A.: Role of the climatological and current variability on shelf-slope exchanges of particulate matter: Evidence from the rhone continental margin (nw mediterranean), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 46, 1513-1538, 1999.

De Madron, X. D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J. C., Radakovitch, O., Giresse, P., Buscail, R., and Kerherve, P.: Particulate matter and organic carbon budgets for the Gulf of lions (nw mediterranean), Oceanol. Acta, 23, 717-730, 2000.

De Madron, X. D., Denis, L., Diaz, F., Garcia, N., Guieu, C., Grenz, C., Loye-Pilot, M. D., Ludwig, W., Moutin, T., Raimbault, P., and Ridame, C.: Nutrients and carbon budgets for the gulf of lion during the moogli cruises, Oceanol. Acta, 26, 421-433, 2003.

Deflandre, B., Mucci, A., Gagne, J. P., Guignard, C., and Sundby, B.: Early diagenetic processes in coastal marine sediments disturbed by a catastrophic sedimentation event, Geochim. Cosmochim. Acta, 66, 2547-2558, 2002.

Dell'Anno, A., Pusceddu, A., Langone, L., and Danovaro, R.: Biochemical composition and early diagenesis of organic matter in coastal sediments of the nw adriatic sea influenced by riverine inputs, Chemistry and Ecology, 24, 75-85, 10.1080/02757540701814580, 2008.

Denis, L., Grenz, C., Alliot, E., and Rodier, M.: Temporal variability in dissolved inorganic nitrogen fluxes at the sediment-water interface and related annual budget on a continental shelf (nw mediterranean), Oceanol. Acta, 24, 85-97, 2001.

Denis, L. and Grenz, C.: Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean), Oceanol. Acta 26, 373–389, 2003.

Epping, E. and Helder, W.: Oxygen budgets calculated from in situ oxygen microprofiles for Northern Adriatic sediments, Cont. Shelf Res., 17 (14), 1737-1764, 1997.

Epping, E., van der Zee, C., Soetaert, K., and Helder, W.: On the oxidation and burial of organic carbon in sediments of the iberian margin and nazare canyon (ne atlantic), Progress In Oceanography, 52, 399-431, 2002.

Eyre, B.D. and Ferguson, A.J.P.: Impact of a flood event on benthic and pelagic coupling in a sub-tropical east Australian estuary (Brunswick), Estuar. Coast. Shelf Sci., 66, 111-122, 2006.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V.: Early oxidation of organic-matter in pelagic sediments of the eastern equatorial atlantic - suboxic diagenesis, Geochim. Cosmochim. Acta, 43, 1075-1090, 1979.

Galy, V., France-Lanord, C., Beyssac, O., Faure, P., Kudrass, H., and Palhol, F.: Efficient organic carbon burial in the bengal fan sustained by the himalayan erosional system, Nature, 450, 407-U406, 2007.

Gattuso, J. P., Frankignoulle, M., and Wollast, R.: Carbon and carbonate metabolism in coastal aquatic ecosystems, Annual Review of Ecology and Systematics, 29, 405-434, 1998.

Glud, R.N., Gundersen, J.K., Jorgensen, B.B, Revsebech, N.P., and Schulz, H.D.: Diffusive and total oxygen uptake of deep-sea sediments in the eastern South Atlantic Ocean: in situ and laboratory measurements. Deep-Sea Res. Part I - Oceanogr. Res. Pap., 41 (11-12), 1767-1788, 1994.

Glud, R.H., Jensen, K., Revsbech, N.P.: Diffusivity in suficial sediments and benthic mats determined by use of a combined N20-O2 microsensor. Geochim. Cosmochim. Acta. 59 (2), 231-237, 1995.

Glud, R. N., Holby, O., Hoffmann, F., and Canfield, D. E.: Benthic mineralization and exchange in arctic sediments (svalbard, norway), Mar. Ecol.-Prog. Ser., 173, 237-251, 1998.

Glud, R. N., Risgaard-Petersen, N., Thamdrup, B., Fossing, H., and Rysgaard, S.: Benthic carbon mineralization in a high-arctic sound (young sound, ne greenland), Mar. Ecol.-Prog. Ser., 206, 59-71, 2000.

Glud, R. N., Gundersen, J. K., Roy, H., and Jorgensen, B. B.: Seasonal dynamics of benthic o-2 uptake in a semienclosed bay: Importance of diffusion and faunal activity, Limnol. Oceanogr., 48, 1265-1276, 2003.

Glud, R. N., Berg, P., Fossing, H., and Jorgensen, B. B.: Effect of the diffusive boundary layer on benthic mineralization and o-2 distribution: A theoretical model analysis, Limnol. Oceanogr., 52, 547-557, 2007.

Grasshoff, K., Ehrhardt, M., and Kremling, K.: Methods of seawater analysis, 419, 1983.

Hedges, J. I.: Global biogeochemical cycles: Progress and problems, Mar. Chem., 39, 67-93, 1992.

Hedges, J. I., and Keil, R. G.: Sedimentary organic-matter preservation - an assessment and speculative synthesis, Mar. Chem., 49, 81-115, 1995.

Hedges, J. I., Keil, R. G., and Benner, R.: What happens to terrestrial organic matter in the ocean?, Organic Geochemistry, 27, 195-212, 1997.

Hulth, S., Tengberg, A., Landen, A., and Hall, P. O. J.: Mineralization and burial of organic carbon in sediments of the southern weddell sea (antarctica), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 44, 955-981, 1997.

Hunter, K. S., Wang, Y. F., and Van Cappellen, P.: Kinetic modeling of microbially-driven redox chemistry of subsurface environments: Coupling transport, microbial metabolism and geochemistry, Journal of Hydrology, 209, 53-80, 1998.

Hyacinthe, C., Anschutz, P., Carbonel, P., Jouanneau, J. M., and Jorissen, F. J.: Early diagenetic processes in the muddy sediments of the bay of biscay, Mar. Geol., 177, 111-128, 2001.

Iversen N. and Jorgensen, B.B.: Diffusion coefficients of sulfate and methane in marine sediments: Influence of porosity, Geochim. Cosmochim. Acta, 57, 57 l-578, 1993.

Jorgensen, B. B., and Revsbech, N. P.: Diffusive boundary-layers and the oxygen-uptake of sediments and detritus, Limnol. Oceanogr., 30, 111-122, 1985.

Keil, R. G., Montlucon, D. B., Prahl, F. G., and Hedges, J. I.: Sorptive preservation of labile organic matter in marine sediments, Nature, 370, 549-552, 1994.

Kelly-Gerreyn, B. A., Hydes, D. J., and Waniek, J. J.: Control of the diffusive boundary layer on benthic fluxes: A model study, Mar. Ecol.-Prog. Ser., 292, 61-74, 2005.

Lansard, B., Rabouille, C., and Massias, D.: Variability in benthic oxygen fluxes during the winter-spring transition in coastal sediments: An estimation by in situ micro-electrodes and laboratory mini-electrodes, Oceanol. Acta, 26, 269-279, 2003.

Lansard, B., Charmasson, S., Gasco, C., Anton, M. P., Grenz, C., and Arnaud, M.: Spatial and temporal variations of plutonium isotopes (pu-238 and pu-239,pu-240) in sediments off the rhone river mouth (nw mediterranean), Sci. Total Environ., 376, 215-227, 10.1016/j.scitotenv.2007.01.069, 2007.

Lansard, B., Rabouille, C., Denis, L., and Grenz, C.: Benthic remineralization at the land-ocean interface: A case study of the rhone river (nw mediterranean sea), Estuar. Coast. Shelf Sci., 81, 544-554, 10.1016/j.ecss.2008.11.025, 2009.

Leithold, E. L., and Hope, R. S.: Deposition and modification of a flood layer on the northern california shelf: Lessons from and about the fate of terrestrial particulate organic carbon, Mar. Geol., 154, 183-195, 1999.

Lisitsyn, A. P.: The marginal filter of the ocean, Oceanology, 34, 671-682, 1995.

Lorke, A., Muller, B., Maerki, M., and Wuest, A.: Breathing sediments: The control of diffusive transport across the sediment-water interface by periodic boundary-layer turbulence, Limnol. Oceanogr., 48, 2077-2085, 2003.

Maerki, M., Wehrli, B., Dinkel, C. and Müller B.: The influence of tortuosity on molecular diffusion in freshwater sediments of high porosity. Geochim. Cosmochim. Acta, 68 (7), 1519–1528, 2004.

Mayer, L. M.: Surface area control of organic carbon accumulation in continental shelf sediments, Geochim. Cosmochim. Acta, 58, 1271-1284, 1994.

McKee, B. A., Aller, R. C., Allison, M. A., Bianchi, T. S., and Kineke, G. C.: Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: Benthic boundary layer and seabed processes, Cont. Shelf Res., 24, 899-926, 2004.

Millot, C.: The gulf of lions hydrodynamics, Cont. Shelf Res., 10, 885-894, 1990.

Miralles, J., Radakovitch, O., and Aloisi, J. C.: Pb-210 sedimentation rates from the northwestern mediterranean margin, Mar. Geol., 216, 155-167, 2005.

Miserocchi, S., Langone, L., and Tesi, T.: Content and isotopic composition of organic carbon within a flood layer in the po river prodelta (adriatic sea), Cont. Shelf Res., 27, 338-358, 2007.

Monaco, A., de Madron, X. D., Radakovitch, O., Heussner, S., and Carbonne, J.: Origin and variability of downward biogeochemical fluxes on the rhone continental margin (nw mediterranean), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 46, 1483-1511, 1999.

Morse, J. W., and Rowe, G. T.: Benthic biogeochemistry beneath the mississippi river plume, Estuaries, 22, 206-214, 1999.

Mucci, A., Boudreau, B., and Guignard, C.: Diagenetic mobility of trace elements in sediments covered by a flash flood deposit: Mn, fe and as, Applied Geochemistry, 18, 1011-1026, 2003.

Naudin, J. J., Cauwet, G., ChretiennotDinet, M. J., Deniaux, B., Devenon, J. L., and Pauc, H.: River discharge and wind influence upon particulate transfer at the land-ocean interaction: Case study of the rhone river plume, Estuar. Coast. Shelf Sci., 45, 303-316, 1997.

Neveux, J., and Lantoine, F.: Spectrofluorometric assay of chlorophylls and pheopigments using the least-squares approximation technique, Deep-Sea Res. Part I-Oceanogr. Res. Pap., 40, 1747-1765, 1993.

Pont, D., Simonnet, J. P., and Walter, A. V.: Medium-term changes in suspended sediment delivery to the ocean: Consequences of catchment heterogeneity and river management (rhone river, france), Estuar. Coast. Shelf Sci., 54, 1-18, 2002.

Rabouille, C., Denis, L., Dedieu, K., Stora, G., Lansard, B., and Grenz, C.: Oxygen demand in coastal marine sediments: Comparing in situ microelectrodes and laboratory core incubations, Journal Of Experimental Marine Biology And Ecology, 285, 49-69, 2003.

Radakovitch, O., Charmasson, S., Arnaud, M., and Bouisset, P.: Pb-210 and caesium accumulation in the rhone delta sediments, Estuar. Coast. Shelf Sci., 48, 77-92, 1999a.

Radakovitch, O., Cherry, R. D., and Heussner, S.: Pb-210 and po-210: Tracers of particle transfer on the rhone continental margin (nw mediterranean), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 46, 1539-1563, 1999b.

Rees, G.N., Bowen, P.M. and Watson, G.O.: Variability in benthic respiration in three southeastern australian lowland rivers, River Res. Applic., 21, 1147–1156, 2005.

Reimers, C. E., Jahnke, R. A., and McCorkle, D. C.: Carbon fluxes and burial rates over the continental slope and rise off central california with implications for the global carbon cycle, Global Biogeochem. Cycles, 6, 1992.

Revsbech, N. P.: An oxygen microsensor with a guard cathode, Limnol. Oceanogr., 34, 474-478, 1989.

Roy, H., Huttel, M., and Jorgensen, B. B.: The role of small-scale sediment topography for oxygen flux across the diffusive boundary layer, Limnol. Oceanogr., 47, 837-847, 2002.

Sempere, R., Charriere, B., Van Wambeke, F., and Cauwet, G.: Carbon inputs of the rhone river to the mediterranean sea: Biogeochemical implications, Glob. Biogeochem. Cycle, 14, 669-681, 2000.

Smith, S. V., and Hollibaugh, J. T.: Coastal metabolism and the oceanic organic-carbon balance, Reviews Of Geophysics, 31, 75-89, 1993.

Sommerfield, C. K., and Nittrouer, C. A.: Modern accumulation rates and a sediment budget for the eel shelf: A flood-dominated depositional environment, Mar. Geol., 154, 227-241, 1999.

Sundby, B.: Transient state diagenesis in continental margin muds, Mar. Chem., 102, 2-12, 2006.

Sweerts, J., Stlouis, V., and Cappenberg, T. E.: Oxygen concentration profiles and exchange in sediment cores with circulated overlying water, Freshwater Biology, 21, 401-409, 1989.

Tesi, T., Langone, L., Goni, M. A., Miserocchi, S., and Bertasi, F.: Changes in the composition of organic matter from prodeltaic sediments after a large flood event (po river, italy), Geochim. Cosmochim. Acta, 72, 2100-2114, 10.1016/j.gca.2008.02.005, 2008.

Ullman, W.J. and Aller, R.C.: Diffusion coefficients in nearshore marine sediments, Limnol. Oceanogr., 27(3), 552-556.

Ulses, C., Estournel, C., de Madron, X. D., and Palanques, A.: Suspended sediment transport in the gulf of lions (nw mediterranean): Impact of extreme storms and floods, Cont. Shelf Res., 28, 2048-2070, 10.1016/j.csr.2008.01.015, 2008.

Wheatcroft, R. A., and Borgeld, J. C.: Oceanic flood deposits on the northern california shelf: Large-scale distribution and small-scale physical properties, Cont. Shelf Res., 20, 2163-2190, 2000.

Wright, L. D., and Friedrichs, C. T.: Gravity-driven sediment transport on continental shelves: A status report, Cont. Shelf Res., 26, 2092-2107, 10.1016/j.csr.2006.07.008, 2006.

CHAPITRE 3. SOURCES AND FATE OF PARTICULATE ORGANIC CARBON EXPORT FROM THE RHÔNE RIVER IN THE MEDITERRANEAN SEA: COMBINED USE OF Δ^{14}C AND δ^{13}C

CHAPITRE 3. Sources and fate of particulate organic carbon export from the Rhône River in the Mediterranean Sea: combined use of $\Delta^{14}C$ and $\delta^{13}C$

CATHALOT C. [1], **RABOUILLE C.** [1], **TISNERAT-LABORDE N.** [1], **BUSCAIL R.** [2], **KERHERVE P.** [2], **GONTIER G.** [3]

[1].Laboratoire des Sciences du climat et de l'Environnement, Gif-sur-Yvette, France
[2].Centre de Formation et de Recherche sur l'Environnement Marin, Perpignan, France
[3].Institut de Radioprotection et Sûreté Nucléaire, Saint Paul Lez Durance, France

Keywords: Organic carbon, Stable carbon isotopes, Radiocarbon, Rhône River, surface sediment, coastal sediments

3.1 ABSTRACT

The biogeochemical fate of the Rhône River particles was studied using coupled isotopic tracers. In June 2005 and April 2007, isotopic compositions ($\Delta^{14}C$ and $\delta^{13}C$) of Organic Carbon (OC) were analysed in 13 surface sediments to determine the distribution and sources of organic matter in the Rhône delta system.

Values of $\delta^{13}C_{OC}$ ranged from – 27.18 ‰ to -23.88 ‰ with a significant enrichment offshore tracing the dispersal of terrestrial organic matter on the continental shelf. A similar pattern was observed for $\Delta^{14}C$ with values around 100 ‰ at the river outlet dropping to – 400 ‰ further offshore. Combining both isotopic signals, a mixing curve was created and highlighted the negligible contribution of marine phytoplankton to the Rhône River delta sediments. A new pool corresponding to resuspended particles from the adjacent continental shelf was identified. These particles are constituted of a mixture of old marine and terrigeneous material, poorly degradable that are resuspended, redeposited and recirculating over the shelf with residence times up to 3000 years.

Thus, riverine contribution to the Rhône River delta sediment is the result of 1) the dilution by this refractory material and 2) the intense burial taking place at the immediate vicinity of the river mouth that traps most of the inputs and sustain high benthic degradation fluxes.

3.2 INTRODUCTION

Continental margins despite their small surface regarding the global ocean (only ~8%) play a significant part in the global biogeochemical cycles, and particularly for carbon. Up to 25% of the global primary production occurs in these areas and they are acting as real "deposit centres" for organic carbon, concentrating around 80% of the global sediment burial (Hedges and Keil, 1995;Hedges *et al.*, 1997;Smith and Hollibaugh, 1993). Located at the continent-ocean interface, coastal areas receive large inputs of organic carbon from rivers: important burial and mineralization represent substantial sinks and sources terms in carbon budget in coastal oceans and allow insight on the underlying processes (Borges, 2005;Hedges, 1992). Indeed, the terrestrial organic carbon is selectively deposited, buried and degraded in coastal waters and sediments, before a fraction of it can be exported to the global ocean. Thus, studying the structure, distributions and quantities of terrestrial organic matter, as well as the processes governing its fate in the coastal ocean, before its delivery to the open oceans is a key factor for assessing global cycles (Raymond and Bauer, 2001a;Galy *et al.*, 2007).

Since the Nile River has been dammed, the Rhône River is the largest Mediterranean river, both in term of liquid and particulate discharge rates (Unesco, 1993). It constitutes 80% of the total riverine inputs in the Gulf of Lion shelf, the major Mediterranean continental margin, and provides 1.6 ±0.5 10^{10} molC y^{-1} to the Mediterranean Sea (Sempere *et al.*, 2000;Cauwet *et al.*, 1990;Copinmontegut, 1993). In this context, the Rhône River has been the subject of many intensive physical and biogeochemical oceanographic studies trying to assess the export and the fate of this terrestrial material (Tesi *et al.*, 2007a;Roussiez *et al.*, 2006;Ulses *et al.*, 2008;Estournel *et al.*, 2001;Radakovitch *et al.*, 1999b). Many of these studies have used radionuclide tracers that bring knowledge on particles transfer but give no information about the organic fraction, its lability or origin. And, until recently, the studies interested in particulate organic carbon mainly concentrated on outshelf and canyon transfers, with no focus on inner shelf distribution and processes: thus, although giving an integrated composition, they brought no insight to the terrestrial fraction of particulate organic carbon exported. Lansard *et al.* (2009) completing the work of Tesi *et al.* (2007a) brought a first quantification of the terrigeneous fraction of the Rhône River particles using carbon stable isotopes and C/N ratios and lignin-derived biomarkers consideration. But their estimation relies in the assessment of the two end-member sources, which is constrained by the narrow range of $\delta^{13}C$ values and the possible overlap between terrestrial and marine isotopic signature.

Therefore, in order to provide a more pertinent understanding of the system, an additional tracer is required to determine the fate of organic matter and to estimate the contribution of terrestrial organic matter to continental margins. Radiocarbon abundances have become an additional tracer of terrestrial versus marine sources because nuclear weapons testing in the 1950s injected large quantities of ^{14}C into the atmosphere. Indeed, natural radioisotope of carbon provides additional and unique information on the sources, ages and residence times of Particulate Organic Matter (POM). Organic matter in river suspended particles presents a wide range of $\Delta^{14}C$ signatures from -980 to +75‰ (Nagao *et al.*, 2005;Raymond and Bauer, 2001a) whereas plankton and marine POC usually display enriched values from -45 to + 110‰ (Williams *et al.*, 1992;Wang *et al.*, 1998). Nevertheless, each single river system exhibits a narrow range of $\Delta^{14}C$ values of corresponding to the resultant of run-off and erosion in the watershed and local autochthonous production (Goni *et al.*, 2006). This dynamic range of values provides an opportunity to distinguish sources of the deposited material (Goni *et al.*, 1997). Accelerator mass spectrometry measured $\Delta^{14}C$ values have thus been proven to be a powerful tool to investigate the dynamics of organic carbon in rivers systems and marine environments (Hedges *et al.*, 1986a;Raymond and Bauer, 2001b;Druffel *et al.*, 2005;Megens *et al.*, 2001).The simultaneous use of $\Delta^{14}C$ and $\delta^{13}C$ adds a second dimension to isotopic studies of carbon cycling in river influenced environments, especially to the study of the fate and geochemical behaviour of particulate organic carbon at continental margins.

This study applies a combined use of $\Delta^{14}C$ and $\delta^{13}C$ to surface sediments from the Rhône river mouth and prodelta. It intends to elucidate the fate of terrestrial particulate organic matter released from the river to the coastal marine environment.

3.3 MATERIAL AND METHODS

3.3.1 Study area

The Gulf of Lions is a large continental shelf located in the NW Mediterranean Sea. A general cyclonic circulation is imposed by the north western Mediterranean current flowing southwestward along the slope. The water column is seasonally stratified and vertical intense mixing events inducing major nutrient export occur mainly in winter or early spring due to strong regional winds (Millot, 1990;de Madron *et al.*, 1999). The Gulf of Lions is microtidal with a moderate swell-dominated wave-energy.

The Rhône River is the major source of freshwater, nutrients and organic carbon for the Gulf of Lions (Sempere *et al.*, 2000;Pont *et al.*, 2002;De Madron *et al.*, 2000). 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 ± 6 10^4 tC/an.. The hydrological regime of the Rhône River shows strong seasonal contrast with a large difference between low (<700 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 60m depth (Wright and Friedrichs, 2006). Net sedimentation rates in the prodelta range from 30 to 50cm yr^{-1} at shallow stations (20 m) near 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 20km (Miralles *et al.*, 2005).

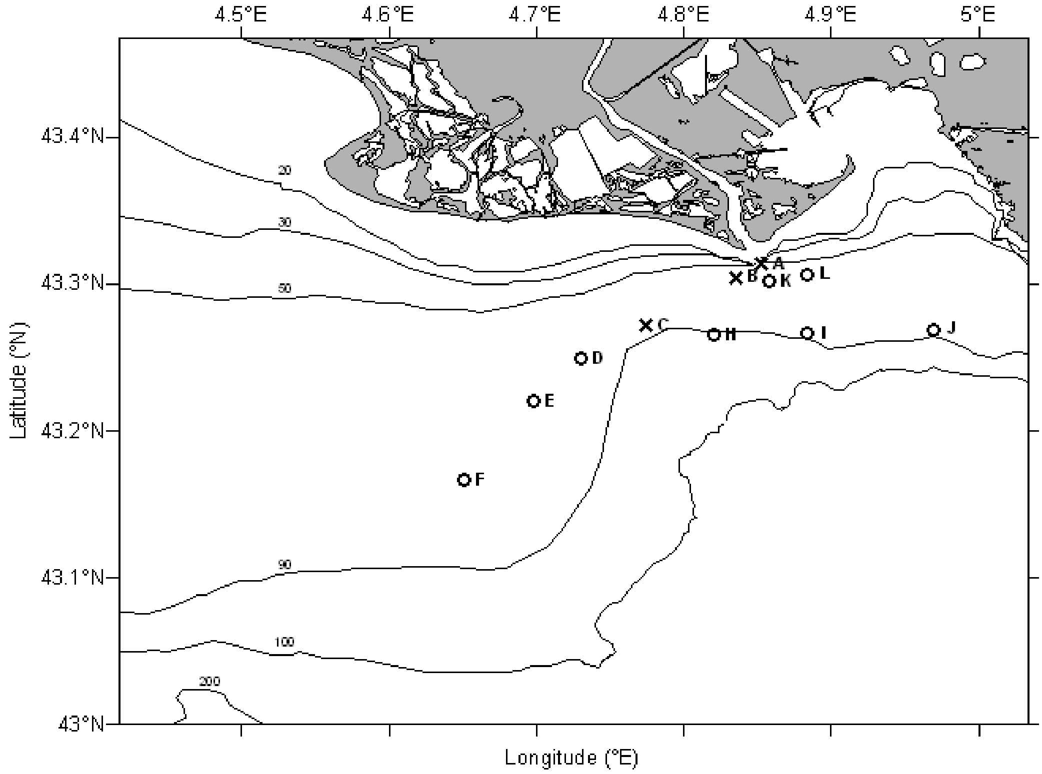

Figure 1. Map of the Rhône prodelta indicating the locations of sampling stations. Circles indicate sampling stations for $\delta^{13}C$ and $\Delta^{14}C$ ($\delta^{13}C$ measured during both cruises). Filled symbols indicate that stations were sampled for $\Delta\ ^{14}C$ at both cruises. Crosses indicate stations sampled only for $\delta^{13}C$ and just once (April 2007 cruise).

3.3.2 Samples

Sediment samples from the Rhône river prodelta were collected with a multicorer MUC 8/100 (Oktopus GmbH) that collect simultaneously eight P.C cores (I.D. 9.5 cm): two cruises were performed, the first one occurred in June 2005 and the second in April 2007. Cores were sliced at 1 cm depth intervals and the subsampled sediments were then stored at -20°C until analysis. Sediment samples were freeze-dried and then ground using an agate mortar.

June 2005 sediment samples were acidified with a 1% HCl solution during 3 to 5 days to ensure complete decarbonation, rinsed three times with MilliQ water. This procedure was completed three times. The sediments were then dried again at 60°C.

Sediments from the April 2007 cruise were acidified in cup with 2N HCl (overnight, at 50°C) in order to remove carbonates prior to the analyses of OC (Cauwet *et al.*, 1990). In addition, sediments from stations A, B, C and F visited in April 2007 were subsampled and decarbonated following the June 2005 protocole.

3.3.3 Analysis

a) Organic Carbon content

Sediment Organic Carbon (OC) was measured in surface sediment (0–1 cm) after carbon removal (see above). OC content for June 2005 sediments were determined at LSCE using an automatic Fisons Instrument NA 1500 Element Analyzer, whereas OC measurements on April 2007 sediment samples were also performed at CEFREM in an automatic CN – analyser LECO 2000. Precisions for OC for both types of analyses were 2%.

b) Stable isotopic composition of organic carbon

Stable carbon isotope contents of surface sediment OC for carbonate-free samples were determined after carbon removal. June 2005 analyses were performed at the LSCE by using a continuous flow ThermoFinigan Delta + XP Isotope-Ratio Mass Spectrometer. Isotopic signature of April 2007 sediments were measured at CEFREM on a ConFlo II interface Finnigan MAT-252 mass spectrometer (some being measured also at LSCE).

The 4 subsampled sediments from April 2007 decarbonated following the June 2005 protocole were also measured at LSCE. Analyses on these samples were performed using both equipments: there was no significant difference between the values obtained ($p<0.01$, non parametric Mann-Whitney test).

The isotopic compositions were reported using the standard δ-notation (‰) with respect to the Vienna Pee Dee Belemnite (PDB) standard.

$$\delta^{13}C = \left(\frac{\left. \frac{^{13}C}{^{12}C} \right|_{sample}}{\left. \frac{^{13}C}{^{12}C} \right|_{PDB}} - 1 \right) * 1000$$

Isotopic results were obtained with uncertainties of ± 0.15 ‰.

c) Radiocarbon organic carbon content

^{14}C measurements were performed either by the Artémis accelerator mass spectrometer (AMS) at the Laboratoire de Mesure du Carbone 14, Gif-sur-Yvette (for sediment samples) or by the NSF - Arizona AMS facility, Tucson (suspended particles samples). Measurements were performed on sediments at two different depths: surface samples (0-1 cm) and samples from 3-4 cm depth. After the decarbonation, the entire sample is combusted in a sealed quartz tube at 850°C with copper oxide and silver wool. The released CO_2 is dried, volumetrically measured, and collected in a glass ampoule. Then, the CO_2 sample is converted to graphite target in an atmosphere of H_2 over an iron powder catalyst at 600°C. The sample ^{14}C /^{12}C ratio was then measured with an NEC 3 MV AMS system. The ^{14}C activities are determined with respect to the international standard of oxalic acid. Final ^{14}C activities are reported in $\Delta^{14}C$. The $\Delta^{14}C$ is defined as the deviation in parts per mil from the modern standard. All $\Delta^{14}C$ values were corrected from 1950, and from the delay between sampling and measurement years (Mook and van der Plicht, 1999). Ages were calculated from the $\Delta^{14}C$ values using the conventional ^{14}C half-life. The $\Delta^{14}C$ precisions of measurements were ± 0.09 ‰.

Table 1. Summary of sediment organic carbon content (C_{org}) and isotopic composition ($\delta^{13}C$ and $\Delta^{14}C$)

Stations	Lat. (°N)	Long. (°N)	Depth (m)	Distance (km)	Cruise	Sediment Depth (cm)	C_{org} (%)	$\delta^{13}C$ (‰)	Δ14C (‰)		
A	43° 18' 47"	4° 51' 4"	24	1.93	Jun-05	0 - 1	1.81	-26.83	134.1	±	-13.9
						3 - 4	1.92	-27.10	119.6	±	-14.3
					Apr-07	0 - 1	1.99	-27.18	59.4	±	-2.3
B	43° 18' 14"	4° 50' 4"	54	3.02	Jun-05	0 - 1	1.68	-26.71	6.0	±	-14.3
						3 - 4	1.55	-26.70	45.7	±	-13.2
					Apr-07	0 - 1	1.61	-26.61	7.3	±	-2.7
C	43° 16' 17"	4° 46' 33"	76	8.57	Jun-05	0 - 1	1.02	-25.32	-224.0	±	-8.9
						3 - 4	1.03	-25.27	-228.1	±	-7.9
					Apr-07	0 - 1	1.25	-25.38	-226.1	±	-2.2
D	43° 14' 54"	4° 43' 46"	74	13.01	Jun-05	0 - 1	0.93	-24.52	-268.0	±	-8.0
						3 - 4	0.93	-24.73	-260.2	±	-8.2
					Apr-07	0 - 1	1.05	-24.77			
E	43° 13' 12"	4° 41' 54"	75	17.03	Jun-05	0 - 1	0.89	-24.27	-317.5	±	-6.8
						3 - 4	0.90	-24.31	-324.4	±	-7.4
					Apr-07	0 - 1		-24.48			
F	43° 10' 1"	4° 41' 59"	78	21.61	Jun-05						
					Apr-07	0 - 1	1.43	-24.19	-400.2	±	-3.9
H	43° 15' 53"	4° 49' 10"	86	7.52	Jun-05	0 - 1	1.03	-25.20	-222.4	±	-8.3
						3 - 4	1.03	-25.46	-254.9	±	-7.4
					Apr-07	0 - 1	1.17	-25.55			
I	43° 16' 0"	4° 53' 1"	89	7.68	Jun-05	0 - 1	0.82	-24.35	-227.9	±	-8.9
						3 - 4	0.88	-24.48	-227.9	±	-8.9
					Apr-07	0 - 1	1.03	-25.14			
J	43° 16' 7"	4° 58' 6"	86	12.09	Jun-05	0 - 1	0.82	-23.88	-390.7	±	-5.7
						3 - 4	0.97	-24.06	-397.1	±	-6.2
					Apr-07	0 - 1	1.08	-24.34			
K	43° 18' 7"	4° 51' 29"	62	3.28	Jun-05	0 - 1	1.18	-26.22	-15.0	±	-13.9
						3 - 4	1.10	-26.22	-86.9	±	-12.5
					Apr-07	0 - 1	1.79	-26.7			
L	43° 18' 24"	4° 52' 59"	62	4.03	Jun-05	0 - 1	1.15	-25.91	-127.3	±	-10.2
						3 - 4	1.28	-25.98	-108.6	±	-10.2
					Apr-07	0 - 1	1.51	-26.33			
N	43° 17' 33"	4° 47' 59"	67	5.54	Jun-05						
					Apr-07	0 - 1	1.43	-25.94			
O	43° 17' 0"	4° 50' 6"	79	5.22	Jun-05						
					Apr-07	0 - 1	1.43	-25.65			

3.4 RESULTS

Table 1 summarized organic content, ^{13}C and ^{14}C values obtained among all stations.

3.4.1 Organic carbon content and isotopic composition

The distribution and values of organic carbon (OC) content in surface sediments were stable over the two cruises and ranged between 2% at the vicinity of the river mouth and 1% offshore. OC content were slightly lower offshore during the June 2005 cruise but the overall prodelta distribution was not significantly different from April 2007 ($p>0.05$).

$\delta^{13}C$ values in June 2005 are the one reported by Lansard *et al.* (2009). $\delta^{13}C$ signatures in surface sediment did not show any significant changes between the two cruises ($p>0.05$): they ranged from -27.18 ‰ at station A (outlet of the river) to -23.88 ‰ at station J (south-eastward) (Figure 2). All $\delta^{13}C$ values increased with distance from the Rhône river mouth ($r^2 = 0.8451$, $n = 27$, $p<0.01$). Stations A, B, K located in a 2 km radius presented strongly depleted values close together around -27 – 26 ‰, associated with high OC content (~ 2 %). Getting offshore, values rise up to -25 ‰ to reach at the far most end of the South-West transect and eastern station signals about -24 ‰ corresponding to the lowest OC contents (~0.8 – 1 %). $\delta^{13}C$ signature of the Rhône river particles was -27.2 ‰ whereas the marine one was -23.3 ‰.

3.4.2 $\Delta^{14}C$ distribution

^{14}C signature of surface sediments presented a wide range of values in the prodelta from 142.5 ‰ to -400.2 ‰. All $\Delta^{14}C$ values decreased with distance from the Rhône river mouth ($r^2 = 0.9417$, $n = 14$, $p<0.01$). Surface sediment in the immediate vicinity of the Rhône River mouth present modern signal close to the current atmospheric $\Delta^{14}C\text{-}CO_2$ level: slightly enriched at station A (~ 100 ‰) and around 0 ‰ at B and K (Figure 3). Getting offshore, the sediment displays much more depleted signatures decreasing rapidly with distance: from -200 ‰ at station C to -400 ‰ at the furthest most stations (F, J). These depleted samples correspond to an age of about 4000 years AD old sediment.

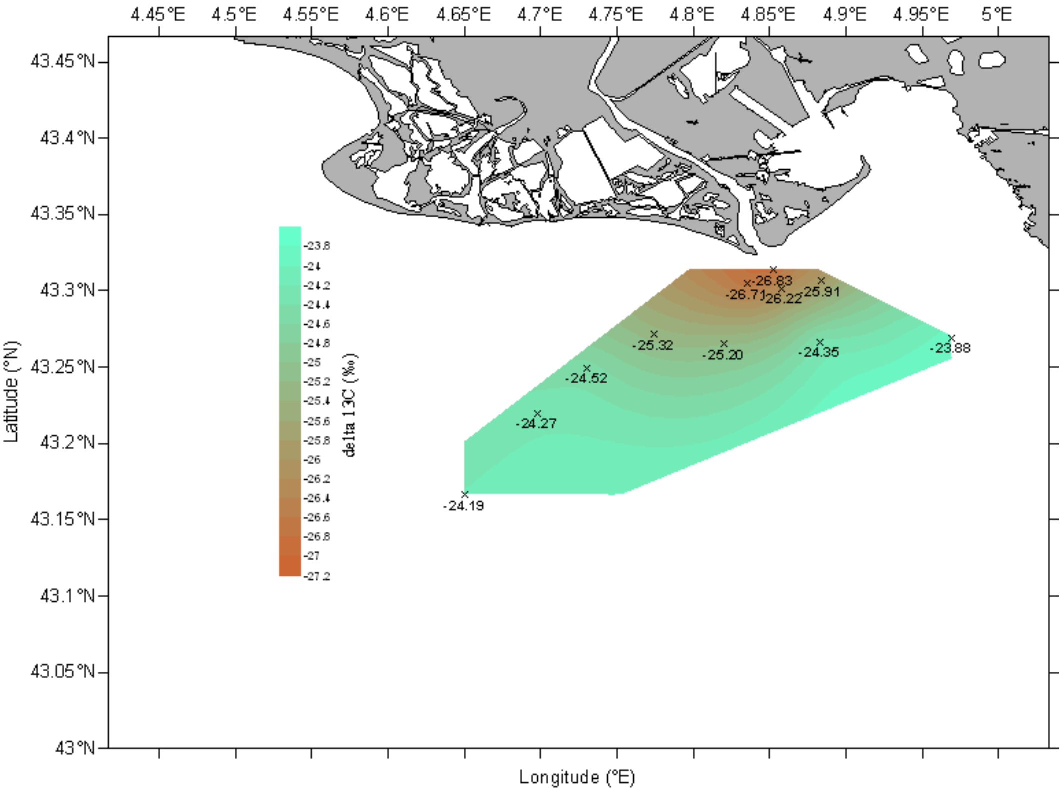

Figure 2. δ^{13}C spatial distribution in the Rhône River prodelta. Values close to -27.2 ‰ correspond to terrestrial material whereas -22 ‰ indicate marine material.

3.5 DISCUSSION

3.5.1 *Particulate Organic Matter (POM) sources in the Rhône River prodelta: End-members terms*

POM in coastal environments results of a complex mixture of multiple sources including estuarine phytoplankton, marine phytoplankton, soil-derived OM and woody debris, each of them having distinct biogeochemical characteristics (Fry and Sherr, 1984;Hedges *et al.*, 1997;Tesi *et al.*, 2007b). In terms of δ^{13}C signatures, studies assessing sources of POM usually use a dichotomous approach with two contributors. A terrigeneous fraction which can be constituted by C4 vascular plants with signals ranging between -10 – 14 ‰ (Smith and Epstein, 1971;France-Lanord and Derry, 1994;Fry and Sherr, 1984) and by C3 vascular plants whose signatures are around -26 - 35 ‰ (Smith and Epstein, 1971;Goni *et al.*, 1997;Tesi *et al.*, 2007b). A fresh and estuarine phytoplankton generally displays depleted signal around -30‰ down to -45 ‰ (Forsberg *et al.*, 1993;Rau, 1978;delGiorgio and France, 1996;France, 1995). A marine fraction constituted by POM originating from autochthonous phytoplankton with $\delta^{13}C$ shows values ranging between -19 and -22 ‰ (Hedges *et al.*, 1997;Fry and Sherr, 1984)

Previous studies have characterized terrestrial and marine sources in the Gulf of Lions: e.g. Darnaude *et al.* (2004b), Lansard *et al.* (2009) and Tesi *et al.* (2007a) defined the $\delta^{13}C_{OC}$ signature of the two main sources of OM for the Rhône delta sediment as: ~ 27.7 ‰ for terrestrial-derived POM and ~ 22.4 ‰ for marine-derived POM. Rhône River suspended particulate matter (SPM) was also sampled in April 2007 (about ca. 1km inland from the sea) and displayed a $\delta^{13}C_{OC}$ of -27.2 ‰ (data not shown). This is fairly consistent with the signatures of surface sediment in stations A, B, K located at the immediate vicinity of the river mouth that were around -27 ‰. Moreover, Cathalot *et al*, (Chapitre 4) measured $\delta^{13}C$ in POC of SPM in bottom and intermediate waters and found a similar value around -27 ‰. Thus, this typical terrigeneous signature correlates well with the previous studies mentioned above and indicates C3-soil and vascular plants derived organic matter inputs by the Rhône River. Kerhervé *et al*, In Prep, realized a 3 years monitoring series of suspended particulate matter in the Rhône River and found out that $\delta^{13}C$ signature of the riverine POC was stable over time and did not vary significantly even with flood events: -27.5 ± 0.5 ‰.

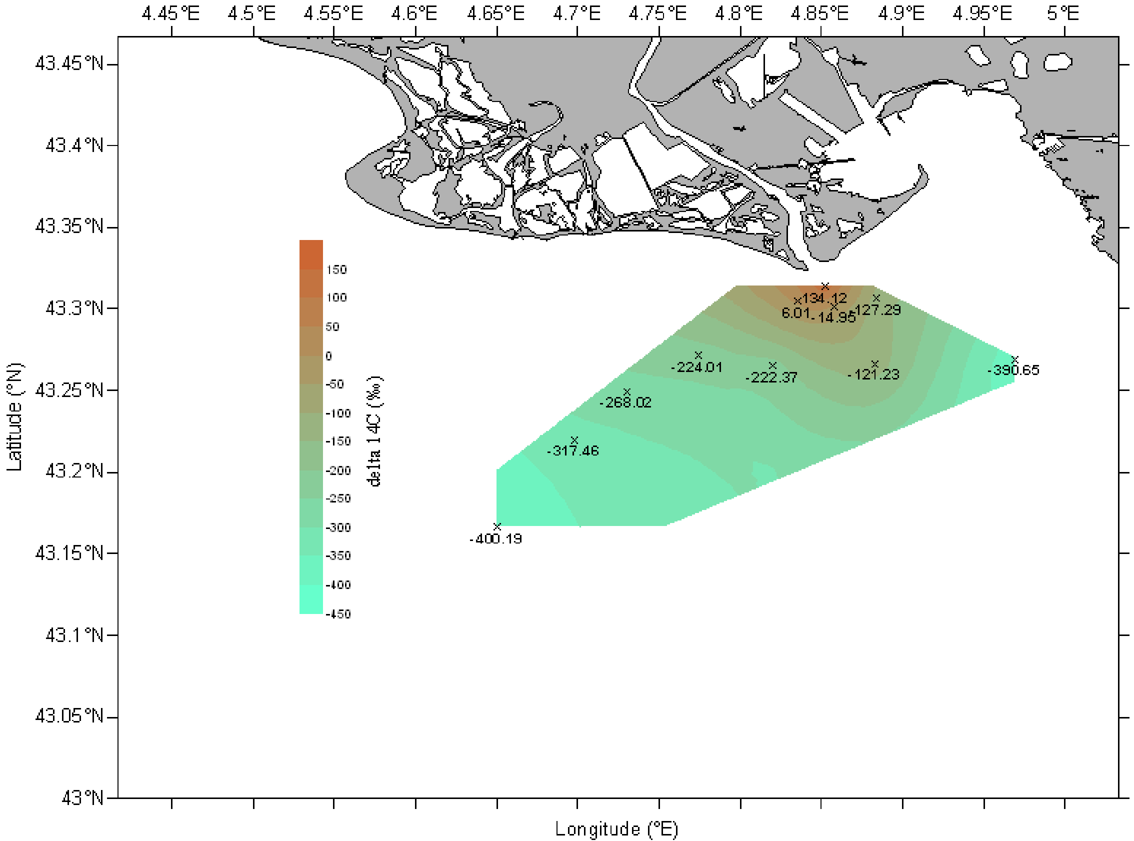

Figure 3. $\Delta^{14}C$ spatial distribution in the Rhône River prodelta. Values close to 150 ‰ correspond to terrestrial enriched material whereas -400 ‰ indicates continental shelf old material.

Marine phytoplankton in North-Western Mediterranean usually present a $\delta^{13}C$ signature of -22 ‰ (Darnaude *et al.*, 2004a).

Contrary to other riverine systems with ^{14}C signatures mostly resulting from run-off and erosion in the watershed (Hedges *et al.*, 1986b;Nagao *et al.*, 2005;Raymond and Bauer, 2001a), the Rhône river $\Delta^{14}C$ signature reflects the nuclear power plants activities occurring along its sides. Indeed, Gilles Gontier's recorded $\Delta^{14}C$ signals in SPM in the Rhône River around 250-300 Bq/kgC, i.e. ~100 ‰ $\Delta^{14}C$, which is coherent with enrichment values found in other nuclear plants influenced coastal oceans (Begg *et al.*, 1992;Baena *et al.*, 2007). This signal also reflects what Cathalot *et al*, *(*Chapitre 4). found in the POC of intermediate waters SPM at the river outlet (station A: $\Delta^{14}C$ = 29.3 ‰). Consequently, we defined the Rhône River source term as having $\Delta^{14}C$ = 100 ‰ and $\delta^{13}C$ = -27.2 ‰.

Marine phytoplankton usually displays a slightly enriched signature between -50 and 150 ‰ corresponding to photosynthesis pumping bomb ^{14}C atmospheric CO_2. Thus the marine associated POC should have a ^{14}C signature close to the ^{14}C-DIC of surface oceanic waters around 100 ‰ (Druffel and Williams, 1992;Williams *et al.*, 1992;Bauer *et al.*, 2001;Druffel *et al.*, 1992;Druffel *et al.*, 1986) Williams & Bauer, 2001). As a matter of fact, $\Delta^{14}C$-DIC values reported for the Mediterranean Sea surface waters are 100 - 120‰ (Yechieli *et al.*, 2001;Stuiver and Ostlund, 1983). We assumed thus a typical marine POC signature of $\Delta^{14}C$ = 100 ‰ and $\delta^{13}C$ = -22.4 ‰.

Based on these biogeochemical ranges, we plotted $\Delta^{14}C$ vs. $\delta^{13}C$ values in order to spot any dependencies and determine the potential sources of sediment OC in the prodelta. We observed a strong linear correlation between $\Delta^{14}C$ and $\delta^{13}C$ values ($\Delta^{14}C = -146.0 * \delta^{13}C - 3876.2$; $r^2 = 0.9173$; $p<0.001$; $n = 14$) that excludes the marine phytoplankton as a significant end-member term (Figure 4). Nevertheless, this straight line supports the idea of an aged pool of particles as the second major contributor to sediment OC in the Rhône River prodelta and the adjacent shelf. Thus, contrary to what was reported in previous studies, marine phytoplankton contribution seems to be negligible and sediment OC distribution in the prodelta most likely result from a mixing between aged material and the terrestrial POM brought by the Rhône River. Based on combined isotopic signatures, this old pool can be identified as particles originated from the adjacent continental shelf. Indeed, sedimentary signatures of stations far from the Rhône river mouth (F, J) were homogeneous with a $\Delta^{14}C$ of -300 - 400 ‰ and a $\delta^{13}C$ of -23.8 ‰ corresponding to an undistinguished (i.e. mixture between terrestrial and marine) old organic carbon. These $\Delta^{14}C$ and $\delta^{13}C$ signature are the same than the SPM in the prodelta reported by Cathalot *et al*, (Chapitre 4). Tesi *et al.* (2007a) studied the whole Gulf of Lions and found similar $\delta^{13}C$ values in the distal Rhône river delta and the continental shelf. The strong cyclonic circulation in the overall Gulf of Lions associated with many resuspension events homogenise suspended particles over the continental shelf and facilitate Rhône River particle export in the south west direction (Ulses *et al.*, 2008;Ferre *et al.*, 2008). Therefore, this second pool is most likely constituted by particles from the shelf with a long residence time on the shelf as indicated by their old radiocarbon ages. This shelf particles pool would therefore be a complex mixture between previously deposited terrigeneous locally produced marine material that underwent many cycles of resuspension/deposition/degradation.

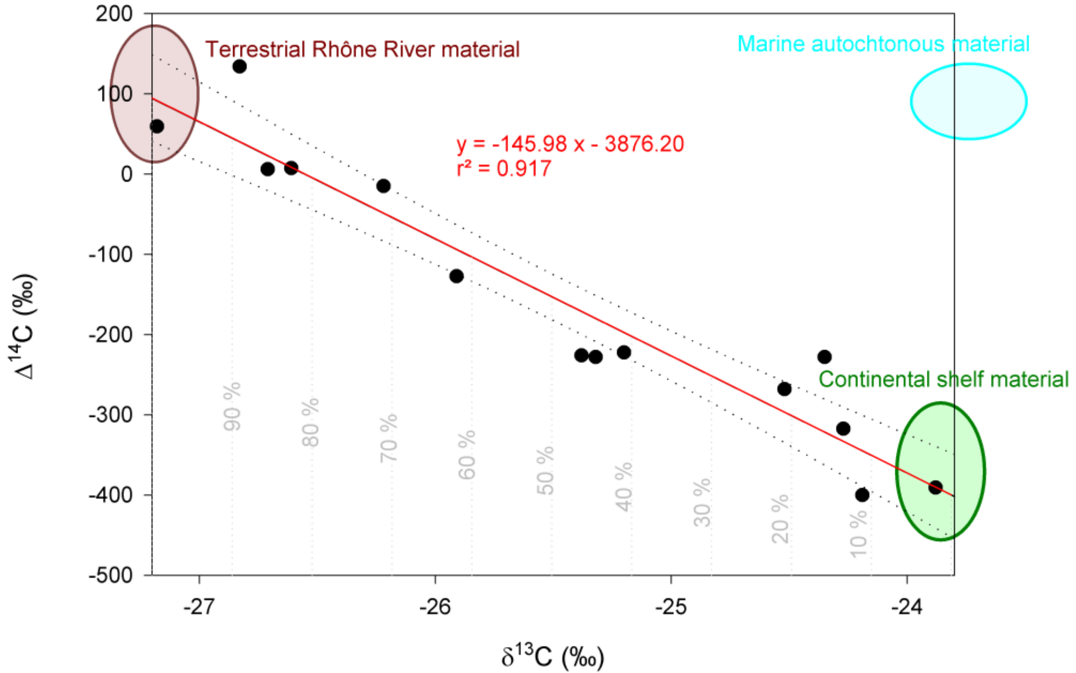

Figure 4. $\delta^{13}C$ - $\Delta^{14}C$ mixing curve with the 3 potential sources indicated. In dotted line, 95% confidence interval for the mixing curve (corresponding to the linear regression)

Since the Gulf of Lions is a heavily human-impacted area with important navigation traffic of fuel tankers, anthropogenic hydrocarbons are present in the sediment of the continental shelf and could explain part of the old age observed in the shelf sediment (Tolosa *et al.*, 1996). Indeed, fossil fuels and the compounds emitted from their combustion contain nearly no ^{14}C because the geologic age of these fuels is much greater than the half-life of radiocarbon (5730 year): fossil fuel sources thus usually have a $\Delta^{14}C$ of −1000 ‰ (Mandalakis *et al.*, 2005;Sheesley *et al.*, 2009). The depleted signal found in the shelf could therefore arise not from long residence time but from a significant contribution of these fossil fuels compounds. Indeed, considering their very distinct signature, and the modern signal of the two other potential sources (marine and terrestrial), they would need a contribution of 37 % in the sediment to dilute the signal enough to lead to the observed shelf particles signatures of – 300 ‰. Polycyclic Aromatic Hydrocarbon (PAH), for instance, are common products of oil industry induced by fossil fuels pyrolysis (during combustion at high temperature of fossil materials such as coal, or compounds deriving from crude oils) and have been observed in the Gulf of Lions sediments (Larsen *et al.*, 1986;Lipiatou and Saliot, 1991). Nevertheless, the observed contents up to 300 µg g^{-1} gives a contribution of only 1-2 % which is far not enough to generate such a variation in the $\Delta^{14}C$ signal. Thus, the second pool of particles we identified from the combined $\delta^{13}C$ - $\Delta^{14}C$ mixing curve as a major contributor of OC in sediment of the Rhône River delta is most likely to be constituted by resuspended shelf particles with long residence time rather than by marine phytoplankton diluted by anthropogenic hydrocarbon compounds.

We thus assumed that sediment in the prodelta results of the dilution between the riverine inputs and this remobilized shelf material.

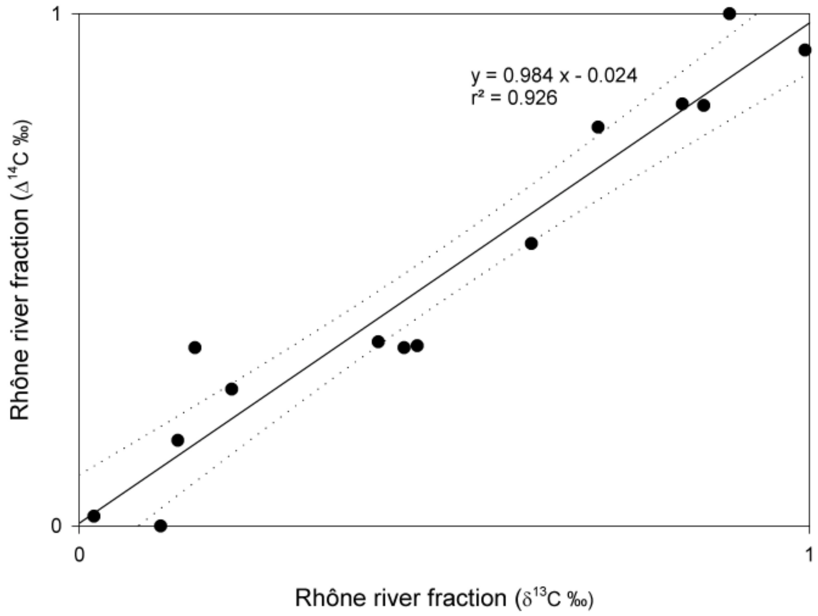

Figure 5. Riverine fraction derivated from $\delta^{13}C$ and $\Delta^{14}C$ measurements. Dotted line 95% confidence interval.

3.5.2 Distribution of POC in the Rhône River prodelta

Following the same procedure than Lansard *et al.* (2009) and assuming only these two sources we can calculate a fraction of riverine organic carbon (%OC_{River}) deposited within the Rhône prodelta system. To do so, we used two two-end member mixing model of $\delta^{13}C_{OC}$ and $\Delta^{14}C_{OC}$ signatures respectively with a terrigeneous and a continental shelf source ($\delta^{13}C_{OC}$ = -27.2 ‰ and -23.8 ‰ respectively, and $\Delta^{14}C_{OC}$ = 100 ‰ and -400 ‰). The only factor affecting the compositional relationship between isotopic signatures and terrestrial organic carbon in sediments is dilution with continental shelf aged and $\delta^{13}C$-heavier material. Fractions calculated with both isotopes were statistically equivalent ($p<0.05$, see Figure 5). We used the linear regression of $\delta^{13}C_{OC}$ vs $\Delta^{14}C_{OC}$ as the experimentally achieved mixing curve to confirm our end members choice (($\Delta^{14}C_{OC}$ = 94 ‰, $\delta^{13}C_{OC}$ = -27.2 ‰) and ($\Delta^{14}C_{OC}$ = - 400 ‰, $\delta^{13}C_{OC}$ = -23.8 ‰)) and calculate %OC_{River} fractions (Figure 4).

Stations in the immediate vicinity of the Rhône River mouth (radius 2km) exhibit high fractions of riverine material (85%), which decrease exponentially with distance from the outlet to reach low homogeneous content close to 0% at distal stations. The large deposition of riverine POC in the prodelta front is in good agreement with the previous quantification and established mixing curve of Lansard *et al.* (2009). Nevertheless, the previous assumptions of marine production being exported to the sea floor seem very unlikely in the Gulf of Lions: it does not seem to have a tight intense pelagic-benthic coupling as previously recorded in others coastal environments (Hedges *et al.*, 1997;Heip *et al.*, 1995;Belviso *et al.*, 2006).

Table 2. Riverine fraction buried in the Rhône River prodelta.

Station	**distance**	**Area**	**w**	**OC content**	**OC burial rate**	**annual OC burial**	**riverine fraction f**	**riverine OC burial rate**	**annual riverine OC burial**
	km	*km²*	*cm y^{-1}*	*%*	*gC m^{-2} y^{-1}*	*10^4 tC y^{-1}*	*%*	*gC m^{-2} y^{-1}*	*10^4 tC y^{-1}*
A	1.9	5.6	10	2	2120	1.19	0.96	2045	1.15
B	3.0	18.3	2	1.3	276	0.50	0.82	227	0.41
C	8.6	50.3	0.5	0.98	52	0.26	0.35	18	0.09
D	13.0	82.8	0.2	0.98	21	0.17	0.27	6	0.05
E	17.0	102.8	0.1	0.4	4	0.04	0.17	1	0.01
F	21.6	42.0	0.1	0.4	4	0.02	0.00	0	0.00
H	7.5	72.7	0.2	0.98	21	0.15	0.36	7	0.05
I	7.7	89.1	0.1	0.75	8	0.07	0.35	3	0.02
J	12.1	114.6	0.1	0.6	6	0.07	0.02	0	0.00
K	3.3	7.7	1	1.2	127	0.10	0.78	99	0.08
L	4.0	24.3	1	1.2	127	0.31	0.55	70	0.17
					TOTAL	**2.90**		**TOTAL**	**2.04**

Fed by high riverine material inputs, delta environments also constitute important burial zones since they sequester nearly half of the OC buried in the marine environment (Blair *et al.*, 2004;Burdige, 2005). By combining previously measured sediment accumulation rates in the Rhône delta, and our estimated riverine fraction, we were able to calculate the amount of Rhône River material buried (Table 2). Therefore at each station we assumed a sediment accumulation rates from the data set available among (Charmasson *et al.*, 1998;Radakovitch *et al.*, 1999a;Zuo *et al.*, 1997). Using a R routine to generate spatial Thiessen's polygon interpolation among our stations network, we defined and calculated areas allocated to each station. Sediment OC accumulation rates in each area were then calculated as follow: $riverine\ buried\ flux = f * r\ (1-\phi)\ \rho * A * \%OC$, where f stands for the riverine OC fraction in the sediment we determined, r is the sedimentation rate, ϕ the porosity, ρ the sediment dry density (2.65 g cm^{-3}), A the surface area and %OC the OC content, for each station respectively. Since, the calculated buried flux is directed downward, we took porosity and OC content values from bottom core samples i.e. 30 cm deep (Pastor *et al*, *In prep.*). Porosity at depth was around 0.6. This leads to a total amount of riverine OC buried in the Rhône River delta of ~ 2.0 10^4 tC y^{-1} with 80% of it occurring in a narrow area of 15 km² around the river mouth (about less than 3 km away; Figure 7).

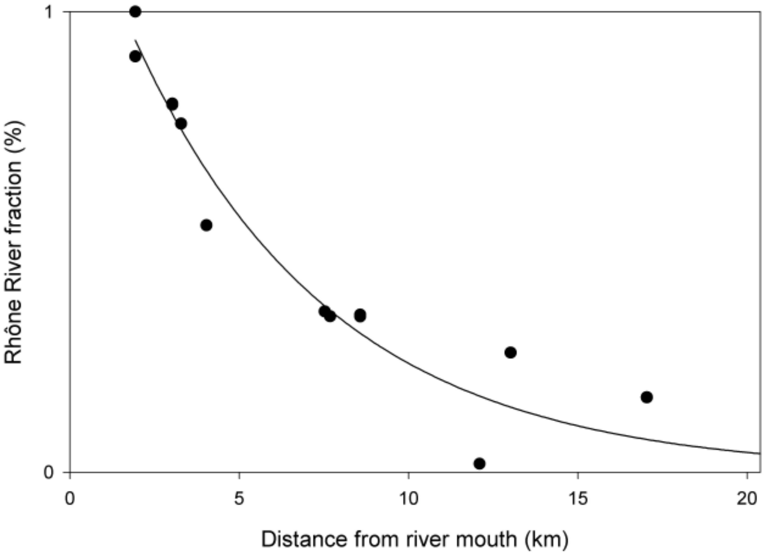

Figure 6. Distribution of terrigeneous material originated by the Rhône River to the continental shelf

Our results corroborate thus the high accumulation rates and previous particles deposit scenario of almost 80 % of the Rhône river material being stuck in a really narrow area about 20km² (Cauwet *et al.*, 1990;Lansard *et al.*, 2007;Miralles *et al.*, 2005). The rest of the material is to be exported all over the shelf, preferentially first in a south-westward direction through resuspension events, and mixed with the overlying resuspended shelf material. Given the radiocarbon age, the residence time of these circulating particles could be more than thousand years. It appears thus that the particles exported from the river feed the benthic prodelta system with high quantity of poor quality terrestrial material (Pastor *et al*, *In prep.*) sustaining high benthic recycling fluxes. Indeed, this terrestrial particulate distribution correlates well with the spatial pattern of Diffusive Oxygen Uptakes (DOU) in the prodelta sediments (Cathalot *et al*, *submitted*; Lansard *et al.*, 2005). These DOU rates display large values near the river mouth and low values in the shelf: this discrepancy in benthic OC degradation activity is directly correlated with the lability of the input material. High activity in the prodelta is sustain by fresh and reactive deposited POC whereas low DOU values in the shelf material are consistent with an old low-reactivity organic material, most likely already partially degraded. This feature again highlights the role of deltaic environments as active benthic reactors capable of processing supposed-refractory terrigeneous material (Aller, 1998;Aller *et al.*, 2004;Buscail *et al.*, 1995).

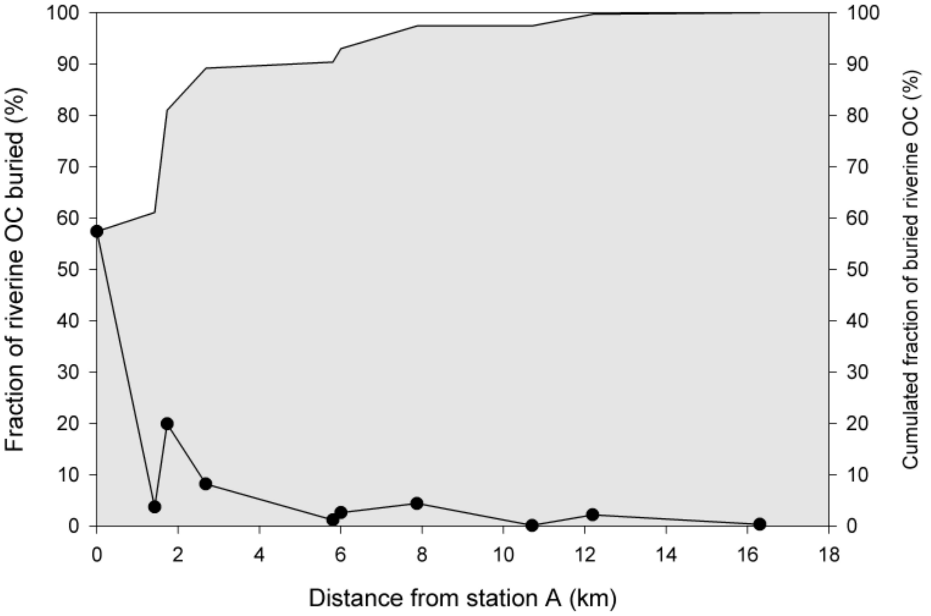

Figure 7. Distribution of the fraction of total riverine OC buried as a function of distance from the river outlet. The shadow area represents the cumulative amount of riverine material buried as getting offshore

3.6 CONCLUSION

The combined use of $\delta^{13}C$ and $\Delta^{14}C$ was a powerfool tool to better constrain the sources of OC in the Rhône River delta and understand the mechanisms involved in the transport and fate of river inputs in the continental shelf. Several features were highlighted:

Benthic-pelagic coupling is not significant in the Rhône River prodelta. Contrary to previous studies' assessments marine phytoplankton produced by local primary production is not a significant component of the sediment organic matter. It is most likely that only very few amount of marine material reaches the bottom and degradation may occur in the water column during vertical export.

The Rhône River delta sediments originate thus from two sources: the Rhône river particles and resuspended particles from the adjacent shelf. These resuspended particles are a complex mixture of old terrigeneous and marine material, partially degraded, that undergo many cycles of deposition and resuspension. These shelf particles have a residence time of more than 3000 years and constitute then a rather refractory pool responsible compared to the Rhône River material delivered.

The high benthic mineralization rates observed by Cathalot *et al* (submitted) near the river mouth is linked the good lability of the riverine deposited material. The OC degradation in the prodelta sediments clearly reflects export mechanisms involved: river deposits are rapidly trapped and accumulates near the river outlet, where they are actively degraded and buried.

3.7 REFERENCES

Aller, R. C.: Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors, Mar. Chem., 61, 143-155, 1998.

Aller, R. C., Hannides, A., Heilbrun, C., and Panzeca, C.: Coupling of early diagenetic processes and sedimentary dynamics in tropical shelf environments: The gulf of papua deltaic complex, Cont. Shelf Res., 24, 2455-2486, 2004.

Baena, A., Fowler, S. W., and Miquel, J. C.: Particulate organic carbon : Natural radionuclide ratios in zooplankton and their freshly produced fecal pellets from the nw mediterranean (medflux 2005), Limnol. Oceanogr., 52, 966-974, 2007.

Bauer, J. E., Druffel, E. R. M., Wolgast, D. M., and Griffin, S.: Sources and cycling of dissolved and particulate organic radiocarbon in the northwest atlantic continental margin, Glob. Biogeochem. Cycle, 15, 615-636, 2001.

Begg, F. H., Cook, G. T., Baxter, M. S., Scott, E. M., and McCartney, M.: Anthropogenic radiocarbon in the eastern irish sea and scottish coastal waters, Radiocarbon, 34, 707-716, 1992.

Belviso, S., Thouzeau, G., Schmidt, S., Reigstad, M., Wassmann, P., Arashkevich, E., and Stefels, J.: Significance of vertical flux as a sink for surface water dmsp and as a source for the sediment surface in coastal zones of northern europe, Estuar. Coast. Shelf Sci., 68, 473-488, 2006.

Blair, N. E., Leithold, E. L., and Aller, R. C.: From bedrock to burial: The evolution of particulate organic carbon across coupled watershed-continental margin systems, Mar. Chem., 92, 141-156, 2004.

Borges, A. V.: Do we have enough pieces of the jigsaw to integrate co2 fluxes in the coastal ocean?, Estuaries, 28, 3-27, 2005.

Burdige, D. J.: Burial of terrestrial organic matter in marine sediments: A re-assessment, Glob. Biogeochem. Cycle, 19, 2005.

Buscail, R., Pocklington, R., and Germain, C.: Seasonal variability of the organic-matter in a sedimentary coastal environment - sources, degradation and accumulation (continental-shelf of the gulf-of-lions, northwestern mediterranean-sea), Cont. Shelf Res., 15, 843-869, 1995.

Cauwet, G., Gadel, F., de Souza Sierra, M. M., Donard, O., and Ewald, M.: Contribution of the rhône river to organic carbon inputs to the northwestern mediterranean sea, Cont. Shelf Res., 10, 1025-1037, 1990.

Cauwet, G., Miller, A., Brasse, S., Fengler, G., Mantoura, R. F. C., and Spitzy, A.: Dissolved and particulate organic carbon in the western mediterranean sea, Deep-Sea Research Part Ii-Topical Studies In Oceanography, 44, 769-779, 1997.

Charmasson, S., Bouisset, P., Radakovitch, O., Pruchon, A. S., and Arnaud, M.: Long-core profiles of cs-137, cs-134, co-60 and pb-210 in sediment near the rhone river (northwestern mediterranean sea), Estuaries, 21, 367-378, 1998.

Copinmontegut, C.: Alkalinity and carbon budgets in the mediterranean-sea, Glob. Biogeochem. Cycle, 7, 915-925, 1993.

Darnaude, A. M., Salen-Picard, C., and Harmelin-Vivien, M. L.: Depth variation in terrestrial particulate organic matter exploitation by marine coastal benthic communities off the rhone river delta (nw mediterranean), Mar. Ecol.-Prog. Ser., 275, 47-57, 2004a.

Darnaude, A. M., Salen-Picard, C., Polunin, N. V. C., and Harmelin-Vivien, M. L.: Trophodynamic linkage between river runoff and coastal fishery yield elucidated by stable isotope data in the gulf of lions (nw mediterranean), Oecologia, 138, 325-332, 10.1007/s00442-003-1457-3, 2004b.

de Madron, X. D., Radakovitch, O., Heussner, S., Loye-Pilot, M. D., and Monaco, A.: Role of the climatological and current variability on shelf-slope exchanges of particulate matter: Evidence from the rhone continental margin (nw mediterranean), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 46, 1513-1538, 1999.

De Madron, X. D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J. C., Radakovitch, O., Giresse, P., Buscail, R., and Kerherve, P.: Particulate matter and organic carbon budgets for the gulf of lions (nw mediterranean), Oceanol. Acta, 23, 717-730, 2000.

de Madron, X. D., Denis, L., Diaz, F., Garcia, N., Guieu, C., Grenz, C., Loye-Pilot, M. D., Ludwig, W., Moutin, T., Raimbault, P., and Ridame, C.: Nutrients and carbon budgets for the gulf of lion during the moogli cruises, Oceanol. Acta, 26, 421-433, 2003.

delGiorgio, P. A., and France, R. L.: Ecosystem-specific patterns in the relationship between zooplankton and pom or microplankton delta c-13, Limnol. Oceanogr., 41, 359-365, 1996.

Druffel, E. R. M., Honjo, S., Griffin, S., and Wong, C. S.: Radiocarbon in particulate matter from the eastern sub-arctic pacific ocean - evidence of a source of terrestrial carbon to the deep sea, Radiocarbon, 28, 397-407, 1986.

Druffel, E. R. M., and Williams, P. M.: Importance of isotope measurements in marine organic geochemistry, Mar. Chem., 39, 209-215, 1992.

Druffel, E. R. M., Williams, P. M., Bauer, J. E., and Ertel, J. R.: Cycling of dissolved and particulate organic matter in the open ocean, Journal of Geophysical Research-Oceans, 97, 15639-15659, 1992.

Druffel, E. R. M., Bauer, J. E., and Griffin, S.: Input of particulate organic and dissolved inorganic carbon from the amazon to the atlantic ocean, Geochem. Geophys. Geosyst., 6, 2005.

Estournel, C., Broche, P., Marsaleix, P., Devenon, J. L., Auclair, F., and Vehil, R.: The rhone river plume in unsteady conditions: Numerical and experimental results, Estuar. Coast. Shelf Sci., 53, 25-38, 2001.

Ferre, B., de Madron, X. D., Estournel, C., Ulses, C., and Le Corre, G.: Impact of natural (waves and currents) and anthropogenic (trawl) resuspension on the export of particulate matter to the open ocean application to the gulf of lion (nw mediterranean), Cont. Shelf Res., 28, 2071-2091, 10.1016/j.csr.2008.02.002, 2008.

Forsberg, B. R., Araujolima, C., Martinelli, L. A., Victoria, R. L., and Bonassi, J. A.: Autotrophic carbon sources for fish of the central amazon, Ecology, 74, 643-652, 1993.

France-Lanord, C., and Derry, L. A.: [delta]13c of organic carbon in the bengal fan: Source evolution and transport of c3 and c4 plant carbon to marine sediments, Geochim. Cosmochim. Acta, 58, 4809-4814, 1994.

France, R. L.: ^{13}c enrichment in benthic compared to planktonic algae - foodweb implications, Mar. Ecol.-Prog. Ser., 124, 307-312, 1995.

Fry, B., and Sherr, E. B.: Δ^{13}c measurements as indicators of carbon flow in marine and freshwater ecosystems, Contributions in Marine Science, 27, 13-47, 1984.

Galy, V., France-Lanord, C., Beyssac, O., Faure, P., Kudrass, H., and Palhol, F.: Efficient organic carbon burial in the bengal fan sustained by the himalayan erosional system, Nature, 450, 407-U406, 2007.

Goni, M. A., Ruttenberg, K. C., and Eglinton, T. I.: Source and contribution of terrigenous organic carbon to surface sediments in the gulf of mexico, Nature, 389, 275-278, 1997.

Goni, M. A., Monacci, N., Gisewhite, R., Ogston, A., Crockett, J., and Nittrouer, C.: Distribution and sources of particulate organic matter in the water column and sediments of the fly river delta, gulf of papua (papua new guinea), Estuar. Coast. Shelf Sci., 69, 225-245, 2006.

Hedges, J. I., Clark, W. A., Quay, P. D., Richey, J. E., Devol, A. H., and Santos, U. D.: Compositions and fluxes of particulate organic material in the amazon river, Limnol. Oceanogr., 31, 717-738, 1986a.

Hedges, J. I., Ertel, J. R., Quay, P. D., Grootes, P. M., Richey, J. E., Devol, A. H., Farwell, G. W., Schmidt, F. W., and Salati, E.: Organic ^{14}c in the amazon river system, Science, 231, 1129-1131, 1986b.

Hedges, J. I.: Global biogeochemical cycles: Progress and problems, Mar. Chem., 39, 67-93, 1992.

Hedges, J. I., and Keil, R. G.: Sedimentary organic-matter preservation - an assessment and speculative synthesis, Mar. Chem., 49, 81-115, 1995.

Hedges, J. I., Keil, R. G., and Benner, R.: What happens to terrestrial organic matter in the ocean?, Organic Geochemistry, 27, 195-212, 1997.

Heip, C. H. R., Goosen, N. K., Herman, P. M. J., Kromkamp, J., Middelburg, J. J., and Soetaert, K.: Production and consumption of biological particles in temperate tidal estuaries, in: Oceanography and marine biology - an annual review, vol 33, Oceanography and marine biology, U C L Press Ltd, London, 1-149, 1995.

Lansard, B., Rabouille, C., Denis, L., and Grenz, C.: In situ oxygen uptake rates by coastal sediments under the influence of the rhone river (nw mediterranean sea), Symposium on Coastal Ecosystem Responses to Changing Nutrient Inputs from Large Temperate and Sub-Tropical Rivers, Fujian, PEOPLES R CHINA, 2005, ISI:000257620200012, 1501-1510,

Lansard, B., Charmasson, S., Gasco, C., Anton, M. P., Grenz, C., and Arnaud, M.: Spatial and temporal variations of plutonium isotopes (pu-238 and pu-239,pu-240) in sediments off the rhone river mouth (nw mediterranean), Sci. Total Environ., 376, 215-227, 10.1016/j.scitotenv.2007.01.069, 2007.

Lansard, B., Rabouille, C., Denis, L., and Grenz, C.: Benthic remineralization at the land-ocean interface: A case study of the rhone river (nw mediterranean sea), Estuar. Coast. Shelf Sci., 81, 544-554, 10.1016/j.ecss.2008.11.025, 2009.

Larsen, P. F., Gadbois, D. F., and Johnson, A. C.: Polycyclic aromatic-hydrocarbons in gulf of maine sediments - distributions and mode of transport, Marine Environmental Research, 18, 231-244, 1986.

Lipiatou, E., and Saliot, A.: Fluxes and transport of anthropogenic and natural polycyclic aromatic hydrocarbons in the western mediterranean sea, Mar. Chem., 32, 51-71, 1991.

Mandalakis, M., Gustafsson, O., Alsberg, T., Egeback, A. L., Reddy, C. M., Xu, L., Klanova, J., Holoubek, I., and Stephanou, E. G.: Contribution of biomass burning to atmospheric polycyclic aromatic hydrocarbons at three european background sites, Environmental Science & Technology, 39, 2976-2982, 10.1021/es048184v, 2005.

Megens, L., van der Plicht, J., and de Leeuw, J. W.: Temporal variations in c-13 and c-14 concentrations in particulate organic matter from the southern north sea, Geochim. Cosmochim. Acta, 65, 2899-2911, 2001.

Millot, C.: The gulf of lions hydrodynamics, Cont. Shelf Res., 10, 885-894, 1990.

Miralles, J., Radakovitch, O., and Aloisi, J. C.: Pb-210 sedimentation rates from the northwestern mediterranean margin, Mar. Geol., 216, 155-167, 2005.

Mook, W. G., and van der Plicht, J.: Reporting c-14 activities and concentrations, Radiocarbon, 41, 227-239, 1999.

Nagao, S., Usui, T., Yamamoto, M., Minagawa, M., Iwatsuki, T., and Noda, A.: Combined use of delta c-14 and delta c-13 values to trace transportation and deposition processes of terrestrial particulate organic matter in coastal marine environments, Chemical Geology, 218, 63-72, 2005.

Pont, D., Simonnet, J. P., and Walter, A. V.: Medium-term changes in suspended sediment delivery to the ocean: Consequences of catchment heterogeneity and river management (rhone river, france), Estuar. Coast. Shelf Sci., 54, 1-18, 2002.

Radakovitch, O., Charmasson, S., Arnaud, M., and Bouisset, P.: Pb-210 and caesium accumulation in the rhone delta sediments, Estuar. Coast. Shelf Sci., 48, 77-92, 1999a.

Radakovitch, O., Cherry, R. D., and Heussner, S.: Pb-210 and po-210: Tracers of particle transfer on the rhone continental margin (nw mediterranean), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 46, 1539-1563, 1999b.

Rau, G.: C-13 depletion in a subalpine lake - carbon flow implications, Science, 201, 901-902, 1978.

Raymond, P. A., and Bauer, J. E.: Riverine export of aged terrestrial organic matter to the north atlantic ocean, Nature, 409, 497-500, 2001a.

Raymond, P. A., and Bauer, J. E.: Use of c-14 and c-13 natural abundances for evaluating riverine, estuarine, and coastal doc and poc sources and cycling: A review and synthesis, Organic Geochemistry, 32, 469-485, 2001b.

Roussiez, V., Ludwig, W., Monaco, A., Probst, J. L., Bouloubassi, I., Buscail, R., and Saragoni, G.: Sources and sinks of sediment-bound contaminants in the gulf of lions (nw mediterranean sea): A multi-tracer approach, Cont. Shelf Res., 26, 1843-1857, 2006.

Sempere, R., Charriere, B., Van Wambeke, F., and Cauwet, G.: Carbon inputs of the rhone river to the mediterranean sea: Biogeochemical implications, Glob. Biogeochem. Cycle, 14, 669-681, 2000.

Sheesley, R. J., Krusa, M., Krecl, P., Johansson, C., and Gustafsson, O.: Source apportionment of elevated wintertime pahs by compound-specific radiocarbon analysis, Atmospheric Chemistry and Physics, 9, 3347-3356, 2009.

Smith, B. N., and Epstein, S.: 2 categories of c-13/c-12 ratios for higher plants, Plant Physiology, 47, 380-&, 1971.

Smith, S. V., and Hollibaugh, J. T.: Coastal metabolism and the oceanic organic-carbon balance, Reviews Of Geophysics, 31, 75-89, 1993.

Stuiver, M., and Ostlund, H. G.: Geosecs indian-ocean and mediterranean radiocarbon, Radiocarbon, 25, 1-29, 1983.

Tesi, T., Miserocchi, S., Goni, M. A., and Langone, L.: Source, transport and fate of terrestrial organic carbon on the western mediterranean sea, gulf of lions, france, Mar. Chem., 105, 101-117, 2007a.

Tesi, T., Miserocchi, S., Goni, M. A., Langone, L., Boldrin, A., and Turchetto, M.: Organic matter origin and distribution in suspended particulate materials and surficial sediments from the western adriatic sea (italy), Estuar. Coast. Shelf Sci., 73, 431-446, 2007b.

Tolosa, I., Bayona, J. M., and Albaiges, J.: Aliphatic and polycyclic aromatic hydrocarbons and sulfur/oxygen derivatives in northwestern mediterranean sediments: Spatial and temporal variability, fluxes, and budgets, Environmental Science & Technology, 30, 2495-2503, 1996.

Ulses, C., Estournel, C., de Madron, X. D., and Palanques, A.: Suspended sediment transport in the gulf of lions (nw mediterranean): Impact of extreme storms and floods, Cont. Shelf Res., 28, 2048-2070, 10.1016/j.csr.2008.01.015, 2008.

Unesco: Discharge of selected rivers of the world. Volume ii (part iii) : Monthly and annual discharges recorded at various selected stations : 20-year catalogue (1965-1984), Unesco, Paris, 600, 1993.

Wang, X. C., Druffel, E. R. M., Griffin, S., Lee, C., and Kashgarian, M.: Radiocarbon studies of organic compound classes in plankton and sediment of the northeastern pacific ocean, Geochim. Cosmochim. Acta, 62, 1365-1378, 1998.

Williams, P. M., Robertson, K. J., Soutar, A., Griffin, S. M., and Druffel, E. R. M.: Isotopic signatures (c-14, c-13, n-15) as tracers of sources and cycling of soluble and particulate organic-matter in the santa-monica basin, california, Progress In Oceanography, 30, 253-290, 1992.

Wright, L. D., and Friedrichs, C. T.: Gravity-driven sediment transport on continental shelves: A status report, Cont. Shelf Res., 26, 2092-2107, 10.1016/j.csr.2006.07.008, 2006.

Yechieli, Y., Sivan, O., Lazar, B., Vengosh, A., Ronen, D., and Herut, B.: Radiocarbon in seawater intruding into the israeli mediterranean coastal aquifer, Radiocarbon, 43, 773-781, 2001.

Zuo, Z., Eisma, D., Gieles, R., and Beks, J.: Accumulation rates and sediment deposition in the northwestern mediterranean, Deep-Sea Research Part Ii-Topical Studies In Oceanography, 44, 597-609, 1997.

CHAPITRE 4. STUDYING SEDIMENT AND WATER COLUMN INTERACTION IN THE RHÔNE RIVER CONTINENTAL MARGIN: ASSESSING THE ORIGIN AND MINERALISATION OF PARTICULATE ORGANIC CARBON (POC) IN A COASTAL ECOSYSTEM

CHAPITRE 4. STUDYING SEDIMENT AND WATER COLUMN INTERACTION IN THE RHÔNE RIVER CONTINENTAL MARGIN: ASSESSING THE ORIGIN AND MINERALISATION OF PARTICULATE ORGANIC CARBON (POC) IN A COASTAL ECOSYSTEM

CATHALOT, C. [1]**, RABOUILLE, C.** [1]**, TISNERAT-LABORDE, N.** [1]**, JOUX, F.** [2]**, BUSCAIL, R.** [3]**, KERHERVE, P.** [3]

[1].Laboratoire des Sciences du climat et de l'Environnement, Gif-sur-Yvette, France

[2].Observatoire Océanologique de Banyuls-sur-mer, Banyusl-sur-mer, France.

[3].Centre de Formation et de Recherche sur l'Environnement Marin, Perpignan, France

Keywords: Bacterial respiration, bacterial production, particulate organic carbon, Rhône River, stable carbon isotopes, radiocarbon, coastal ocean

4.1 ABSTRACT

The fate and origin of suspended particulate organic carbon (POC) in the Rhône River prodelta and adjacent shelf were studied using carbon isotopes and bacterial metabolism measurements. Suspended Particulate Matter (SPM) and POC content and Bacterial metabolism (Community Respiration (CR) rates, Bacterial Abundance, Bacterial Production (BP)) were investigated on a selected set of 10 stations during three cruises performed under normal discharge conditions (in April 2007 and September 2007) and under flood conditions (in June 2008). In addition, $\Delta^{14}C$ and $\delta^{13}C$ signatures of POC were determined in bottom and water column over the area in April 2007.

Under normal discharge rates, CR values highlighted the important role of the water column in POC degradation, with average rates of 46 ± 20 µgC l^{-1} d^{-1} exceeding local primary production and benthic oxygen demand: bottom and intermediate waters in the Rhône River prodelta are major terms in both carbon and oxygen budgets. In June 2008, under flood conditions, CR rates in bottom waters were lower and associated with low BP (~ 0.7 µgC l^{-1} d^{-1}). Statistical calculations seem to indicate that bacteria account for a significant part of CR and rely directly to the Rhône River inputs and their lability.

$\delta^{13}C$ in bottom and intermediate water POC signals were homogeneous over the whole prodelta and adjacent shelf, and displayed values around -23.5 ‰. $\Delta^{14}C$ on the contrary presented a rapid decrease offshore from null values (~0 ‰) at the immediate vicinity of the Rhône River mouth to heavily depleted values (~ -300 ‰) further away on the continental shelf. Coupled $\Delta^{14}C$ and $\delta^{13}C$ signatures shows a clear deconnexion between suspended particles and sediment, and points out a dual mechanism for the export of Rhône River POC inputs. 1) The riverine particles settle down quickly near the river mouth since the ^{14}C enriched material corresponding to the Rhône River inputs is confined in the prodelta. 2) They are diluted with a pool of old particles (~ 3000 yr) corresponding to resuspended particles from the continental shelf sediment, likely to be a mixture of degraded marine and terrestrial material.

4.2 INTRODUCTION

Continental margins are critical buffer regions between land and open ocean. Autochtonous primary production supported by river nutrient inputs from land and coastal upwellings coupled with allochtonous terrigeneous inputs of particulate organic matter and sediment resuspension make these environments areas of tight pelagic and benthic coupling and high organic matter deposition. Hedges *et al.* (1997) reported that the Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) discharged by rivers were sufficient to sustain the current global ocean DOC pool and the global organic carbon burial in marine sediments. Many processes can occur and transform the riverine material after its delivery into the coastal and prior to its offshore export (Raymond and Bauer, 2001a): quantifying and qualifying the amounts of terrestrial organic matter sequestrated in and exported off the continental shelves is thus an important concern when assessing carbon cycle.

Since the damming of the Nile, the Rhône River is the major source of fresh water and terrigeneous particles to the Mediterranean Sea (Copin-Montegut, 1993). Many studies have tried to quantify the Rhône River exports to the Mediterranean Basin: Sempere *et al.* (2000a) proposed a first budget mainly focused on the inputs and discussed with data from literature and De Madron *et al.* (2000) made another budget at the Gulf of Lions' scale using mainly data from sediment traps at the shelf break and canyon heads. Hydrodynamic mechanisms involved in riverine particulate matter export off the Rhône River are well constrained, and have been studied extensively using sediment traps, and organic, radionuclides or trace metals tracers (Buscail and Germain, 1997; Heussner *et al.*, 1990; Lansard *et al.*, 2007; Monaco *et al.*, 1990a; Naudin and Cauwet, 1997). Based on these "offshore" measurements, it has been highlighted that a significant fraction of this export occurs with a nepheloid benthic layer, and that the shelf entraps at least 70% of the riverine material (Bonnin *et al.*, 2008; Ulses *et al.*, 2008b). Therefore, in an attempt to better quantify this buried fraction, several authors focused on the particles sequestration in the Rhône River prodelta and the Gulf of Lions (Lansard *et al.*, 2009; Tesi *et al.*, 2007) or turbidity measurement across the shelf (Naudin and Cauwet, 1997). Nevertheless, so far, the Rhône River POC inputs in this nepheloid layer, their composition as well as their distribution in the prodelta have not been studied using a direct organic carbon tracer on the riverine particles. Characterizing the carbon in the nepheloid layer of the Rhône River prodelta is thus needed to assess its origin, its reactivity and further transforming processes.

Moreover, in coastal and estuaries environments, many studies have reported that degradation of POC by particle-attached bacteria respiration is an important process, in particular via a high extracellular enzyme activity. Aggregates representing potential important microhabitats for microorganisms, particle-bound bacteria may represent a dominant and active community in waters with high SPM (Crump *et al.*, 1998; Smith *et al.*, 1992; Vallières *et al.*, 2008): up to 90% of the bacterial activity can be associated with particles in estuaries. POC degradation in the water column due to bacterial respiration is thus likely to be a major process in river-dominated environments, especially in turbid ones. We therefore surmised that the benthic nepheloid layer would play a key role in the Rhône River prodelta bacterial dynamics and subsequently in the degradation state of the POC reaching the sea floor. Changes in riverine POC inputs are likely to impact the bacterial degradation rates inside this bottom water layer, and thus to change the reactivity of the carbon exported and deposited further offshore.

Our aim in the present study is to characterize the particles in the Rhône River prodelta, their sources and their distribution, by coupling carbon isotopes ($\delta^{13}C$ and $\Delta^{14}C$) on POC in bottom and intermediate waters. Indeed, both isotopes are powerful tools in indicating both the origin and the potential residence time of organic carbon, since marine plankton and terrestrial organic carbon generally display different signatures (delGiorgio and France, 1996; Raymond and Bauer, 2001b). We also measured community respiration rates in normal river discharge rates conditions to evaluate the degradation of organic matter in the water column. Bacterial abundance, bacterial production and community respiration rates were measured during flood conditions, in order to assess the impact of hydrodynamics changes in this coastal ecosystem.

4.3 MATERIALS AND METHODS

4.3.1 Study area and sampling conditions

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 and vertical intense mixing events inducing major nutrient export occur due strong regional winds (de Madron *et al.*, 1999; Millot, 1990). The Gulf of Lions is microtidal and the moderate wave-energy is swell-dominated. The Rhône River has a drainage basin of 97 800 km², a mean water flow of 1700 m^3 s^{-1}, and an annual particulate organic carbon discharge of 19.2 ± 6 10^4 tC/an. The Rhône river is thus the main source of freshwater, nutrients and organic for the Gulf of Lions (De Madron *et al.*, 2000; Pont *et al.*, 2002; Sempere *et al.*, 2000a). The hydrological regime of the Rhône River shows strong seasonal contrast with a large difference between low (<700 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 60m depth (Wright and Friedrichs, 2006). Net sedimentation rates in the prodelta range from 30 to 50cm 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 20km (Miralles *et al.*, 2005).

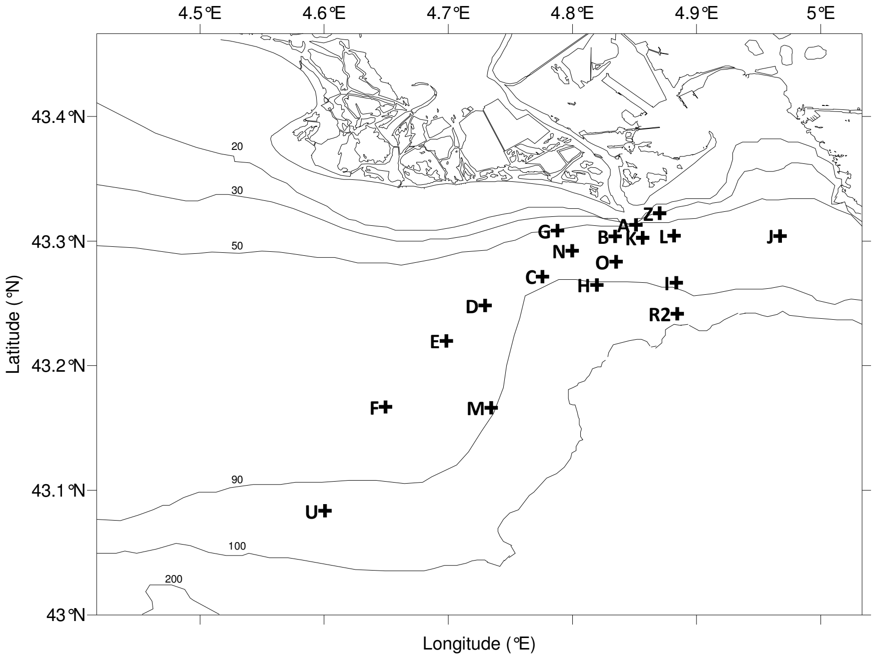

Figure 1. Location of the sampling stations.

4.3.2 Sampling

Samples were collected by Niskin bottles in the Rhône River prodelta (Figure 1) during April 2007, September 2007 and June 2008 (cf. Table 1, Table 2 and Table 3). Samples were collected in intermediate and bottom waters. The Figure 2 shows the Rhône River conditions when sampling was performed.

Samples were filtered on Whatman GF/F precombusted quartz filters (april 2007) or glass fibre filters (september 2007 and june 2008) in an all-glass filter holder. After filtration, filters are washed with distilled water to eliminate the remaining salt and immediately frozen on board at -20°C. They are then dried for 24 h at 65°C and weighted to evaluate the total suspended particulate matter. Subsamples of the filtrate were collected in 10 ml glass tubes with Teflon-lined screw caps and poisoned with $HgCl_2$ (10 mg l^{-1}) until Dissolved Organic Carbon (DOC) analyses.

Table 1. Summary of bottom and intermediate waters conditions in April 2007 cruise

Stations	Long. (°N)	Lat. (°N)	Distance (km)	Depth (m)	T (°C)	[O_2] (µM)	MES mg l^{-1}	[POC] (µgC l^{-1})	[DOC] (µgC l^{-1})	$\delta^{13}C$ (‰)	$\Delta^{14}C$ (‰)	Radiocarbon ages (yr)
A	43° 18' 48"	4° 51' 6"	1.9	13	14.9	259	1.63	152	-	-23.4	29.2 +- -15.8	post-bomb
				25	15.2	244	2.79	152	1080	-24.1	-72.8 +- -9.8	609 ± 87
B	43° 18' 11"	4° 50' 8"	3.1	25	14.8	249	2.09	248	-	-21.7	-168.0 +- -8.7	1479 ± 86
				57	14.8	214	4.99	208	1068	-24.4	-212.8 +- -10.8	1930 ± 110
C	43° 16' 21"	4° 46' 44"	8.3	40	14.8	243	1.88	-	-	-	-	-
				76	14.5	239	4.06	159	1300	-23.8	-298.2 +- -8.4	2847 ± 98
D	43° 15' 3"	4° 43' 48"	12.8	73	14.3	244	2.79	152	951	-23.7	-	-
E	43° 13' 18"	4° 41' 59"	16.8	35	14.5	245	1.82	117	-	-23.2	-67.8 +- -9.8	561 ± 86
				75	14.2	245	3.45	146	1472	-24.4	-320.4 +- -7.8	3106 ± 92
F	43° 10' 10"	4° 39' 1"	23.8	40	14.4	257	1.62	120	-	-23.9	-	-
				78	14.2	242	3.13	155	870	-24.1	-	-
G	43° 18' 30"	4° 47' 17"	5.2	47	14.8	249	4.97	-	958		-	-
H	43° 15' 54"	4° 49' 11"	7.5	40	15.1	251	1.28	106	-	-23.1	-	-
				86	14.5	236	2.26	137	1027			
I	43° 15' 59"	4° 53' 0"	7.7	89	15.1	231	5.37	181	1024	-23.8	-	-
J	43° 18' 15"	4° 58' 2"	10.3	86	14.1	243	1.33	105	1373	-24.3	-111.8 +- -9.8	958 ± 92
K	43° 18' 7"	4° 51' 28"	3.3	31	15.3	249	0.94	106	-	-24.1	-	-
				63	14.8	241	2.86	137	1060	-23.5	-	-
L	43° 18' 6"	4° 52' 48"	4.2	66	14.3	247	1.99		1756		-	-
M	43° 9' 59"	4° 44' 4"	20.3	91	14.1	241	2.07		923		-	-
N	43° 17' 29"	4° 48' 3"	5.6	3	15.2	253	2.41	266	-	-23.0	-	-
				32	15.2	217	2.40	124	-	-23.2	-	-
				67	14.5	240	5.19	-	1080	-	-	-
O	43° 16' 58"	4° 49' 44"	5.4	79	14.4	251	2.84	137	937	-24.4	-	-
R2	43° 14' 28"	4° 52' 55"	10.3	98	14.1	242	0.80	77	-	-23.8	-	-

4.3.3 Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) measurements

Bottom waters DOC is analysed according to a previous method (Cauwet, 1984). After acidification, the sample is bubbled with nitrogen to eliminate the inorganic carbon. It is then pumped through a peristaltic pump, mixed with a potassium persulfate solution and irradiated by a UV lamp. The CO_2 formed is swept by nitrogen to a catalytic unit where it is reduced in CH_4 and analysed in a FID (flame ionization detector). The sensitivity of the method is given as 10 µg C l^{-1} (Cauwet, 1984).

For all cruises, POC from bottom waters is measured by dry combustion of the filters in an automatic CN - analyser LECO 2000 at CEFREM. After being dried and weighed the filters are folded in crucibles and 2 N HCl is added in order to destroy carbonates. They are then dried at 60°C to eliminate the inorganic carbon and most of the remaining acid and water (Cauwet *et al.*, 1990). The precision for organic carbon was 2%.

Specifically for April 2007, others samples were collected in bottom and intermediate waters. Measurements on these samples were performed at LSCE using an automatic Fisons Instrument NA 1500 Element Analyzer. Decarbonation treatment was different from above: filters were acidified with H_3PO_4 1% during 24 hours. The remaining acid was removed by percolating through the filters, which were then dried at 65°C during two days (Druffel and Williams, 1992). The precision for organic carbon was 3%.

4.3.4 Isotopic POC signatures

All carbon isotopic analyses were performed only for April 2007 on the POC samples treated at LSCE, i.e. with decarbonation using H_3PO_4.

Stable isotopic analyses of particulate organic carbon ($\delta^{13}C_{POC}$) were carried out on the same samples than for POC by using a continuous flow ThermoFinigan Delta plus XP Isotope-Ratio Mass Spectrometer. The isotopic compositions were reported using the standard δ-notation (‰) with respect to the Vienna Pee Dee Belemnite (PDB) standard. Stable isotopic results were obtained with uncertainties of ± 0.15 ‰.

^{14}C measurements were performed by the NSF - Arizona AMS facility, Tucson (suspended particles samples). After the decarbonation, the entire sample is combusted in a sealed quartz tube at 850°C with copper oxide and silver wool. The released CO_2 is dried, volumetrically measured, and collected in a glass ampoule. Then, the CO_2 sample is converted to graphite target in an atmosphere of H_2 over an iron powder catalyst at 600°C. The sample ^{14}C /^{12}C ratio was then measured with an NEC 3 MV AMS system. The ^{14}C activities are determined with respect to the international standard of oxalic acid. Final ^{14}C activities are reported in $\Delta^{14}C$. The $\Delta^{14}C$ is defined as the deviation in parts per mil (‰) from the modern standard. All $\Delta^{14}C$ values were corrected from 1950, and from the delay between sampling and measurement years (Mook and van der Plicht, 1999).Ages were calculated from the $\Delta^{14}C$ values using the conventional ^{14}C half-life. The precisions of measurements were ± 10 % on $\Delta^{14}C$ values.

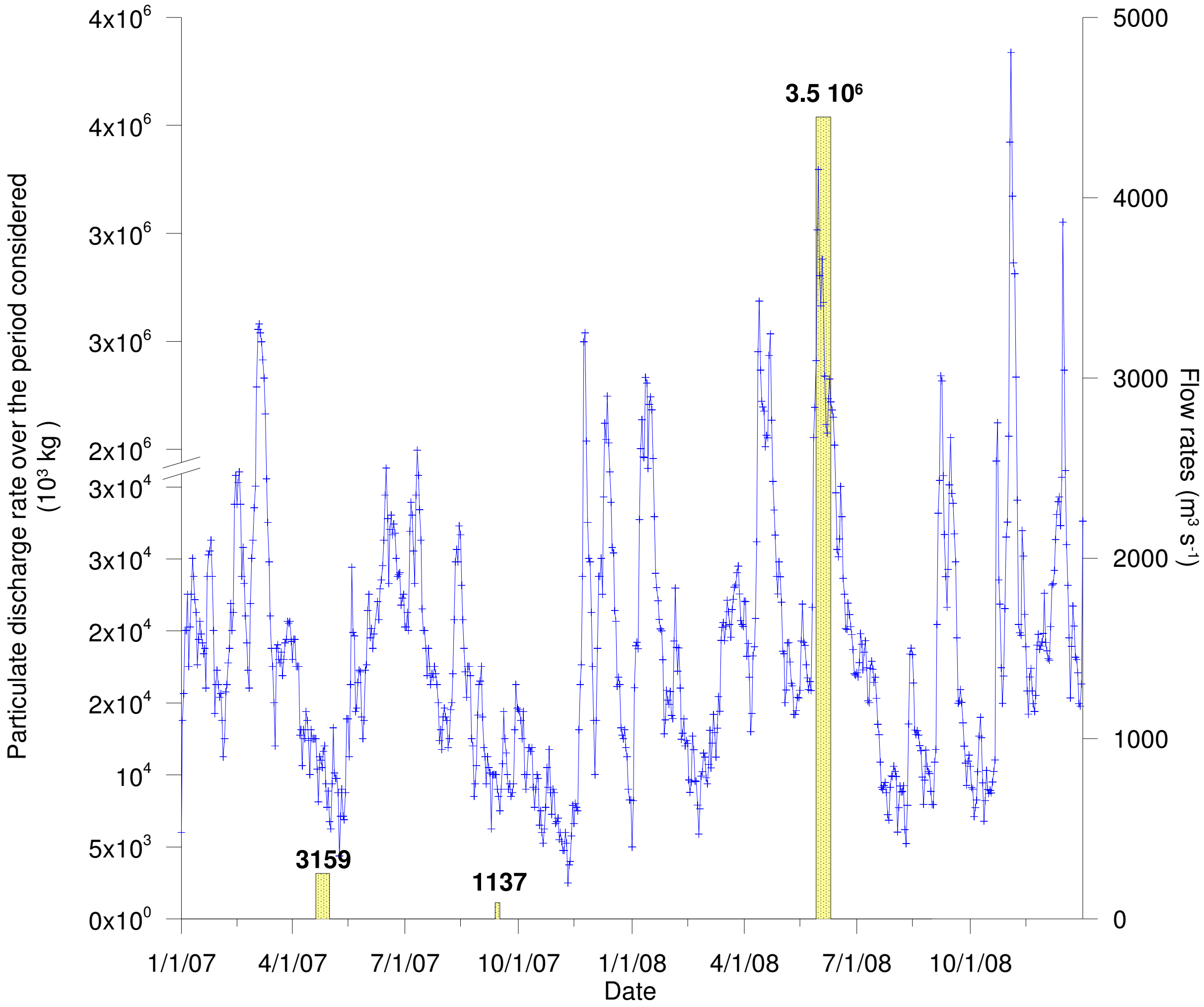

Figure 2. Mean daily flow and particulate discharge rates of the Rhône River. The integrated SPM amount delivered during the sampling cruises period are indicated in yellow.

4.3.5 Bacterial data collection

a) Bacterial abundance

For determination of bacterial abundance by flow cytometry, duplicate 3 ml samples in cryovials were preserved in buffered formalin (2% final concentration). The samples were gently mixed and left in the dark at room temperature for 10 min before quick-freezing in liquid nitrogen and storage at -80°C. The samples were later thawed at room temperature, stained with SYBR Green I (final concentration 0.01% (v/v) of the commercial solution; Molecular Probes Inc., OR) for at least 15 min at 20°C in the dark and analyzed on a flow cytometer (FACScan, Becton Dickinson, San Jose, CA) equipped with a 488 nm, 15 mW argon laser. Bacteria were detected on a plot of green fluorescence (FL1: 515-545 nm) *versus* right angle light scatter (SSC), using the green fluorescence as threshold parameter. Fluorescent beads (1.0 µm; Polysciences Inc., Warrington, PA) were added to each sample analyzed to normalize SSC and green fluorescence. Analytical accuracy of measurements gave a CV of less than 5%. We differenciated two clusters of cells, Low Nucleic Acid and High Nucleic Acid content, according to their differing signals of SSC and FL1.

b) Bacterial production

Bacterial production (BP) was measured by ^{3}H-leucine incorporation (Simon and Azam, 1989) as modified by (Smith and Azam, 1992). Samples (2.5 ml in triplicate) were added to sterile Eppendorf tubes (5 ml), containing 8 nM [4,5-^{3}H]-leucine (specific activity 117 Ci mmole^{-1}, Perkin Elmer) and 32 nM of unabelled leucine. One killed control was prepared for each assay by addition of 250 µl 50% trichloroacetic acid (TCA), 15 min before the addition of leucine. Tubes were incubated in the dark for 1 h in water maintained at *in situ* temperature. Incubations were stopped by adding 100 µl of 50% TCA. Samples were then frozen and kept stored at -20°C until final processing. Tubes were then thawed, vortexed and then centrifuged for 15 min at 12,000 x g. The precipitate was rinsed once with 5% TCA and once with 70% ethanol. The precipitates were resuspended in 1.0 ml of liquid scintillation cocktail (FilterCount, Perkin Elmer) and radioactivity determined by liquid scintillation counter (LS 5000CE Beckman). Leucine incorporation rates were converted into carbon production using the conversion factor of 1.55 kg C produced by mole of leucine incorporated (Simon and Azam, 1989). Analytical accuracy of measurements gave a CV of less than 4%.

Table 2. Summary of bottom and intermediate waters conditions in September 2007 cruise

Cruise	Stations	Long. (°N)	Lat. (°N)	Distance (km)	Depth (m)	T (°C)	$[O_2]$ (µM)	S (p.s.u.)	MES mg l^{-1}	[POC] (µgC l^{-1})	[DOC] (µgC l^{-1})
sept-07	A	43° 18' 47"	4° 51' 6"	1.9	19	17.7	244	34.40	8.36	201	1118
	B	43° 17' 60"	4° 50' 5"	3.1	59	14.5	214	35.60	6.87	209	1020
	C	43° 16' 17"	4° 46' 20"	8.3	75	14.8	207	-	5.83	142	1061
	D	43° 18' 2"	4° 43' 39"	13.0	73	15.0	217	35.02	4.54	121	1060
	H	43° 15' 55"	4° 49' 11"	7.5	85	15.0	202	35.90	6.05	141	1109
	I	43° 15' 60"	4° 53' 3"	7.7	88	14.8	210	36.80	5.24	127	949
	K	43° 18' 35"	4° 52' 47"	3.3	56	18.2	241	37.10	5.64	157	811
	L	43° 18' 35"	4° 52' 47"	5.4	56	18.0	238	37.30	5.74	172	837
	N	43° 17' 28"	4° 47' 50"	5.7	67	14.5	217	33.00	4.95	133	825
	O	43° 17' 5"	4° 49' 48"	5.1	77	16.1	226	32.10	4.51	142	690

c) Community Respiration

For community respiration (CR), sample from Niskin bottle was dispensed into six 60 ml biological oxygen demand (BOD) bottles. All BOD bottles were washed with 10% HCl and rinsed with Milli-Q water prior to use. The BOD bottles were allowed to overflow ~ 3 times the volume of the bottle, ensuring that no bubbles remained in the bottles, and capped free of headspace with ground glass stoppers. . The BOD bottles were incubated in the dark at *in situ* temperature in a water bath to prevent gas exchange. At time zero and then at 24 h, 3 BOD bottles were fixed with Winkler reagents for the determination of dissolved O_2 (DO) concentration. Concentrations of DO were estimated by Winkler titration procedure. The whole BOD bottle was titrated to increase sensitivity of the rate estimates. Analytical accuracy of measurements of O_2 gave a CV of less than 0.5% between replicate measurements. CR rates were determined by following the decrease in DO during incubation experiments. CR was calculated as the difference between DO at time 0 and time 24h: the significance of this difference was statistically tested by a non-parametric Mann-Whitney test among time 0 and time 24h replicates. Values were rejected when p>0.1. Uncertainty on CR was calculated from the standard deviation of the replicates using the classical following formula: $\sigma_{CR} = \sqrt{{\sigma_{O_2(t_0)}}^2 + {\sigma_{O_2(t+24h)}}^2}$.

d) Statistical calculation

In order to assess statistical correlation between water column and heterotrophic community parameters (CR, BR, BA) we calculated the non parametric Spearman correlation coefficient (rho). We thus assumed that correlation were significant were different when $p < 0.05$. We also compared POC and DOC concentrations and CR rates during cruises. To do so, we used the non parametric the Mann Whitney test ($\alpha = 0.05$). Spatial interpolations have been performed using krigging tool provided by the Surfer® software.

Table 3. Summary of bottom and intermediate waters conditions in June 2008 cruise

Cruise	Stations	Long. (°N)	Lat. (°N)	Distance (km)	Depth (m)	T (°C)	[O_2] (µM)	S (p.s.u.)	MES mg l^{-1}	[POC] (µgC l^{-1})	[DOC] (µgC l^{-1})
June 08	A	43° 18' 42"	4° 51' 6"	2.1	19	17.7	238	37.90	22.61	291.71	6207.60
	B	43° 18' 10"	4° 50' 2"	3.0	59	17.4	239	37.80	3.76	130.17	1798.80
	C	43° 16' 18"	4° 46' 30"	8.6	75	14.7	239	38.30	3.14	97.19	963.24
	D	43° 14' 49"	4° 43' 39"	13.0	73	13.7	226	38.50	4.49	99.61	849.48
	E	43° 18' 2"	4° 43' 39"	17.0	73	15.6	245	38.30	5.07	135.82	1402.50
	H	43° 15' 55"	4° 49' 11"	7.6	85	14.0	245	38.30	0.71	61.55	1320.00
	I	43° 15' 60"	4° 53' 3"	7.7	88	15.9	238	38.30	2.09	80.32	1150.80
	J	43° 15' 60"	4° 53' 3"	12.0	88	13.3	227	38.60	2.72	68.69	749.04
	K	43° 18' 35"	4° 52' 47"	3.4	56	16.8	240	38.00	7.68	146.00	-
	L	43° 18' 35"	4° 52' 47"	4.1	56	16.7	229	38.30	2.29	97.28	954.96
	N	43° 17' 28"	4° 47' 50"	5.7	67	16.3	240	38.30	5.18	105.57	1394.40
	O	43° 17' 5"	4° 49' 48"	5.3	77	15.3	248	38.30	3.94	89.16	1356.00
	U	43° 18' 2"	4° 43' 39"	33.8	73	13.8	231	38.10	4.21	96.86	939.36
	Z	43° 18' 2"	4° 43' 39"	1.9	73	17.6	236	38.30	24.23	291.15	954.24

4.4 RESULTS

4.4.1 Stations characteristics: intermediate and bottom water column environmental characteristics

Table 1, Table 2 and Table 3 summarize all bottom and intermediate water column data, and Rhône River discharge conditions.

a) Temperature and Suspended Particulate matter

Temperatures were homogeneous over the prodelta waters between cruises, ranging between 13 and 18°C. Suspended Particulate Matter (SPM) contents were statistically different between cruises ($p<0.01$). In April 2007, SPM contents varied between 1.4 and 5.2 mg l^{-1}, with no significant spatial pattern over the prodelta. In September 2007, values were homogeneous with an average SPM concentration of 5.8 ± 1.2 mg l^{-1}, station A displaying a single higher value of 8.4 mg l^{-1}. The same tendency was observed in June 2008: stations A, Z and K at the immediate vicinity of the river outlet presented high values with homogeneous lower content elsewhere in the prodelta.

b) Dissolved organic carbon

Dissolved organic carbon (DOC) contents were homogeneous over the shelf, except station A in June 2008 which displayed a significant high value directly related to the Rhône River flood inputs. DOC values were not statistically different from one cruise to another ($p>0.05$).: excluding this single value, mean DOC concentration in the Rhone River prodelta (all cruises taken into account) was 1082.2 ± 246.3 µgC l^{-1}, corresponding to a variation of only 22%.

c) Particulate Organic Carbon

For the April 2007 cruise, POC measurements in bottom waters were performed both at LSCE and Cefrem (cf. Materials and Methods). Decarbonation processes were different and resulted in values obtained at the LSCE lower by 66.8 ± 9.5 %. Solubilisation and removal of a portion of the organic matter as a consequence to carbonate removal by acidification is a well-known issue (Bisutti *et al.*, 2004; Froelich, 1980). The two set of data were significantly and strongly correlated (Figure 3; y = 1.77 x + 60.64, r² = 0.7723, p<0.001). As POC data from all cruises have been measured at Cefrem, and the technique they used prevented samples from OC losses (Nieuwenhuize *et al.*, 1994), we chose to correct the LSCE values obtained in April 2007 using the relationship observed between both data sets in bottom waters. The relative error resulting from transformation was 27 µgC l^{-1}. Anyway, comparison between cruises was made using only Cefrem bottom water POC contents, allowing reliable conclusions. For April 2007, comparing stations and bottom and intermediate water concentrations using the LSCE data s*et al*low us to draw relative tendency.

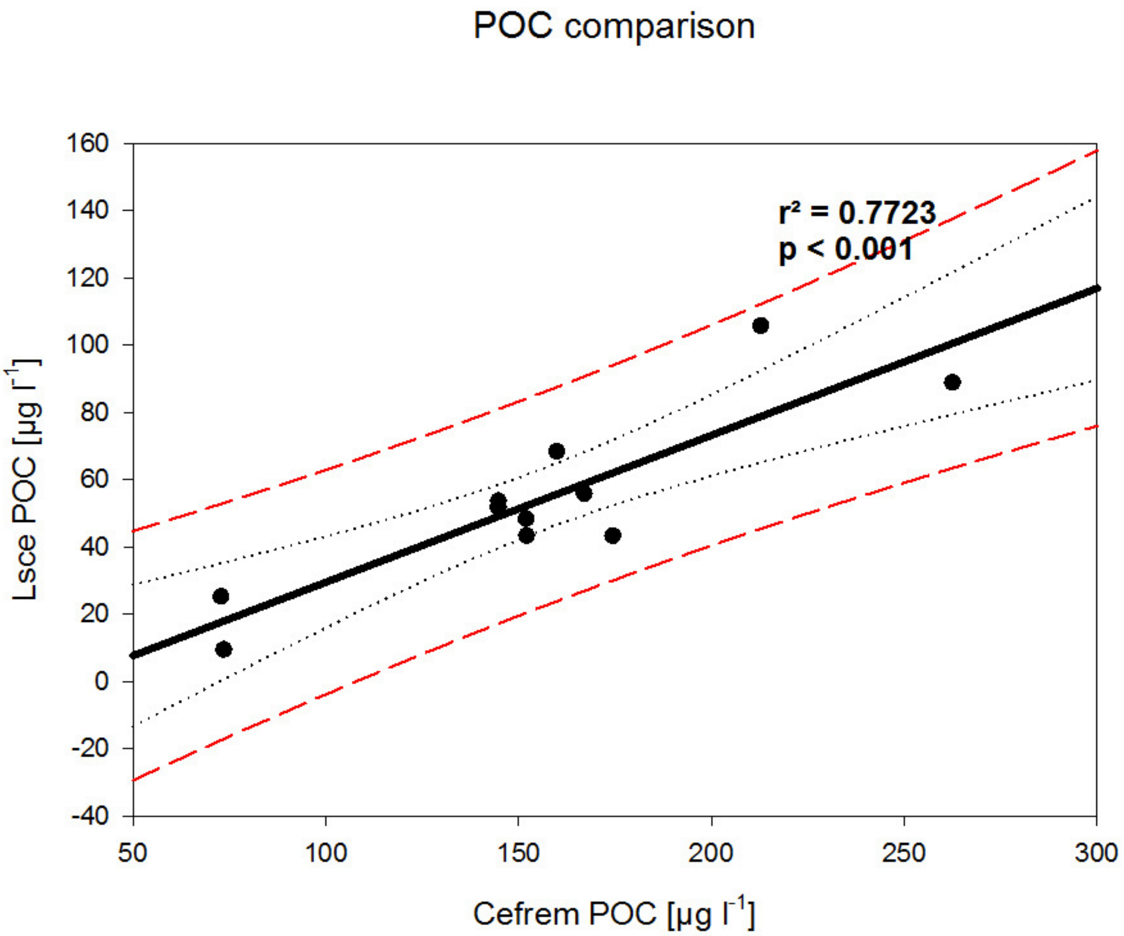

Figure 3. Comparison of POC values obtained at LSCE and Cefrem. Plain line: linear regression (Pearson coefficient and associated probability bottom right), dotted line: 95 confidence interval, dashed line: 95% prediction interval.

Bottom water particulate organic carbon (POC) contents during cruises were statistically different from one to another (p<0.05). Indeed, when comparing the stations that have been sampled during the three cruises, POC contents were the highest in April 2007 (Table 1) and the lowest in June 2008 (Table 3). Nevertheless, as for DOC and SPM, in June 2008 stations close to the river mouth (A and Z) displayed high POC content of 291 µgC l^{-1}: this must be related to the high liquid and particulate discharge rate of the Rhône River at this time. Station F presented also high POC content in June 2008 (Table 3) corresponding to a high organic carbon fraction of SPM (~14%): this outlier value is not consistent with surrounding stations content (E and U) that display much lower content. We thus suspect either an error in the sampling procedure (contamination, sediment resuspension during Niskin bottle sampling) or a local organic matter input from a spatially localized and limited primary production event. Except for this outlier, in all cruises, the spatial distribution pattern was as follows: POC contents were highest near the Rhône River mouth (Stations A, K, B, Z, L) and usually associated with the highest SPM organic fraction, and decreased offshore to low values, both in concentration and OC content.

Intermediate waters presented slightly lower POC contents than bottom water, but given the variability, not significantly different.

d) POC isotopic $\delta^{13}C$ and $\Delta^{14}C$ signals:

Carbon isotopic signatures of POC where determined on LSCE samples. The decarbonation technique is equivalent to the acidification and subsequent rinsing as it implies acid removal before drying. Many authors studied the effect of decarbonation processes on sediment and particulate organic carbon on isotopic signals, and namely compared the acidification + rinsing, the vapour phase acidification and the in situ acidification methods (Batista *et al.*, 1994; Komada *et al.*, 2008; McNichol *et al.*, 1994; Schubert and Nielsen, 2000). For carbonate-rich samples (~30%), they found no influence of methods on both $\delta^{13}C$ and $\Delta^{14}C$ signatures. Batista *et al.*, 1994 and McNichol *et al.*, 1994 even showed a better ^{14}C estimation using the acidification + rinsing protocol on high carbonate content sediments. (Monaco *et al.*, 1990b) analysed particulate matter in intermediate waters on the western Gulf of Lions and found values around 20-30% $CaCO_3$. Moreover, Heussner *et al.* (2006) and Monaco *et al.* (1999) found similar rich carbonate particulate matter at the head of canyons on the northeastern continental slope of the Gulf of Lions. Carbonate content on the Rhône River suspended particles are usually 30% (Aucour *et al.*, 1999; Santiago *et al.*, 1994). Therefore, it is most likely that SPM in the Rhône River prodelta has high carbonates content. We can thus reasonably assume that $\delta^{13}C$ and $\Delta^{14}C$ analyses performed on the LSCE POC were undisturbed by the decarbonation treatment and that their associated results are reliable.

$\delta^{13}C_{POC}$ values in April 2007 were homogeneous in the whole prodelta (Table 1) and different from the sediment pattern (Figure 4). There was no specific trend in spatial $\delta^{13}C_{POC}$ distribution in the prodelta, $\delta^{13}C_{POC}$ signatures being -24.0 ± 0.3 ‰ in bottom waters and -23.2 ± 0.8 ‰ in intermediate waters, respectively.

Except station A, all stations show bottom and intermediate waters with $\Delta^{14}C_{POC}$ < -100 ‰. Station A was markedly enriched with intermediate waters reaching modern carbon values, the $\Delta^{14}C_{POC}$ signals decreasing very quickly offshore down to values around -300 ‰.

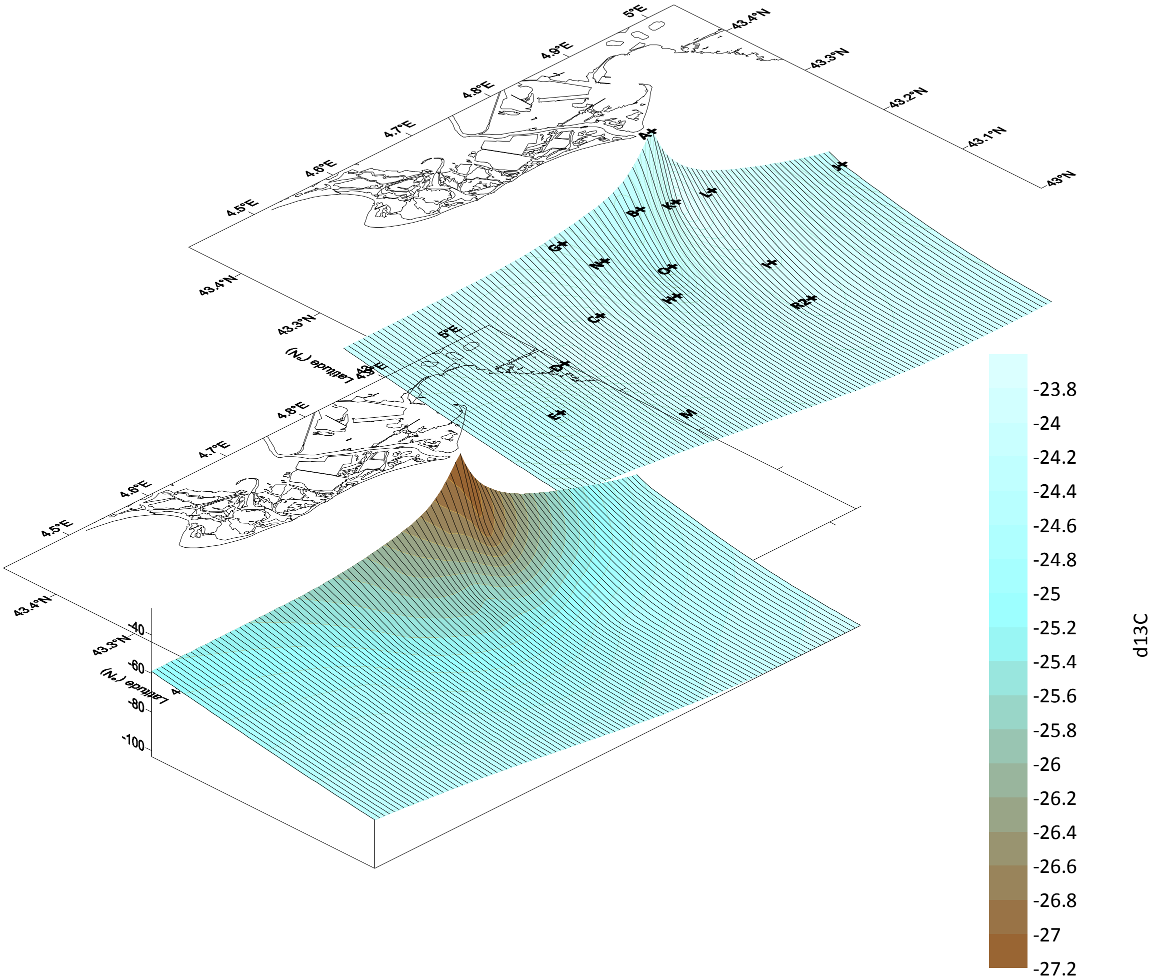

Figure 4. $\delta^{13}C$ (‰) distribution in the Rhône River prodelta. Bottom: surface sediment (from Cathalot *et al*, In prep.). Top: Bottom water POC.

4.4.2 Heterotrophic ecosystem and bacterial bulk properties

a) Community Respiration Rates

When both available, Community Respiration (CR) rates in bottom and intermediate waters were similar ($p>0.05$) (**Figure 5**). Thus in September 2007 and June 2008, we mainly focused on bottom waters assuming that CR was homogeneous in the lower water column. Water column community respiration rates presented significant differences between cruises ($p<0.05$): April and September 2007 CR rates were significantly higher than the June 2008 flood conditions values. CR rates were homogeneous among the shelf with no significant spatial distribution pattern. Nevertheless, in normal conditions (April, September 2007 and early June 2008), the furthest offshore stations tend to display higher CR values (196.8 ± 72.5 µgC L^{-1} d^{-1} vs. 45.6 ± 20.8 µgC L^{-1} d^{-1}).

The other bacterial data (Bacterial Abundance, Bacterial Production) are available only in the bottom water during the June 2008 flood conditions.

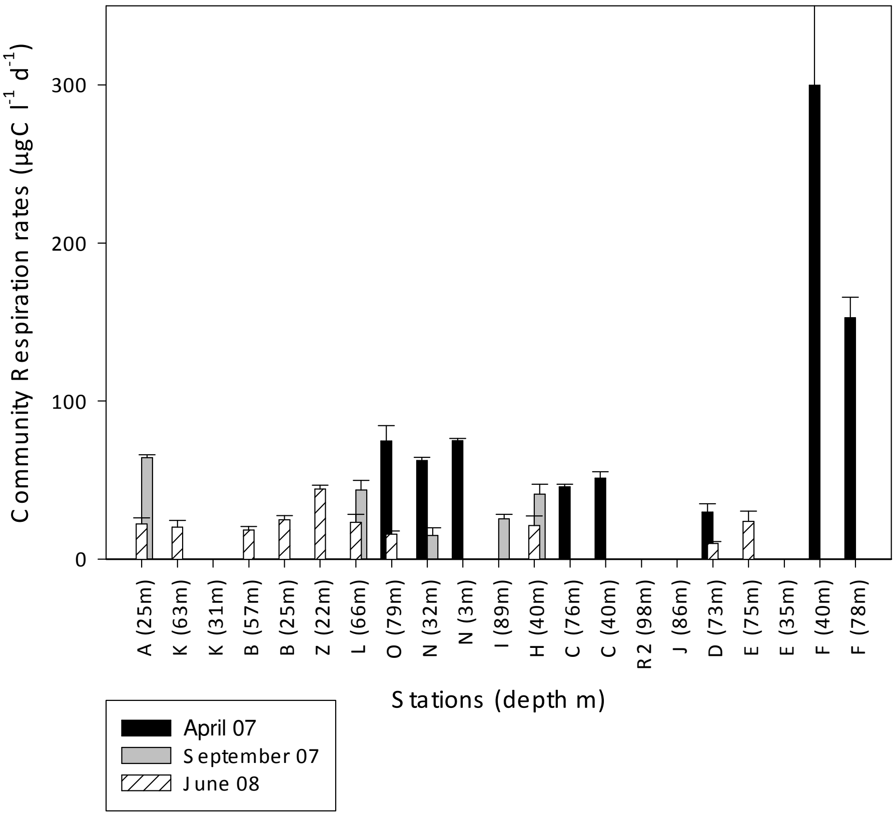

Figure 5. Community Respiration rates during the three cruises. Black: April 07, Gray: September 07, Hashed: June 08

b) Bacterial Abundance

Overall, the total bacterial abundance was minimal at station J and maximal at station L (cf. Figure 6). Highest values were recorded at intermediate distance from the river outlet not at the direct vicinity of the Rhône River mouth (stations L, K, Z, I: distance between 1.3 and 7.6 km from station A). Low Nucleic Acid (LNA) bacteria dominated the community with 64 ± 4% of the total bacterial community. Respectively, High Nucleic Acid (HNA) bacteria represented only 36 ± 4% of the total bacterial community, with abundances ranging between 1.41 10^8 cells L^{-1} and 3.4 10^8 cells L^{-1}.

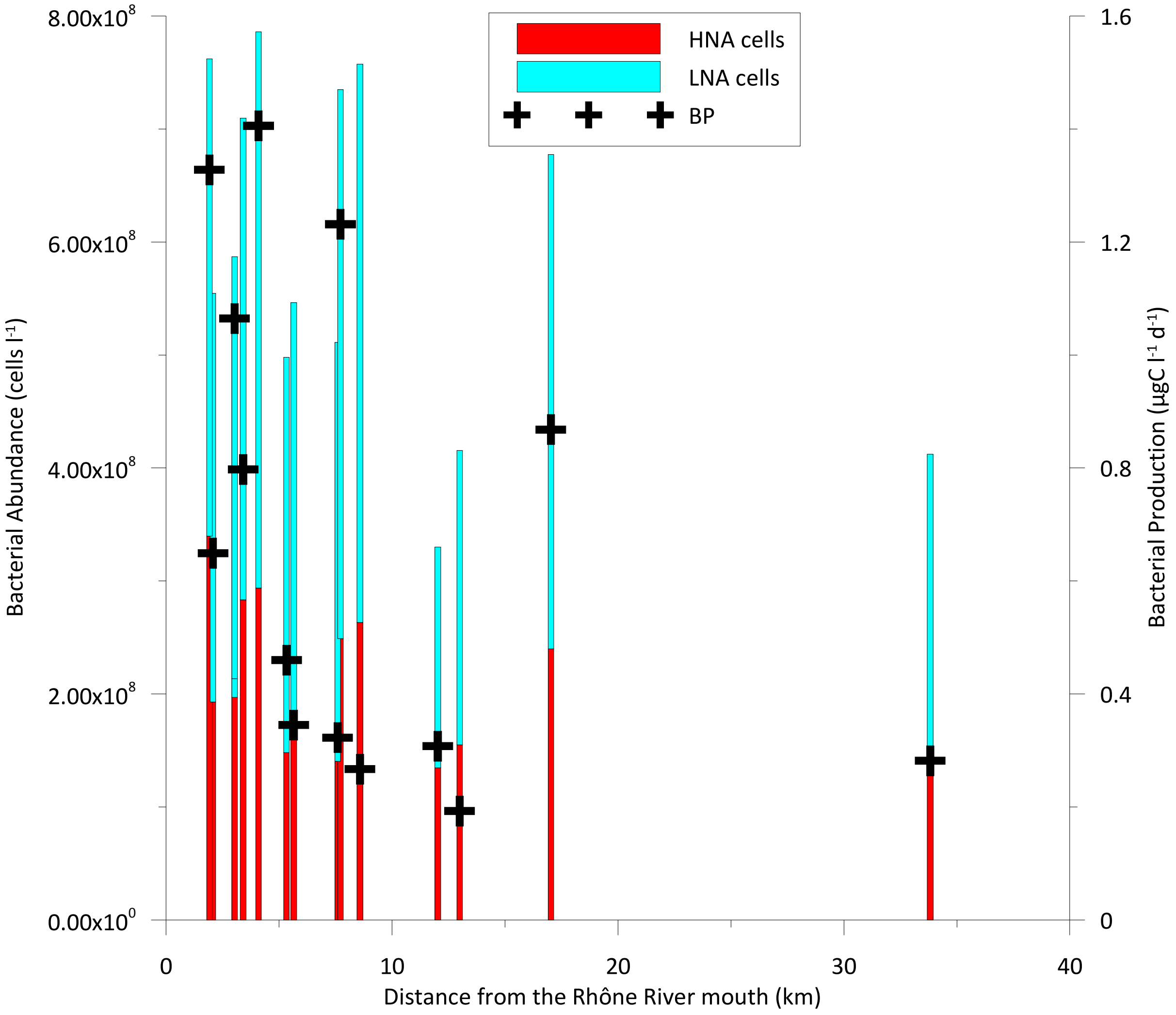

Figure 6. Bacterial Abundance and Production in bottom water during the June 2008 flood.

c) Bacterial production

Bacterial production derived from leucine incorporation rates was much lower than the CR rates. Indeed the leucine incorporation rates ranged between 5.2 pmol Leu L^{-1} h^{-1} at station D and 37.9 pmol Leu L^{-1} h^{-1} at station L, corresponding to a bacterial production varying between 0.2 and 1.4 µgC L^{-1} d^{-1}. As for bacterial abundance, highest values of bacterial production were recorded located at stations at intermediate distance from the river outlet (L, B, Z and I).

d) Relationships between parameters

Relationships among bacterial production, bacterial abundance, community respiration, DOC, POC, temperature and distance to the river outlet are presented in Table 4. Bacterial production was strongly correlated with total bacterial abundance and particularly with HNA cells. Bacterial abundance was correlated to temperature, and particularly HNA cells correlated with POC. Finally, community respiration correlated strongly with bacterial abundance and weakly with bacterial production.

Table 4. Relationships between Bacterial Production (BP, µgC l^{-1} d^{-1}), Bacterial Abundance (Total BA, HNA and LNA, 10^9 cells l^{-1}), Dark Community Respiration (DCR, µgC l^{-1} d^{-1}), Temperature (T, °C), Particulate Organic Carbon (POC, µgC l^{-1}), Dissolved Organic Carbon (DOC, µgC l^{-1}) and distance from river outlet (distance, km). Spearman correlation coefficient (ρ) and significant levels are presented.

	BP	Total BA	HNA	LNA	DCR
Total BA	0.67**				
HNA	0.67**	0.95***			
LNA	0.48	0.93***	0.82***		
DCR	0.67	0.75*	0.65*	0.7*	
Water column properties					
SPM	0.05	0.1	0.24	0.08	0.27
POC	0.38	0.41	0.55*	0.18	0.16
POC (%)	0.1	0.1	0.02	0.27	0.04
DOC	0.32	0.16	0.077	0.15	0.05
T	0.75**	0.61*	0.64*	0.4	0.31
distance	0.59*	0.4	0.43	0.18	0.14

** p<0.05*
***p<0.01*
****p<0.001*

4.5 DISCUSSION

4.5.1 *Distribution and sources of POC in the prodelta bottom and intermediate waters:*

The Suspended Particulate Matter in bottom and intermediate waters the Rhône River delta system displays a decrease in POC concentrations from the river mouth to the adjacent continental shelf. This POC distribution clearly reflects the footprint of the riverine inputs, spreading preferentially in the south-west direction (Naudin *et al.*, 1997). Hydrodynamic mechanisms involved in riverine particulate matter export off the Rhône River have been extensively studied: the continental material is transported to the shelf in a benthic nepheloid layer, mostly alongshore to the southwest (Heussner *et al.*, 1990; Monaco *et al.*, 1990a; Naudin and Cauwet, 1997). Terrigeneous POC transfer to shelf via these benthic turbid layers is thus likely to play an important role in the North Western Mediterranean carbon cycle. Kerhervé *et al*, In Prep, realized a 3 years monitoring series of suspended particulate matter in the Rhône River and found out that $\delta^{13}C_{POC}$ signature of the riverine POC was stable over time and did not vary significantly including flood events: -27.5 ± 0.5 ‰.

Gontier (personal communication) found that SPM $\Delta^{14}C$ signatures in the Rhône River were mostly around 100 ‰: this is coherent with enriched values found in other nuclear plants influenced coastal oceans (Baena *et al.*, 2007; Begg *et al.*, 1992) and with the signal in intermediate waters at the river outlet (station A: $\Delta^{14}C$ = 29.2 ‰). The Rhône River entry term would thus be $\Delta^{14}C$ ~ 100 ‰ and $\delta^{13}C_{POC}$ ~ -27.5 ‰. Marine phytoplankton generally displays a slightly enriched signature between -50 and 150 ‰ corresponding to photosynthesis fixation of bomb ^{14}C atmospheric CO_2 (Bauer *et al.*, 2001; Druffel and Williams, 1992; Williams *et al.*, 1992). Thus the marine associated POC should have a ^{14}C signature close to the ^{14}C-DIC of Mediterranean Sea surface waters around 100 ‰ (Yechieli *et al.*, 2001). The $\delta^{13}C$ values associated with marine POM originating from autochthonous phytoplankton usually range between -19 and -22 ‰ (Fry and Sherr, 1984; Hedges *et al.*, 1997). The marine POC term signal would therefore be $\Delta^{14}C_{POC}$ ~ 100 ‰ and δ^{13} C_{POC} ~ -22.4 ‰ (Darnaude *et al.*, 2004; Fry and Sherr, 1984; Lansard *et al.*, 2009).

$\delta^{13}C_{POC}$ signatures (~ -24.0 ‰) were similar from one station to another in all the prodelta and shelf indicating a homogeneous pool of particles in bottom and intermediate waters, with a mixed terrigeneous/marine signature (Figure 4). This distribution pattern clearly differs from the one observed previously in the prodelta and adjacent shelf sediments (Lansard *et al.*, 2009; Tesi *et al.*, 2007; Cathalot *et al*, (Chapitre 3)): even close to the river outlet, the POC does not display any distinct Rhône River signature, and no correlation was found between the sediment $\delta^{13}C_{OC}$ signals and the POC values in bottom waters. This reflects a clear disconnexion between sediment and suspended particles.

The uncoupling between sedimentary OC and bottom waters POC content is also observed with the $\Delta^{14}C$ signals in bottom waters. Indeed, $\Delta^{14}C$ signals in bottom waters show a rapid decrease offshore, from modern enriched values towards low values indicating aged material. Only at the far end of the South-West transect (station E), sediment OC and bottom waters POC displayed the same $\delta^{13}C$ and $\Delta^{14}C$ signatures ($\Delta^{14}C$ ~ -320 ‰, $\delta^{13}C$ ~ -24.0 ‰)(cf. Figure 7). This intermediate and homogeneous $\delta^{13}C$ signal corresponds to the mid-shelf mud belt signatures reported by Tesi *et al.* (2007), and these signatures may thus reflect the average shelf particles composition: an old (around 3000 yr.) and slightly $\delta^{13}C$ depleted material compared to fresh produced marine phytoplankton. In an attempt to better quantify the terrigeneous fraction in the Rhône River prodelta sediment, Cathalot *et al*, (Chapitre 4) coupled $\delta^{13}C_{OC}$ and $\Delta^{14}C_{OC}$ signals as a discriminatory source factor: they suggested that the marine contribution to OC in the prodelta sediment was almost negligible and that the complementary source would be resuspended and redeposited shelf particles. Our results corroborate this hypothesis and contrast sharply with the previous idea of a simple mixing between the Rhône River and freshly marine material originating from local primary production (Lansard *et al.*, 2009; Tesi *et al.*, 2007).

The observed shift between sediment and bottom water signatures in the proximal prodelta suggests a quick deposition of the riverine input consistently with previous local hydrodynamic and particulate export studies (Roussiez *et al.*, 2006). Indeed, enriched $\Delta^{14}C$ signature of the Rhône River SPM (around 100 ‰) is recorded only in sediments located at the immediate outlet, the bottom and intermediate waters at station A (2km from the mouth) presenting a slightly depleted signal that indicates a mixing with old material. The $\Delta^{14}C$ of bottom waters and sediments reflects thus a dual mechanism for the Rhône River particles export:

- Rapid deposition in the sediment where they can be degraded and buried (Cathalot *et al.*, In prep.)
- Dilution with resuspended shelf particles.

The main transport and distribution of riverine material in the Gulf of Lions shelf waters are ensured by advective transfers via the benthic nepheloid layer, instead of downward vertical settling of particles from overlying layers (Aloisi *et al.*, 1982; deMadron and Panouse, 1996). Combination of sedimentation, erosion and advective transfer processes in the boundary nepheloid layer is thus a major process by which the nearshore deposits and the middle-shelf mud belt are formed, and is responsible of particle exchange between these two units. Roussiez *et al.* (2005) showed that the riverine material is first deposited in the inner-shelf before being subjected to the local hydrodynamics and then partially exported towards the platform and slope (preferentially south-westward). Highly energetic resuspension events are frequent and repeated phenomena affecting the inner-shelf sediment of the Gulf of Lions (Roussiez *et al.*, 2005) and constitute the predominant shelf-slope export process of particulate material (Ferre *et al.*, 2008; Heussner *et al.*, 2006; Ulses *et al.*, 2008a). Yet, this phenomenon seems to be limited since our $\Delta^{14}C$ results show that the enriched material is confined into the prodelta. Using our $\Delta^{14}C$ data, we attempt to calculate the fraction of the prodelta sediment redistributed to the shelf.

Assuming an average concentration of POC in the Gulf of Lions of 5 mmol m^3 (de Madron *et al.*, 2003), a volume of 9.1×10^{11} m^3 this leads to a stock of $4.6\ 10^9$ mol POC. In an attempt to make a quick budget of one year over the Gulf of Lion, let's assume also that this pool has an "initial" $\Delta^{14}C$ signature of -400 ‰ (oldest value recorded in sediment at station J) and is only diluted by the Rhône River POC inputs approx. $1.6 \pm 0.5\ 10^{10}$ mol/an (Sempere *et al.*, 2000a). To lead to a pool of POC particles of -300 ‰ $\Delta^{14}C$ signature (cf. POC signatures), it would need $f_{Rh\hat{o}ne} = \frac{4.6\ 10^{9}(-300+400)}{1.6\ 10^{10}(100+300)} = 7.2\ \%$ of the Rhône River annual input. POC records over the last two years showed an input closer to the ones of Cauwet *et al.* (1997) around $0.7\ 10^{10}$ mol/an: with these lower inputs, the fraction needed to give the average -300 ‰ of suspended particles over the shelf would be 20 %. Since the pool of shelf particles is actually fed by the sediment of the Gulf of Lions continental shelf which constitutes an almost infinite pool compared to the Rhône River inputs, this calculation is, of course, an oversimplification and can only give an insight of the export of the Rhône River POC to the shelf. Nevertheless, as it is consistent with previous estimates based of radionuclides, sediment trap measurements and modelling (Ferre *et al.*, 2008; Heussner *et al.*, 2006; Lansard *et al.*, 2007; Ulses *et al.*, 2008a), we suggest that only 10-20 % of the Rhône River POC is actually exported on the shelf and thus available for ocean export and C biogeochemical cycles of the Mediterranean Sea.

Bottom water $\Delta^{14}C_{POC}$ at station J and intermediate waters $\Delta^{14}C_{POC}$ at station E display a clear enriched signal (around -24.0 ‰) which may reflect inputs of fresh marine material, produced by local primary production in surface waters. Moreover, $\Delta^{14}C_{POC}$ values in intermediate waters were generally greater than bottom waters, reflecting an autochtonous contribution from surface waters. Therefore, the POC in bottom and intermediate waters of the Rhône River prodelta is the result of complex mixture between riverine and circulating resuspended shelf particles, and minor and pulsed marine inputs. Thus, the coupling between fresh water river plume and the particle deposition that has been reported in other coastal areas does not apply to the Rhône River prodelta (Fulweiler and Nixon, 2009; Soetaert and Middelburg, 2009).

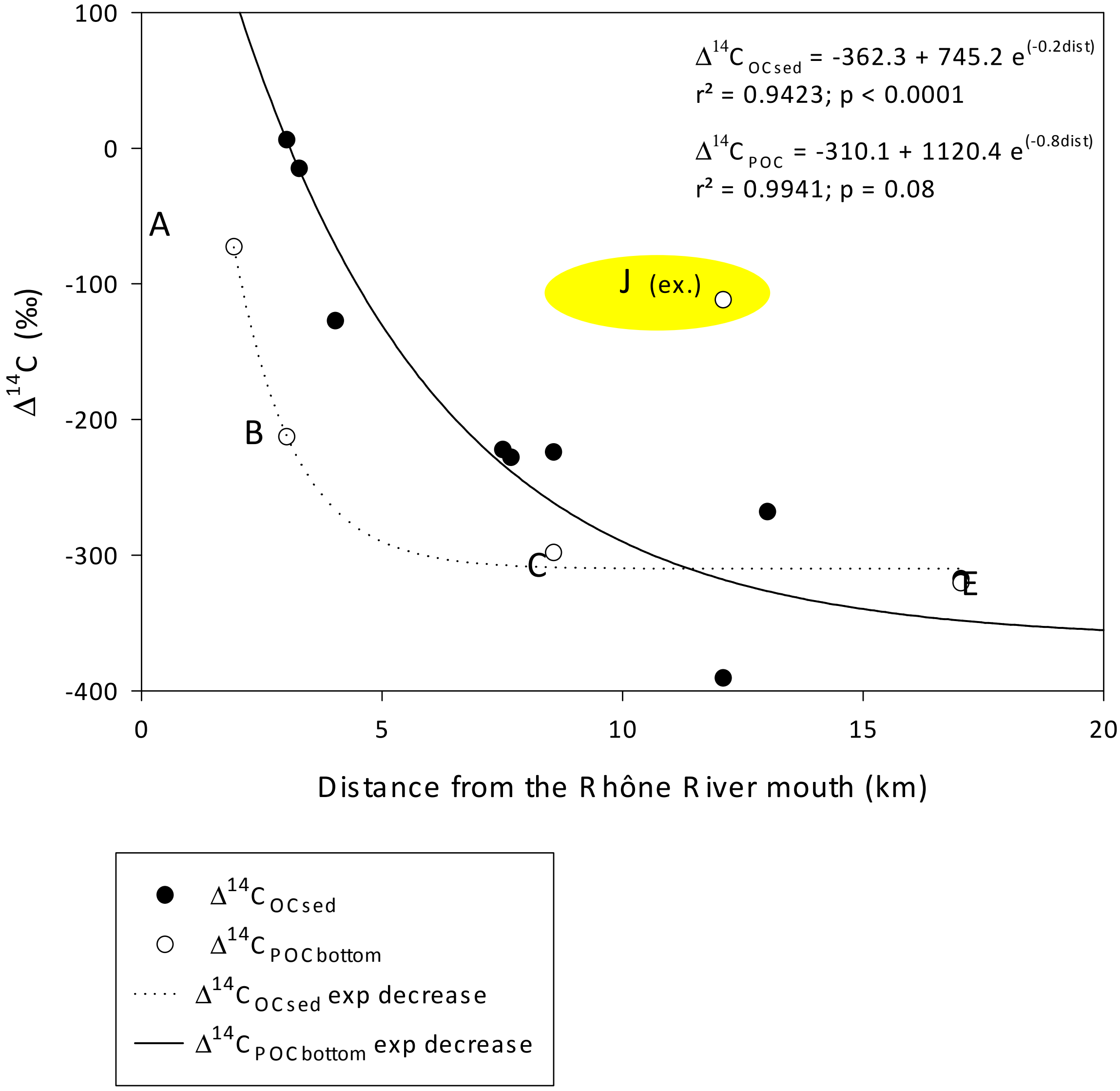

Figure 7. $\Delta^{14}C$ decrease with distance from the river outlet. For POC values, station J was excluded from regression, in order to highlight the south-westward trend.

4.5.2 Metabolism in the Rhône River prodelta: Carbon utilization under various discharge rates conditions

Respiration in water column can account for a significant part in the oxygen consumption of river-dominated margins: it can thus be a major process in the biogeochemical fate of riverine particles (Dagg *et al.*, 2004; Kemp *et al.*, 1992).

Gazeau *et al*, 2004 reported the lack and scarcity of community respiration (CR) rates data available for European coastal ocean. Our values of CR in bottom and intermediate waters in April and September 2007 were in the range of the one measured in the euphotic zone of the Gulf of Lions (42 µgC l^{-1} d^{-1}) and both euphotic and aphotic zones in the Mediterranean, Baltic and North Sea (between 9.6 and 177.6 µgC l^{-1} d^{-1}). They are in the lower ranges of total community rates reported by Witek *et al* (1997) for the shallow Gulf of Gdansk (Poland), but correspond to the bacterial respiration rates measured by Alonso-Saez *et al*, 2008 in the Blanes Bay and Bonilla-Findji *et al*, 2008 in the Bay of Villefranche (NW Mediterranean Sea). This suggests as it has been observed previously in various coastal and marine environments that bacteria are responsible for the major oxygen consumption in the water column (Biddanda *et al*, 1994; Gonzalez *et al*, 2003). As stated above, given the $\delta^{13}C$ and $\Delta^{14}C$ signatures, little marine material sinks into the water column and reaches the seafloor in the prodelta. Except at stations far from the river outlet (J or F) where some local primary production can occur and generate downward exports of particulate organic matter, mainly all the community relies on allochtonous riverine inputs. The common coupling-pelagic benthic picture in coastal systems with a community respiration in the aphotic layers of about 30% the growth primary production may not apply in the Rhône River system, this fraction being likely to be higher. Excluding the distal stations of the prodelta, considering an average CR of 46.3 ± 19.6 µgC l^{-1} d^{-1}, with an average depth of 60 m, the integrated CR in bottom and intermediate waters in the prodelta would be 1.4 ± 0.6 gC m^{-2} d^{-1}. These estimates are in the range of previous studies in coastal areas: Biddanda *et al*, 1994 reported a CR of 1.9 gC m^{-2} d^{-1} for the entire water column of the Louisiana continental shelf. Our CR values are higher than the benthic mineralization rates in the same area, indicating thus the importance of water column degradation processes in the local carbon and oxygen cycle. Indeed, diffusive oxygen uptakes rates for the Rhône River prodelta sediment range between 5 and 22 mmolO_2 m^{-2} d^{-1}. which leads to 0.06 – 0.3 gC m^{-2} d^{-1} (Cathalot *et al.*, submitted). This is consistent with other coastal ocean areas where water column respiration dominates the global ecosystem demand of oxygen and can therefore lead to hypoxia events (Kemp *et al.*, 1992). Moreover, our CR values are higher than the primary production rates in the Gulf of Lions and the Rhône River plume that range between 0.05 and 0.4 gC m^{-2} d^{-1} (Lefevre *et al.*, 1997; Pujo-Pay *et al.*, 2006). This implicates that the local autochthonous production is not enough to support the degradation rates and that the bacterial community may rely on other organic matter supply, most likely the Rhône River inputs. Our CR results also points out the water column as a major term in the carbon budget of the Rhône River prodelta.

The Rhône River prodelta receives some 19.4 ± 11 10^4 tons of POC each year (De Madron *et al.*, 2000), and receives thus high concentrations of allochtonous organic particles. As we saw above, it is also fed by a pool of recirculating and resuspended shelf particles, resulting from previous allochtonous deposits and local primary production and, given their radiocarbon ages (up to 3000 yr), are most likely to have suffered repeated resuspension/redeposit/degradation cycles. In coastal and estuaries aggregates constitute important microhabitat for microorganisms and particle-attached bacteria represent the major part of bacterial activity and organic matter degradation via an enhanced extracellular enzymatic activity (Crump *et al.*, 1998). Vallières *et al.* (2008) also found that the contribution of particle-bound bacteria to total bacterial production (BP) was significantly higher in the bottom waters of the coastal zone of the Mackenzie River shelf. Therefore it is most likely that a large portion of bacterial activity and degradation in the Rhône River prodelta is supported by its POC inputs.

BP rates in bottom waters we found during the Rhône River plume were around 0.7 µgC l^{-1} d^{-1} and in the low range of previously reported values in coastal temperate systems (Alonso-Saez *et al.*, 2008; Biddanda *et al.*, 1994). BP in our study was strongly correlated with temperature. This has widely been observed and many others have included temperature as a parameter in bacterial functional relationships to build accurate bacterial models (Alonso-Saez *et al.*, 2008; del Giorgio and Cole, 1998; delGiorgio *et al.*, 1997; White *et al.*, 1991). Bacterial production was also strongly correlated with bacterial abundance, and specifically with HNA bacteria. This is consistent with many studies reporting that HNA was the major contributor to bacterial activity (Gasol *et al.*, 1999; Moran *et al.*, 2007): in particular (Joux *et al.*, 2005) found HNA bacteria to be the most active fraction in the Rhône River plume, and (Moran and Calvo-Diaz, 2009) in the Bay of Biscay. Andrade *et al.* (2007) suggested that HNA bacteria are most likely to be the most active fraction in high temperature waters influenced by riverine nutrients inputs. HNA bacteria community may thus play a significant role in the bottom waters of the Rhône River prodelta. HNA being significantly correlated with POC contents, it underlines the potential major contribution of particle-bound bacteria in this ecosystem. Therefore, a change in POC riverine inputs both in terms of quantity and quality may have significant consequences to bacterial metabolism in the Rhône River prodelta.

During the flood conditions in June 2008, we observed significantly lower CR rates than during normal discharge rates conditions, associated with low bacterial production rates. This flood was associated with a heavy particulate discharge rates (up to 3g l^{-1} of SPM in the river) and delivered ~0.6 t C. None of the heterotrophic community parameters correlates with DOC, whereas POC seems to control the potentially most active part of bacterial community. In an attempt to assess bacterial response to changes in discharge rates, we calculated Bacterial Production (BP), Bacterial Respiration (BR) and Bacterial Growth Efficiency (BGE) - defined as $\mathrm{BGE} = \frac{\mathrm{BP}}{\mathrm{BP} + \mathrm{BR}}$ - from various available models in the literature (Figure 5). Their coefficients were adjusted to fit our data, since correlation were observed in our data set too. BP was estimated from total bacterial abundance and temperature according to (White *et al.*, 1991).: our BP values were generally 20% lower (BP estimated = 1.22 BPdata + 0.52 , $r^2 = 0.647$, $p<0.001$). BR was calculated both from delGiorgio *et al.* (1997) and del Giorgio and Cole (1998) and exceeded our CR rates, indicating first that BR may contribute to a large proportion of the CR in the prodelta, and second, that bacterial organic matter degradation may be lower than expected during this high particulate discharge rates. BGE was then calculated either as a minimum value using our BP and CR data or using (del Giorgio and Cole, 1998) model: BGE in bottom waters in the Rhône River prodelta may thus ranged between 5 and 30%, which is consistent with previous measurements in coastal areas and Mediterranean Sea ((Alonso-Saez *et al.*, 2008; Sempere *et al.*, 2000b); for a review of BGE in aquatic environments see del Giorgio and Cole (1998)). The decrease of carbon degradation rates through respiration associated to low PB and low BGE during these flood conditions indicates that bacterial metabolism may be limited by the lability of available organic carbon more than its quantity give the high ambient POC and DOC concentrations. Benner *et al.* (1995), Meon and Amon (2004) and Vallières *et al.* (2008) found that bacterial respiration and production were carbon limited in various coastal environments as a consequence to low availability of POC and DOC. We sampled the MES during this flood and the Rhône River displayed at this time a $\Delta^{14}C_{POC}$ of - 495.1 ±1.7 ‰ corresponding to a radiocarbon age of ~ 5500 yr. This new substantially aged material discharged in the prodelta may have been principally constituted with refractory POC. This poorly available POC diluted with the common shelf particles, already partially degraded may thus have limited carbon metabolism during this flood event. This is also coherent with what Cathalot *et al*,(Chapitre 3) found in sediments of the prodelta at the same time i.e. a decrease in benthic carbon mineralization rates corresponding to a lower phytodetritus content in the material delivered during the flood than during normal conditions. During flood conditions, benthic and bottom waters metabolisms may be more coupled: they likely rely on the same and unique source (the Rhône River) whereas in low discharge rates conditions, the allochtonous particles with a more labile carbon settle really quickly in the prodelta feeding the benthic community with fresher material than the refractory old pool of Gulf of Lions shelf particles. The predicted changes in precipitation and runoff and their consequence on the hydrological regime of the Rhône River (increase of flood occurrence) are thus likely to influence coastal metabolism, by slowing down all the degradation processes (IPCC report, 2007).

Table 5. June 08 bacterial parameters: from our data set and calculated from models

Cruise	Stations	BP µgC l^{-1} d^{-1}	CR µgC l^{-1} d^{-1}	Min BGE =BP/(BP+CR)	BA 10^8 cells l^{-1}	HNA 10^8 cells l^{-1}	LNA 10^8 cells l^{-1}	BP (coastal model) White et al, 1991	BR (model I) Del Giorgio et Cole, 1998	BR (model II) Del Giorgio et Cole, 1998	BGE Del Giorgio et Cole, 1998	BR Del Giorgio et al, 1997	Associated BGE Del Giorgio et al, 1997
June 08	A	0.65 ± 0.11	22.29 ± 2.88	2.83%	5.52	1.93	3.62	2.04	74.38	63.06	18.74%	34.91	3.16%
	B	1.06 ± 0.11	18.43 ± 1.69	5.46%	5.32	1.97	3.35	1.83	91.10	85.27	25.45%	33.77	5.34%
	C	0.27 ± 0.01	-		7.56	2.63	4.94	1.14	51.68	36.68	10.19%	46.01	0.88%
	D	0.19 ± 0.02	9.86 ± 1.02	1.92%	4.16	1.55	2.61	0.56	45.22	30.08	8.15%	27.21	1.40%
	E	0.87 ± 0.10	23.83 ± 5.06	3.51%	6.76	2.40	4.38	1.34	83.79	75.28	22.53%	41.71	3.23%
	H	0.32 ± 0.03	21.22 ± 4.71	1.50%	5.12	1.41	3.71	0.71	55.85	41.17	11.62%	32.67	1.76%
	I	1.23 ± 0.17	-		7.33	2.49	4.86	1.54	96.71	93.19	27.62%	44.79	4.08%
	J	0.31 ± 0.04	-		3.28	1.35	1.96	0.42	54.78	40.01	11.25%	22.10	3.00%
	K	0.80 ± 0.07	20.28 ± 3.27	3.78%	7.05	2.83	4.26	1.91	80.93	71.49	21.38%	43.27	2.82%
	L	1.41 ± 0.20	23.21 ± 4.02	5.71%	7.84	2.94	4.92	2.01	102.11	101.03	29.66%	47.53	4.25%
	N	0.34 ± 0.03	-		5.44	1.74	3.72	1.38	57.40	42.88	12.18%	34.48	1.74%
	O	0.46 ± 0.06	15.87 ± 1.55	2.82%	4.97	1.48	3.50	0.98	64.58	51.11	14.87%	31.82	2.60%
	U	0.28 ± 0.02	-		4.12	1.41	2.71	0.57	52.84	37.91	10.58%	27.01	2.05%
	Z	1.33 ± 0.15	44.45 ± 1.82	2.90%	7.60	3.40	4.22	2.50	99.75	97.58	28.78%	46.23	4.19%

4.6 CONCLUSION

The export of the Rhône River POC inputs over the prodelta and the adjacent shelf and their degradation in the bottom and intermediate water column was studied in this paper. The coupled use of $\delta^{13}C$ and $\Delta^{14}C$ isotopes in suspended particles of the prodelta waters allowed us to identify some mechanisms controlling the fate of the Rhône River inputs:

- A quick deposition nearby the river mouth in agreement with hydrodynamic features and previous studies.
- A dilution with resuspended, recirculating particles from the adjacent shelf with a long residence time (up to 3000 yr). This pool of particles is constituted by a mixture of marine and terrestrial material old and partially degraded with a poor reactivity.

Under normal discharge rates conditions, the suspended particles in the Rhône River prodelta are the results of a complex mixture of riverine POC and old refractory shelf material that support high community respiration rates. Water column respiration in the Rhône River prodelta is thus an important term for assessing carbon degradation in the area and should therefore not be neglected in carbon budgets. Under flood conditions, as in June 2008, more particles are discharged in the Rhône River and the increased turbidity induced changes in the bacterial metabolism, slowing down the degradation activity of water column bacteria. Therefore, hydrological variations are likely to induce significant perturbations in the carbon cycle of the Rhône River prodelta.

4.7 REFERENCES

Aloisi, J.C., Cambon, J.P., Carbonne, J., Cauwet, G., Millot, C., Monaco, A., Pauc, H., 1982. Origin and role of the bottom nepheloid layer in the tranfer of particles into the marine environment - Application to the Gulf of Lions. Oceanologica Acta 5 (4), 481-491.

Alonso-Saez, L., Vazquez-Dominguez, E., Cardelus, C., Pinhassi, J., Sala, M.M., Lekunberri, I., Balague, V., Vila-Costa, M., Unrein, F., Massana, R., Simo, R., Gasol, J.M., 2008. Factors controlling the year-round variability in carbon flux through bacteria in a coastal marine system. Ecosystems 11 (3), 397-409.

Andrade, L., Gonzalez, A.M., Rezende, C.E., Suzuki, M., Valentin, J.L., Paranhos, R., 2007. Distribution of HNA and LNA bacterial groups in the Southwest Atlantic Ocean. Brazilian Journal of Microbiology 38 (2), 330-336.

Aucour, A.M., Sheppard, S.M.F., Guyomar, O., Wattelet, J., 1999. Use of C-13 to trace origin and cycling of inorganic carbon in the Rhone river system. Chemical Geology 159 (1-4), 87-105.

Baena, A., Fowler, S.W., Miquel, J.C., 2007. Particulate organic carbon : natural radionuclide ratios in zooplankton and their freshly produced fecal pellets from the NW Mediterranean (MedFlux 2005). Limnology and Oceanography 52 (3), 966-974.

Batista, F., McNichol, A.P., Gerlach, D.S., 1994. The effect of different acid treatments on the radiocarbon age of sedimentary organic matter. . Eos Trans. AGU 84 (52).

Bauer, J.E., Druffel, E.R.M., Wolgast, D.M., Griffin, S., 2001. Sources and cycling of dissolved and particulate organic radiocarbon in the northwest Atlantic continental margin. Global Biogeochemical Cycles 15 (3), 615-636.

Begg, F.H., Cook, G.T., Baxter, M.S., Scott, E.M., McCartney, M., 1992. Anthropogenic radiocarbon in the Eastern Irish Sea and Scottish coastal waters. Radiocarbon 34 (3), 707-716.

Benner, R., Opsahl, S., ChinLeo, G., Richey, J.E., Forsberg, B.R., 1995. Bacterial carbon metabolism in the Amazon River system. Limnology and Oceanography 40 (7), 1262-1270.

Biddanda, B., Opsahl, S., Benner, R., 1994. Plankton respiration and carbon flux through bacterioplankton on the Louisiana shelf. Limnology and Oceanography 39 (6), 1259-1275.

Bisutti, I., Hilke, I., Raessler, M., 2004. Determination of total organic carbon - an overview of current methods. Trac-Trends in Analytical Chemistry 23 (10-11), 716-726.

Bonnin, J., Heussner, S., Calafat, A., Fabres, J., Palanques, A., de Madron, X.D., Canals, M., Puig, P., Avril, J., Delsaut, N., 2008. Comparison of horizontal and downward particle fluxes across canyons of the Gulf of Lions (NW Mediterranean): Meteorological and hydrodynamical forcing. Continental Shelf Research 28 (15), 1957-1970.

Buscail, R., Germain, C., 1997. Present-day organic matter sedimentation on the NW Mediterranean margin: Importance of off-shelf export. Limnology and Oceanography 42 (2), 217-229.

Cathalot, C., Rabouille, C., Pastor, L., Deflandre, B., Viollier, E., Buscail, R., Treignier, C., Pruski, A., submitted. Seasonal dynamics of carbon recycling in coastal sediments influenced by rivers: assessing the impact of flood inputs in the Rhône River prodelta. Biogeosciences.

Cathalot, C., Rabouille, C., Tisnerat-Laborde, N., Buscail, R., Kerherve, P., Gontier, G., In prep. Sources and fate of particulate organic carbon export from the Rhône River in the Mediterranean Sea: combined use of $\Delta^{14}C$ and $\delta^{13}C$

Cauwet, G., 1984. Automatic-determination od Dissolved Organic Carbon in seawater in the sub-ppm range. Marine Chemistry 14 (4), 297-306.

Cauwet, G., Gadel, F., de Souza Sierra, M.M., Donard, O., Ewald, M., 1990. Contribution of the Rhône River to organic carbon inputs to the northwestern Mediterranean Sea. Continental Shelf Research 10 (9-11), 1025-1037.

Cauwet, G., Miller, A., Brasse, S., Fengler, G., Mantoura, R.F.C., Spitzy, A., 1997. Dissolved and particulate organic carbon in the western Mediterranean Sea. Deep-Sea Research Part Ii-Topical Studies in Oceanography 44 (3-4), 769-779.

Charmasson, S., Bouisset, P., Radakovitch, O., Pruchon, A.S., Arnaud, M., 1998. Long-core profiles of Cs-137, Cs-134, Co-60 and Pb-210 in sediment near the Rhone River (Northwestern Mediterranean Sea). Estuaries 21 (3), 367-378.

Copin-Montegut, C., 1993. Alkalinity and carbon budgets in the Mediterranean Sea. Global Biogeochemical Cycles 7 (4), 915-925.

Crump, B.C., Baross, J.A., Simenstad, C.A., 1998. Dominance of particle-attached bacteria in the Columbia River estuary, USA. Aquatic Microbial Ecology 14 (1), 7-18.

Dagg, M., Benner, R., Lohrenz, S., Lawrence, D., 2004. Transformation of dissolved and particulate materials on continental shelves influenced by large rivers: plume processes. Continental Shelf Research 24 (7-8), 833-858.

Darnaude, A.M., Salen-Picard, C., Polunin, N.V.C., Harmelin-Vivien, M.L., 2004. Trophodynamic linkage between river runoff and coastal fishery yield elucidated by stable isotope data in the Gulf of Lions (NW Mediterranean). Oecologia 138 (3), 325-332.

De Madron, X.D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J.C., Radakovitch, O., Giresse, P., Buscail, R., Kerherve, P., 2000. Particulate matter and organic carbon budgets for the Gulf of Lions (NW Mediterranean). Oceanologica Acta 23 (6), 717-730.

de Madron, X.D., Denis, L., Diaz, F., Garcia, N., Guieu, C., Grenz, C., Loye-Pilot, M.D., Ludwig, W., Moutin, T., Raimbault, P., Ridame, C., 2003. Nutrients and carbon budgets for the Gulf of Lion during the Moogli cruises. Oceanologica Acta 26 (4), 421-433.

de Madron, X.D., Radakovitch, O., Heussner, S., Loye-Pilot, M.D., Monaco, A., 1999. Role of the climatological and current variability on shelf-slope exchanges of particulate matter: Evidence from the Rhone continental margin (NW Mediterranean). Deep-Sea Research Part I-Oceanographic Research Papers 46 (9), 1513-1538.

del Giorgio, P.A., Cole, J.J., 1998. Bacterial growth efficiency in natural aquatic systems. Annual Review of Ecology and Systematics 29, 503-541.

delGiorgio, P.A., Cole, J.J., Cimbleris, A., 1997. Respiration rates in bacteria exceed phytoplankton production in unproductive aquatic systems. Nature 385 (6612), 148-151.

delGiorgio, P.A., France, R.L., 1996. Ecosystem-specific patterns in the relationship between zooplankton and POM or microplankton delta C-13. Limnology and Oceanography 41 (2), 359-365.

deMadron, X.D., Panouse, M., 1996. Advective transport of suspended particulate matter on the Gulf of Lions continental shelf. Summer and winter situations. Comptes Rendus De L Academie Des Sciences Serie Ii Fascicule a-Sciences De La Terre Et Des Planetes 322 (12), 1061-1070.

Druffel, E.R.M., Williams, P.M., 1992. Importance of isotope measurements in marine organic geochemistry. Marine Chemistry 39 (1-3), 209-215.

Ferre, B., de Madron, X.D., Estournel, C., Ulses, C., Le Corre, G., 2008. Impact of natural (waves and currents) and anthropogenic (trawl) resuspension on the export of particulate matter to the open ocean Application to the Gulf of Lion (NW Mediterranean). Continental Shelf Research 28 (15), 2071-2091.

Froelich, P.N., 1980. Analysis of organic carbon in marine sediments. Limnology and Oceanography 25 (3), 564-572.

Fry, B., Sherr, E.B., 1984. δ^{13}C measurements as indicators of carbon flow in marine and fresh-water ecosystems. Contributions in Marine Science 27 (SEP), 13-47.

Fulweiler, R.W., Nixon, S.W., 2009. Responses of benthic-pelagic coupling to climate change in a temperate estuary. Hydrobiologia 629 (1), 147-156.

Gasol, J.M., Zweifel, U.L., Peters, F., Fuhrman, J.A., Hagstrom, A., 1999. Significance of size and nucleic acid content heterogeneity as measured by flow cytometry in natural planktonic bacteria. Applied and Environmental Microbiology 65 (10), 4475-4483.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27 (5-6), 195-212.

Heussner, S., Cherry, R.D., Heyraud, M., 1990. 210Po,210Pb in sediment trap particles on a Mediterranean continental margin. Continental Shelf Research 10 (9-11), 989-1004.

Heussner, S., de Madron, X.D., Calafat, A., Canals, M., Carbonne, J., Delsaut, N., Saragoni, G., 2006. Spatial and temporal variability of downward particle fluxes on a continental slope: Lessons from an 8-yr experiment in the Gulf of Lions (NW Mediterranean). Marine Geology 234 (1-4), 63-92.

Joux, F., Servais, P., Naudin, J.J., Lebaron, P., Oriol, L., Courties, C., 2005. Distribution of picophytoplankton and bacterioplankton along a river plume gradient in the Mediterranean Sea. Vie Et Milieu-Life and Environment 55 (3-4), 197-208.

Kemp, W.M., Sampou, P.A., Garber, J., Tuttle, J., Boynton, W.R., 1992. Seasonal depletion of oxygen from bottom waters of Cheapeake Bay: Roles of benthic and planktonic respiration and physical and exchange processes. Marine Ecology-Progress Series 85 (1-2), 137-152.

Komada, T., Anderson, M.R., Dorfmeier, C.L., 2008. Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures, delta C-13 and Delta C-14: comparison of fumigation and direct acidification by hydrochloric acid. Limnology and Oceanography-Methods 6, 254-262.

Lansard, B., Charmasson, S., Gasco, C., Anton, M.P., Grenz, C., Arnaud, M., 2007. Spatial and temporal variations of plutonium isotopes (Pu-238 and Pu-239,Pu-240) in sediments off the Rhone River mouth (NW Mediterranean). Science of the Total Environment 376 (1-3), 215-227.

Lansard, B., Rabouille, C., Denis, L., Grenz, C., 2009. Benthic remineralization at the land-ocean interface: A case study of the Rhone River (NW Mediterranean Sea). Estuarine Coastal and Shelf Science 81 (4), 544-554.

Lefevre, D., Minas, H.J., Minas, M., Robinson, C., Williams, P.J.L., Woodward, E.M.S., 1997. Review of gross community production, primary production, net community production and dark community respiration in the Gulf of Lions. Deep-Sea Research Part Ii-Topical Studies in Oceanography 44 (3-4), 801-&.

McNichol, A.P., Osborne, E.A., Gagnon, A.R., Fry, B., Jones, G.A., 1994. TIC, TOC, DIC, DOC, PIC, POC -- unique aspects in the preparation of oceanographic samples for 14C-AMS.

Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms 92 (1-4), 162-165.

Meon, B., Amon, R.M.W., 2004. Heterotrophic bacterial activity and fluxes of dissolved free amino acids and glucose in the Arctic rivers Ob, Yenisei and the adjacent Kara Sea. Aquatic Microbial Ecology 37 (2), 121-135.

Millot, C., 1990. The Gulf Of Lions Hydrodynamics. Continental Shelf Research 10 (9-11), 885-894.

Miralles, J., Radakovitch, O., Aloisi, J.C., 2005. Pb-210 sedimentation rates from the Northwestern Mediterranean margin. Marine Geology 216 (3), 155-167.

Monaco, A., Biscaye, P., Soyer, J., Pocklington, R., Heussner, S., 1990a. Particle fluxes and ecosystem response on a continental margin: the 1985-1988 Mediterranean ECOMARGE experiment. Continental Shelf Research 10 (9-11), 809-839.

Monaco, A., Courp, T., Heussner, S., Carbonne, J., Fowler, S.W., Deniaux, B., 1990b. Seasonality And Composition Of Particulate Fluxes During Ecomarge .1. Western Gulf Of Lions. Continental Shelf Research 10 (9-11), 959-987.

Monaco, A., de Madron, X.D., Radakovitch, O., Heussner, S., Carbonne, J., 1999. Origin and variability of downward biogeochemical fluxes on the Rhone continental margin (NW Mediterranean). Deep-Sea Research Part I-Oceanographic Research Papers 46 (9), 1483-1511.

Mook, W.G., van der Plicht, J., 1999. Reporting C-14 activities and concentrations. Radiocarbon 41 (3), 227-239.

Moran, X.A.G., Bode, A., Suarez, L.A., Nogueira, E., 2007. Assessing the relevance of nucleic acid content as an indicator of marine bacterial activity. Aquatic Microbial Ecology 46 (2), 141-152.

Moran, X.A.G., Calvo-Diaz, A., 2009. Single-cell vs. bulk activity properties of coastal bacterioplankton over an annual cycle in a temperate ecosystem. Fems Microbiology Ecology 67 (1), 43-56.

Naudin, J.J., Cauwet, G., 1997. Transfer mechanisms and biogeochemical implications in the bottom nepheloid layer. A case study of the coastal zone off the Rhone River (France). Deep-Sea Research Part Ii-Topical Studies in Oceanography 44 (3-4), 551-575.

Naudin, J.J., Cauwet, G., ChretiennotDinet, M.J., Deniaux, B., Devenon, J.L., Pauc, H., 1997. River discharge and wind influence upon particulate transfer at the land-ocean interaction: Case study of the Rhone River plume. Estuarine Coastal and Shelf Science 45 (3), 303-316.

Nieuwenhuize, J., Maas, Y.E.M., Middelburg, J.J., 1994. Rapid analysis of organic carbon and nitrogen in particulate materials. Marine Chemistry 45 (3), 217-224.

Pont, D., Simonnet, J.P., Walter, A.V., 2002. Medium-term changes in suspended sediment delivery to the ocean: Consequences of catchment heterogeneity and river management (Rhone River, France). Estuarine Coastal and Shelf Science 54 (1), 1-18.

Pujo-Pay, M., Conan, P., Joux, F., Oriol, L., Naudin, J.J., Cauwet, G., 2006. Impact of phytoplankton and bacterial production on nutrient and DOM uptake in the Rhone river plume (NW Mediterranean). Marine Ecology-Progress Series 315, 43-54.

Raymond, P.A., Bauer, J.E., 2001a. Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. Nature 409 (6819), 497-500.

Raymond, P.A., Bauer, J.E., 2001b. Use of C-14 and C-13 natural abundances for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis. Organic Geochemistry 32 (4), 469-485.

Roussiez, V., Aloisi, J.C., Monaco, A., Ludwig, W., 2005. Early muddy deposits along the Gulf of Lions shoreline: A key for a better understanding of land-to-sea transfer of sediments and associated pollutant fluxes. Marine Geology 222, 345-358.

Roussiez, V., Ludwig, W., Monaco, A., Probst, J.L., Bouloubassi, I., Buscail, R., Saragoni, G., 2006. Sources and sinks of sediment-bound contaminants in the Gulf of Lions (NW Mediterranean Sea): A multi-tracer approach. Continental Shelf Research 26 (16), 1843-1857.

Santiago, S., Thomas, R.L., Larbaigt, G., Corvi, C., Rossel, D., Tarradellas, J., Gregor, D.J., McCarthy, L., Vernet, J.P., 1994. Nutrient, heavy metal and organic pollutant composition of suspended and bed sediments in the Rhône River. Aquatic Sciences 56 (3), 220-242.

Schubert, C.J., Nielsen, B., 2000. Effects of decarbonation treatments on delta C-13 values in marine sediments. Marine Chemistry 72 (1), 55-59.

Sempere, R., Charriere, B., Van Wambeke, F., Cauwet, G., 2000a. Carbon inputs of the Rhone River to the Mediterranean Sea: Biogeochemical implications. Global Biogeochemical Cycles 14 (2), 669-681.

Sempere, R., Yoro, S.C., Van Wambeke, F., Charriere, B., 2000b. Microbial decomposition of large organic particles in the northwestern Mediterranean Sea: an experimental approach. Marine Ecology-Progress Series 198, 61-72.

Simon, M., Azam, F., 1989. Protein content and protein synthesis rates of planktonic marine bacteria. Marine Ecology-Progress Series 51 (3), 201-213.

Smith, D.C., Azam, F., 1992. A simple, economical method for measuring bacterial protein synthesis rates in seawater using ^{3}H-leucine. Marine Microbial Food Webs 6, 107-114.

Smith, D.C., Simon, M., Alldredge, A.L., Azam, F., 1992. Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution. Nature 359 (6391), 139-142.

Soetaert, K., Middelburg, J.J., 2009. Modeling eutrophication and oligotrophication of shallow-water marine systems: the importance of sediments under stratified and well-mixed conditions. Hydrobiologia 629 (1), 239-254.

Tesi, T., Miserocchi, S., Goni, M.A., Langone, L., 2007. Source, transport and fate of terrestrial organic carbon on the western Mediterranean Sea, Gulf of Lions, France. Marine Chemistry 105 (1-2), 101-117.

Ulses, C., Estournel, C., Bonnin, J., Madron, X.D., Marsaleix, P., 2008a. Impact of storms and dense water cascading on shelf-slope exchanges in the Gulf of Lion (NW Mediterranean). Journal of Geophysical Research-Oceans 113 (C2).

Ulses, C., Estournel, C., de Madron, X.D., Palanques, A., 2008b. Suspended sediment transport in the Gulf of Lions (NW Mediterranean): Impact of extreme storms and floods. Continental Shelf Research 28 (15), 2048-2070.

Vallières, C., Retamal, L., Ramlal, P., Osburn, C.L., Vincent, W.F., 2008. Bacterial production and microbial food web structure in a large arctic river and the coastal Arctic Ocean. Journal of Marine Systems 74 (3-4), 756-773.

White, P.A., Kalff, J., Rasmussen, J.B., Gasol, J.M., 1991. The effect of temperature and algal biomass on bacterial production and specific growth-rate in fresh-water and marine habitats. Microbial Ecology 21 (2), 99-118.

Williams, P.M., Robertson, K.J., Soutar, A., Griffin, S.M., Druffel, E.R.M., 1992. Isotopic Signatures (C-14, C-13, N-15) As Tracers Of Sources And Cycling Of Soluble And Particulate Organic-Matter In The Santa-Monica Basin, California. Progress in Oceanography 30 (1-4), 253-290.

Wright, L.D., Friedrichs, C.T., 2006. Gravity-driven sediment transport on continental shelves: A status report. Continental Shelf Research 26 (17-18), 2092-2107.

Yechieli, Y., Sivan, O., Lazar, B., Vengosh, A., Ronen, D., Herut, B., 2001. Radiocarbon in seawater intruding into the Israeli Mediterranean coastal aquifer. Radiocarbon 43 (2B), 773-781.

CHAPITRE 5. BIOGEOCHEMICAL PROCESSES IN SEDIMENTS FROM THE RHÔNE RIVER PRODELTA (FRANCE): A MODEL OF CARBON MINERALIZATION

CHAPITRE 5. BIOGEOCHEMICAL PROCESSES IN SEDIMENTS FROM THE RHÔNE RIVER PRODELTA (FRANCE): A MODEL OF CARBON MINERALIZATION

L. Pastor[1,*], C. Cathalot[2, *], B. Deflandre[1,3], E. Viollier[1], K. Soetaert[4], R. Buscail[5], A. Grémare[3], C. Ulses[6], C. Rabouille[2]

[1].Laboratoire de Géochimie des Eaux, UMR 7154, Université Paris Diderot – Paris 7 and IPGP, Batiment Lamarck, Case Postale 7052, 75205 Paris cedex 13, France

[2].Laboratoire des Sciences du Climat et de l'Environnement, CEA-CNRS UNMR 1572, Av. de la Terrasse, 91198 Gif sur Yvette, France

[3].UMR 5805 EPOC – OASU, Site de Talence, Université Bordeaux, Avenue des Facultés, 33405 TALENCE CEDEX, France

[4].Netherlands Institute of Ecology, Vierstraat 28, 4401 EA Yerseke, The Netherlands

[5].Centre de Formation et de Recherche sur l'Environnement Marin, Université de Perpignan, CNRS ERS 1745, Avenue de Villeneuve, 66860 Perpignan, France

[6].LA, CNRS-Université de Toulouse, Toulouse, France

* L. Pastor and C. Cathalot have contributed equally to this manuscript

corresponding author: pastor@ipgp.fr

5.1 ABSTRACT

As part of the French national project CHACCRA, interested in carbon fluxes in river-dominated ocean margins, biogeochemical processes in the Rhône River delta (France) were studied. The budgets for degradable organic carbon were calculated from sediment and pore water properties, using a steady-state version of a numerical coupled diagenetic model, OMEXDIA. Data were collected in April 2007 along offshore transects from the river mouth to the shelf.

Diagenetic processes in the delta clearly showed the footprint of the Rhône River inputs. High oxidation rates of organic carbon (OC) were located near the mouth (~450 gC m^{-2} y^{-1}) and declined quickly (down to 25 gC m^{-2} y^{-1}) further away in the adjacent shelf. Our results highlighted the direct relation between the OC oxidation and the quantity (OC flux) and lability (reactivity) of the material deposited. Indeed, intense mineralization activity near the outlet is coupled with massive OC burial: efficient burial occurs in the proximal delta with only 20-40 % of the OC deposited being degraded. This area plays thus the role of a reactive deposit centre for the Rhône River particulate OC inputs.

A clear shift in the diagenetic pathways was also observed from anaerobic oxidation dominated pathways to a system dominated by aerobic oxidation. Although denitrification is homogeneous over the whole area, anaerobic oxidation is enhanced within the prodelta area where it represents up to 90% of the total OC degradation. On the contrary, in the adjacent continental shelf, the oxic pathway dominates and contributes to ~ 60% of the OC degradation. The model outputs pointed out the importance of anaerobic processes in the Rhône River prodelta. Therefore, carbon budgets in river-influenced shelves based solely on sediment oxygen consumption rates may be severely underestimated since products from anoxic mineralization may escape the diagenetic sequence escape through recombination and precipitation processes.

5.2 INTRODUCTION

Continental margins are complex physical, biological and geochemical environments: as they constitute an important buffer zone for continent-shelf-ocean exchange, they play a major role in biogeochemical cycles. High rates of new primary production on the shelf are sustained by the inputs of nutrients from riverine, atmospheric and open ocean sources as well as bentho-pelagic coupling. It is estimated for instance that coastal ocean accounts for 12 to 30 % of the global oceanic primary production (Smith and Hollibaugh, 1993). With their shallow water depths, these environments are also areas of intense benthic-pelagic coupling, since 50% of the material newly produced in the water column is assumed to settle down and be rapidly oxidized in surface sediments (Smith and Hollibaugh, 1993;Middelburg *et al.*, 1997;McKee *et al.*, 2004). In addition to the in situ production of biogenic particles, ocean margins also receive organic and lithogenic particles of terrestrial origin from river discharge and direct run-off. Indeed, river-dominated margins have been shown to be active burial, deposition and organic carbon (OC) oxidizing centres (Aller *et al.*, 2004;Hedges *et al.*, 1997). Mineralization of OC in sediment of river-dominated continental margins plays therefore a crucial role in the carbon cycle but also in the nitrogen and oxygen cycles since they are tightly coupled via the nutrient regeneration and oxidation processes involved.

In active coastal river-dominated environments, with important organic deposition, enhanced sediment accumulation rates and larger concentrations of organic matter, suboxic and anoxic processes become more important: for instance, sulphate reduction can account for more than half of the total mineralization in shelf sediments (Canfield *et al.*, 1993a).

Since the damming of the Nile, the Rhône River is 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;Sempere *et al.*, 2000;Lansard *et al.*, 2009). Several studies highlighted the distribution of organic carbon in the sediments near the Rhone delta and discussed its origin and lability (Lansard *et al.*, 2009;Tesi *et al.*, 2007). Other studies (Lansard *et al.*, 2009; Cathalot *et al.*, submitted) emphasized the tight link between the distribution of Rhône River inputs and the benthic mineralization activity viewed from sediment oxygen fluxes. Nevertheless, suboxic diagenesis was clearly overlooked in these papers and may play an important role in the mineralization of carbon in these organic-rich sediments.

This study intends to combine in situ and pore water measurements and the use of the OMEXDIA diagenetic model developed by Soetaert *et al.* (1996a) to investigate the OC oxidation pathways involved in the Rhône River delta. OMEXDIA is a coupled, nonlinear, general diagenetic model that incorporates oxic mineralization, denitrification, anoxic mineralization, and the oxidation of ammonium (nitrification) and other reduced compounds. We thus give an insight of the cycling of carbon, oxygen, and nitrogen involved in the Rhône River delta, and discuss the influence of the riverine inputs.

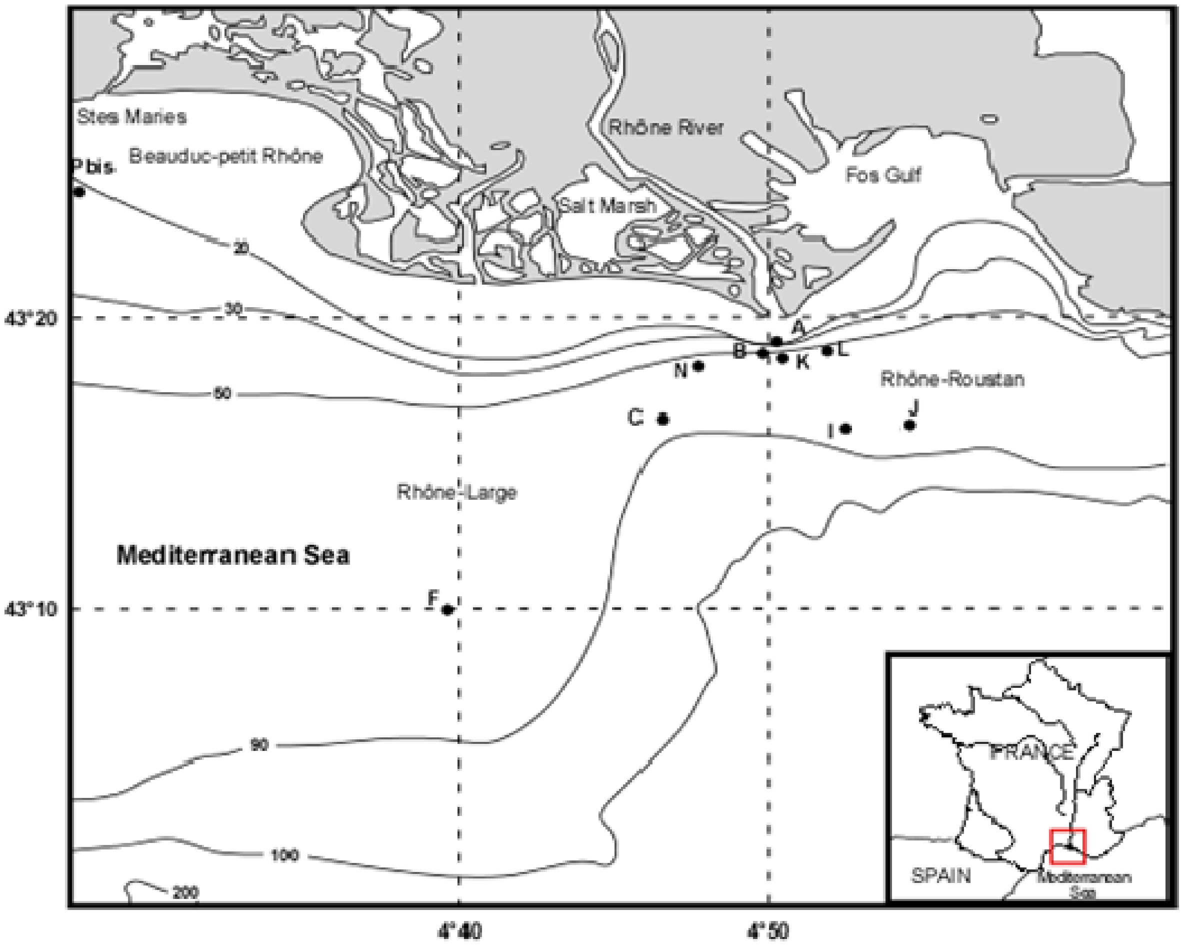

Figure 1. Sampling sites in the vicinity of the Rhône River outlet

5.3 MATERIALS AND METHODS

5.3.1 Study area

The Rhône River is 812 km long and presents an annual average water discharge of 1700 m^3 s^{-1} (Pont *et al.*, 2002;Antonelli *et al.*, 2004). Its main channel, Grand Rhône, encompasses 90 % of the total river water flux. The Rhône prodelta represents a 30 km^2 area close to the Rhône River mouth extending off the deltaic plain (Aloisi *et al.*, 1982;De Madron *et al.*, 2000). It is characterized by very high sedimentation rates (up to 41 cm y^{-1} at the mouth of the river and less than 1 cm y^{-1} on the continental slope) (Zuo *et al.*, 1997) and high organic carbon content (1-3 %). The river’s plume is generally oriented southwestward but eastward currents can occur (up to 18% of the time) and thus change the direction of the plume (Gatti *et al.*, 2006).

Nine sites were chosen (Figure 1). Four sites (A, B, K, L) were located in the prodelta, three sites were located on the Southwest transect (N, C and F) and 2 sites (I and J) were situated in the eastern part of the prodelta, with a lower influence of the Rhone deposition.

Table 1. Sampling site location and surface sediment (0-0.5 cm) properties.

Site	**Lat. (°N)**	**Long. (°E)**	**Depth (m)**	**Dist (km)**	**T_{bw} (°C)**	**O_{2bw} (µM)**	**D_{50} (µm)**	**C_{inorg} (% DW)**	**OC (% DW)**	**C/N**
A	43°18’8	4°51’1	24	1.9	14.9	259	37.4	3.72	2.74	11.64
B	43°18’2	4°50’1	57	3.0	14.8	248	14.8	4.04	2.10	11.50
N	43°17’5	4°48’0	65	5.5	14.5	-	14.0	4.44	1.55	10.73
C	43°16’3	4°46’6	76	8.6	14.5	243	11.4	4.72	1.10	9.24
F	43°10’0	4°42’0	78	21.6	14.2	256	9.2	4.44	1.05	10.36
K	43°18’1	4°51’5	62	3.3	14.7	234	17.5	3.85	1.62	10.77
L	43°18’3	4°52’9	61	4.0	14.3	251	13.6	4.47	1.15	10.63
I	43°16’0	4°53’0	89	7.7	14.2	231	10.7	4.48	1.37	11.76
J	43°16’1	4°58’1	86	12.1	14.2	243	11.6	5.42	1.08	11.51

5.3.2 Experimental work

a) In situ profiling: Oxygen flux measurements

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

The complete description of oxygen profile acquisition is given in Cathalot *et al.* (submitted). Briefly, dissolved oxygen concentration was measured by polarographic oxygen microelectrodes provided with a built-in reference and an internal guard cathode (Revsbech, 1989). The O_2 microsensors had tip outer diameters of 100 µm, a stirring sensitivity of <1%, a 90% response time <10 s, and less than 2% per hour current drift. A linear calibration for the microelectrodes was used, between the bottom water oxygen content estimated by Winkler titration and the anoxic zone of the sediment (Grasshoff *et al.*, 1983). The location of the sediment-water interface relative to the in situ oxygen profiles was determined from O_2 microprofiles. and diffusive oxygen uptake (DOU) was calculated from O_2 microprofiles by using the 1-D Fick's first law of diffusion.

b) Sampling

Sampling sites were situated within 23 km off the Rhône River mouth with water depths ranging between 24 m and 89 m (Table 1). Bottom water measurements of temperature, salinity and oxygen concentration were performed on Niskin bottle samples taken 2 meters above bottom.

Sediment cores from 9 sites were collected in April 2007 with an Oktopus multicorer GmbH deployed from the R.V. Tethys II. Up to eight cores of 10 cm inner diameter were collected at each site with corer penetration depth between 20 and 40 cm. Cores were sampled and maintained at in situ temperature until analysis.

Porewater and solid profiles were measured on a single core: sediments were subsampled under nitrogen atmosphere according to a set grid, typically every 0.5 cm over the 1st cm, every 1 cm over the next 10 cm, and at 2 cm intervals below. Sediments were then transferred into 50 ml polypropylene Falcon™ tubes and centrifuged. Porewaters were extracted and immediately acidified (69% suprapur HNO_3^-, Merck) to ~pH 2 or frozen (-

20°C) depending on the analyses. The remaining solid phase was immediately frozen to keep the anoxic conditions of the sediments. Analyses were completed within a few months after the sampling.

c) Dark core incubations

Sediment incubations were performed in dark on three intact cores at *in situ* conditions. After inspection, cores were selected with undisturbed sediment (i.e. visibly intact sediment surface and clear overlying water). Once sealed, cores were placed in a water bath at *in situ* bottom temperature (±1°C). Overlying water into the cores was constantly stirred at about 30 rpm by using a Teflon coated magnetic stirring bar attached to the core lid. Magnetic stirrers (*Rank Brothers Ltd*), centered on the lid of each cores, made the stirring bars circulate with the same speed in all the three cores. Every 2-4 hours, 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). Total fluxes of nitrates and ammonium were then calculated from the difference in concentration between samples in each incubation core, corrected with the replacement water. The incubation period and sampling intervals were adjusted so that oxygen concentration in the overlying water was not below approximately 20-30% from the original ambient value (Hulth *et al.*, 1997). In general the incubation lasted for 18 hours with sampling intervals of 2-3 hours.

d) Solid phase analyses

Porosity and microporosity were calculated using water content (difference between wet and freeze-dry weight) and assuming a bulk density of 2.65 g cm^{-3} (Berner, 1980). The water content and the salinity were used to correct the analyses for the presence of sea salt.

Organic carbon, nitrogen and sulphur contents were measured using an automatic CHNS analyser Flash 2000 Thermofisher. Pore water free, freeze dried sediment was milled, weighted, and directly acidified with 8% H_3PO_4 in 1 cm diameter tin capsules. Two acidifications were enough to dissolve the carbonates. Once the sediments dried, the capsules were closed and directly used for the measurements of OC content. The same milled sediment was then used without treatment to measure the nitrogen and total carbon content. Two certified soils (Soil reference material for NCS determination, thermo; IHSS 1S101F) were used to check the accuracy of the analyses. Typically the precision for TN and TC analyses is within 5%. All the results were corrected for salinity.

Two different extraction techniques were used to determine the manganese and iron solid phase concentrations. The most reactive manganese and iron oxide fractions (amorphous oxides) were extracted with an ascorbate reagent (Anschutz *et al.*, 1998;Haese *et al.*, 2000;Kostka and Luther, 1994;Anschutz *et al.*, 2000). This reagent consisted of a deaerated solution of 50 g of sodium citrate and 50 g of sodium bicarbonate in 1 L of deionized water to which 20 g of ascorbic acid was slowly added to a final pH of 8. About 250 mg of dry sediment was extracted at room temperature with 12.5 mL of this reagent while shaking continuously for 24 h. A second extraction on a separate 250 mg aliquot was carried out with 12.5 mL of 1 N HCl for 24 h to determine acid soluble Mn and Fe. The centrifuged solutions were then diluted in 0.2 N HCl and analyzed by flame atomic absorption. The ascorbate reagent extracts selectively amorphous iron and manganese oxides and associated elements (Kostka and Luther, 1994). The reactive phases extracted by 1 N HCl represented the operationally defined fraction that comprises amorphous and crystalline Fe and Mn oxides, carbonates and hydrous aluminum silicates (Huertadiaz and Morse, 1990, 1992) but may not include the oxidation products of Fe monosulfides (goethite and hematite; (Raiswell *et al.*, 1994). Consequently, FeAsc is expected to be smaller than FeHCl. There are flaws inherent in any extraction procedure but even critics of these techniques concede that they are useful tools when used and interpreted with caution. We are aware that the solid-phase speciation of metals may change upon oxidation and freeze-drying of the sediments (Rapin *et al.*, 1986). The most significant change is the oxidation of acid volatile sulfides (AVS) to oxides that are not readily extracted by the 1 N HCl reagent (Raiswell *et al.*, 1994).

e) Pore water analyses

Pore water was analyzed for nitrate (Grasshoff *et al.*, 1983), ammonia (Helder, 1989) and sulphate (Bottrell *et al.*, 2009) using an AXFLOW autoanalyser. The acidified subsample was analyzed for Fe^{2+} and Mn^{2+} using a SOLAAR AAS. Total inorganic carbon (DIC) was measured using a flow injection-conductivity detection system as described in (Hall and Aller, 1992). H_2S was measured using the colorimetric method described in Grasshoff *et al.* (1983). The analytical precision was <2% for all solutes.

ODU were calculated using the concentration of dissolved iron, manganese and H_2S using the following formula: $[ODU] = \frac{1}{2}[Mn^{2+}] + \frac{1}{4}[Fe^{2+}] + 2[S^{2-}]$ according to the diagenetic sequence and the stoechiometry involved (Berner, 1989;Canfield *et al.*, 1993b;Froelich *et al.*, 1979).

f) Diagenetic modelling

A steady state version of a numerical diagenetic model, OMEXDIA (Soetaert *et al.*, 1996a), was used and fitted to the measured profiles of oxygen, nitrate, ammonium and TOC to estimate the rates of total carbon oxidation, the relative contribution of the majors pathways of organic matter mineralization (aerobic, anaerobic and denitrification) and the degradability of the organic carbon deposited. For details on this model and parameter values, other than those listed in Table 3, we refer to Soetaert *et al.* (1996b, a).

Briefly, OMEXDIA is a numerical nonlinear coupled model based on the 1-dimensional diagenetic equations (Boudreau, 1997;Berner, 1980). In this model, solutes are transported by molecular diffusion, whereas solid phase compounds are transported by advection, compaction and bioturbation. The model describes aerobic carbon mineralization, nitrification and denitrification and combines anaerobic mineralization processes. It generates steady state profiles of oxygen, nitrate, ammonium, Oxygen Demand Units (ODU; *i.e.* the amount of oxygen used to reoxidize the reduced products resulting from anaerobic mineralization) and carbon. Solid phase organic carbon is modelled as 2 fractions with different degradabilities: they thus have different first order mineralization rates and C/N ratios corresponding to a labile and more refractory organic matter.

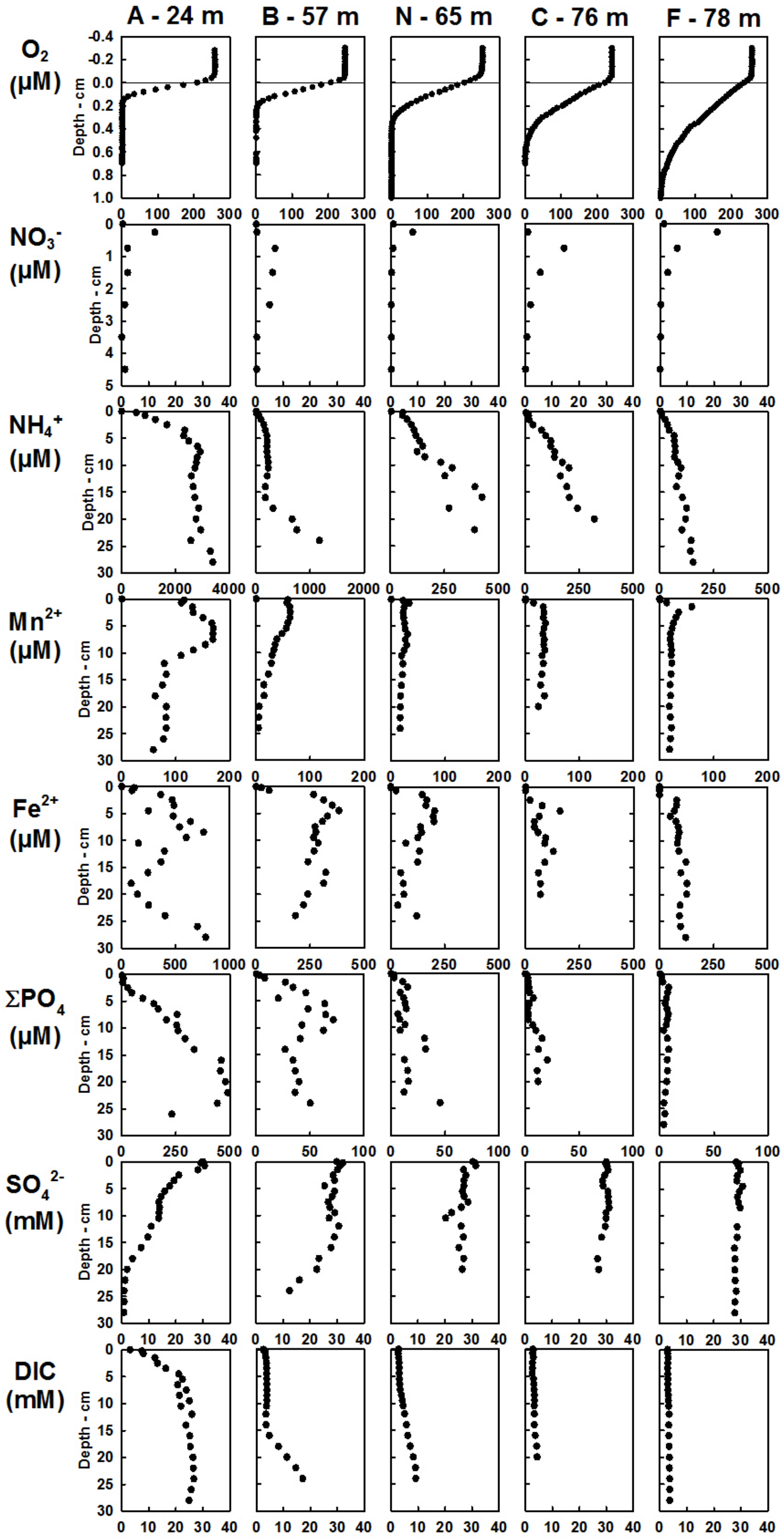

Figure 2 : Measured profiles of dissolved species in sites A, B, N, C and F representing the southwestward gradient. Note that different scale are used for different profiles.

5.4 RESULTS AND DISCUSSION

5.4.1 Characteristics of the Rhone River prodelta and shelf

Bottom water temperature and salinity (Table 1) were homogeneous among all sites: they ranged respectively between 14.2 and 14.9°C and 37.6 and 38.0 p.s.u. Bottom water was well-oxygenated with calculated O_2 saturation between 92 and 100 %.

The sea floor in the sampling area was composed of silt and clay sized particles with a mean grain size decreasing with water depth from 37 µm in site A to 9 µm in site F (Pastor *et al.*, In prep.). Porosity was constant over the sites, between 0.85 and 0.95 in surface and decreased within the sediment to around 0.60-0.70, consistently with profiles reported by *(Cathalot et al., submitted)*. The organic carbon content in the upper 0.5 cm was higher in the close vicinity of the river with 2.7 dw% and decreased proportionally with depths to 1.1 dw% at sites F and J (Table 1).The asymptotic organic carbon contents down cores ranged from 0.6 to 2.4 dw%. The atomic C/N ratios were in average 10.9 ± 0.8. Briefly, in the Rhône River delta, high concentration of benthic organic carbon occur near the river outlet and reflect the Rhône River inputs i.e. the amount and lability of organic carbon discharged originating from erosion and runoff in the drainage basin.

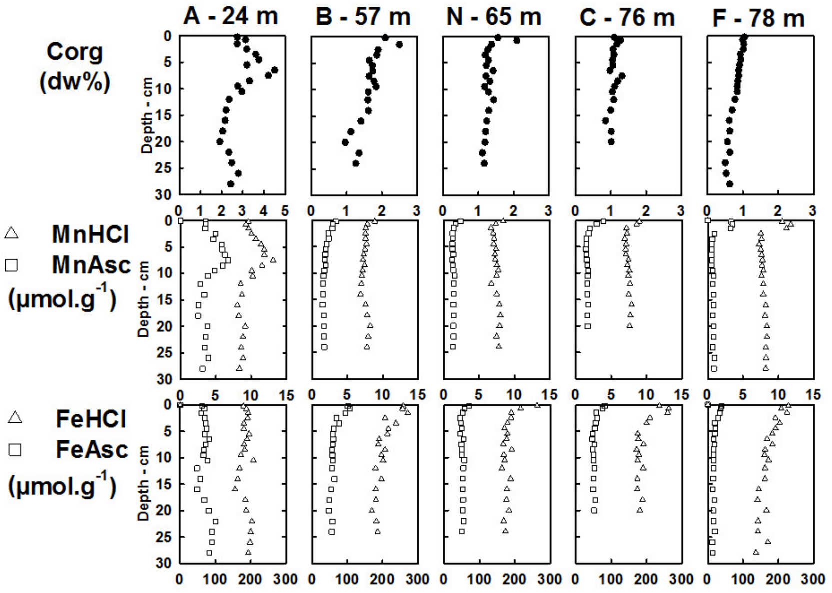

Figure 3 : Measured profiles of solid species in sites A, B, N, C and F representing the southwestward gradient.

5.4.2 Diagenetic sequence

Sites A, B, N, C and F are representative of the southwestward gradient and thus give informations about the Rhône River plume effect on the biogeochemistry of the sediments. Porewater profiles of oxygen, nitrate, ammonium, dissolved manganese and iron, phosphate, sulphate and dissolved inorganic carbon are shown in Figure 2 while solid phase profiles of TOC, manganese and iron oxi-hydroxides are shown in Figure 3. The surface organic carbon content is clearly decreasing with depth and distance from the mouth (Table 1). This suggests a decrease in organic carbon loading from the river with distance coupled to an increase in organic carbon degradation throughout the water column as water depth increase (Buscail *et al.*, 1995;Pastor *et al.*, In prep.;Lansard *et al.*, 2005). Similarly, the diffusive oxygen uptakes are also decreasing with depth and distance (Table 2) from 21.5 mmol m^{-2} d^{-1} in site A to 5.3 mmol m^{-2} d^{-1} in site F as previously presented in (Cathalot *et al.*, submitted). This is consistent with previous measurements in the same area showing high diffusive oxygen uptake rates correlated with organic matter content (Lansard *et al.*, 2009) These authors highlighted the intense microbial degradation activity associated with relatively elevated retention time and important burial rates occurring in the prodelta (Tesi *et al.*, 2007).

Table 2. Sediment oxygen consumption fluxes (DOU) and ODUs reoxydation fluxes calculated from profiles, nitrate and ammonium release to the bottom water measured from core incubation, compared to values estimated by the model; expressed in mmol m^{-2} d^{-1}. OPD is the oxygen penetration depth in mm as deducted from the profiles.

Sites	DOU		OPD		NO_3^- flux		NH_4^+ flux		ODUs reoxyd	
	data	model	data	model	data	model	data	model	data	model
A	21.5 ± 3.9	20.0	1.4 ± 0.2	1.8	/	4.1	5.00 ± 3.00	2.01	0.26	0.18
B	15.7 ± 2.1	17.5	2.2 ± 0.3	2.2	0.2 ± 0.1	1.3	0.60 ± 0.50	0.47	0.33	0.58
N	9.5 ± 1.2	11.2	3.3 ± 0.6	3.6	/	1.1	/	0.04	0.08	0.15
C	10.3 ± 3.2	8.2	4.7 ± 1.5	4.8	0.4 ± 0.1	0.8	/	<0.01	0.03	0.08
F	5.3 ± 0.7	4.9	9.7 ± 2.1	9.7	/	0.5	/	0.06	0.04	0.02
K	10.8 ± 2.2	13.5	2.6 ± 0.7	2.7	0.4 ± 0.3	1.6	0.32 ± 0.16	0.33	0.14	0.22
L	7.0 ± 3.9	7.5	4.9 ± 2.1	4.9	0.3 ± 0.1	0.2	2.01 ± 1.91	0.71	0.05	0.10
I	4.6 ± 0.8	5.4	6.7 ±0.3	7.1	0.1 ± 0.1	0.5	/	0.04	0.03	0.03
J	7.2 ± 3.3	5.5	7.5 ± 2.2	6.8	0.3 ± 0.1	0.3	/	<0.01	0.03	0.04

/ : not exploited. Errors for DOU and OPD are determined for n profiles, errors for nitrate and ammonium are determined for 2 or 3 cores.

In most cores, a peak of nitrate in the oxic zone is observed from 21 µM in site F to 7 µM in site B. As the concentration in nitrate in the bottom water never exceeded 1 µM during the cruise, we thus conclude that the nitrate present in the oxic zone is being produced within the sediment by the oxidation of ammonium by nitrification. Nitrates are then rapidly consumed by denitrifying bacteria. Nitrates and ammonium peaks match each other, indicating a potential tight coupling between denitrification and nitrification processes. As the oxygen penetration depths do not exceed 9.7 mm in site F and is < 3 mm in sites close to the mouth, It is most likely that anoxic degradation is an important process.

Just below the nitrate reduction zone, the reduction of manganese and iron degradable oxides occurs as indicate by the decrease in MnAsc and FeAsc respectively (Figure 3) as predicted by (Froelich *et al.*, 1979). These reactions produced dissolved manganese and iron with concentration up to 170 µM and 640 µM respectively in site A (Figure 2). These concentrations decreased with depths and distance from the mouth to reach an average value of 25 µM of dissolved manganese and 100 µM of dissolved iron in site F. The diffusion of these species up to the oxic layer with their reoxidation is responsible for the authigenic oxides layer at the oxic/anoxic interface (Figure 2). In this area, the stock of manganese and iron degradable oxides stay constant at a certain depth, between 1 and 4 µmol g^{-1} for manganese and between 20 and 100 µmol g^{-1} for iron. Thus, the degradation of organic carbon using these oxides as electron acceptors is still possible.

Nethertheless, sulphate reduction is clearly observable in sites A and B and weakly in sites N and C by a reduction in sulphate concentrations throughout the sediment (Figure 2). The reduction of sulphate produced no detectable sulphide in these sediments (data not shown). The absence of sulphide and the accumulation of reduced manganese and iron in the pore water as well as their declining concentration downcore are characteristic of an intense cycling of metal oxides and of a significant precipitation of sulphides in these sediments (van der Zee *et al.*, 2001). The high accumulation of ammonium, phosphate and dissolved inorganic carbon as end products of the organic carbon mineralization underline the high organic degradation rates in the close vicinity of the Rhône, and its decrease with water depth and distance from the mouth.

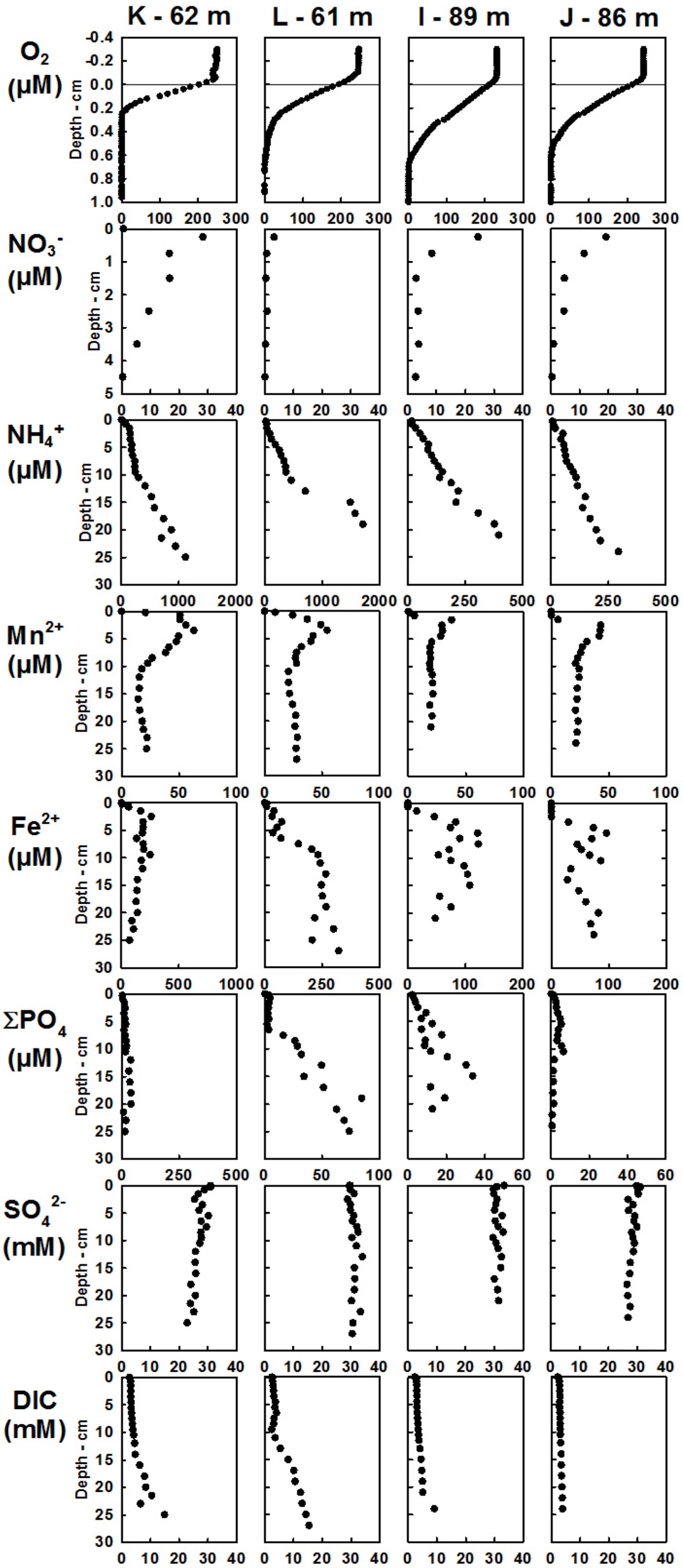

Figure 4 : Measured profiles of dissolved species in sites K, L, I and J representing the eastern zone. Note that different scale are used for different profiles.

Sites K and L are situated in the close vicinity of the Rhône River in the same area than site B. Their sediment biogeochemistry is very similar to the one in site B with the same order of value for reduced species (Mn^{2+}, Fe^{2+}, NH_4^+, DIC) (Figure 4; Figure 5). We even observe the same non steady state feature between 10 and 15 cm depth, especially in the ammonium and DIC profiles. This suggests that these 3 sites are under the same sedimentary regime with a similar sediment organic carbon degradation rate.

Finally, sites I and J represent the eastern part of the prodelta area and are likely to be less influenced by the river inputs. Indeed, many studies underlined the preferential particles dispersal pathway toward the southwest and the high prodelta particles retention (Monaco *et al.*, 1990;Naudin and Cauwet, 1997;Heussner *et al.*, 1990),. Therefore, these sites may be similar to site F located offshore, with a deeper oxygen penetration depth and less accumulation of reduced species (Figure 4). This confirms that site F situated at 23 km offshore of the river mouth is probably under a weak influence of the Rhône river plume.

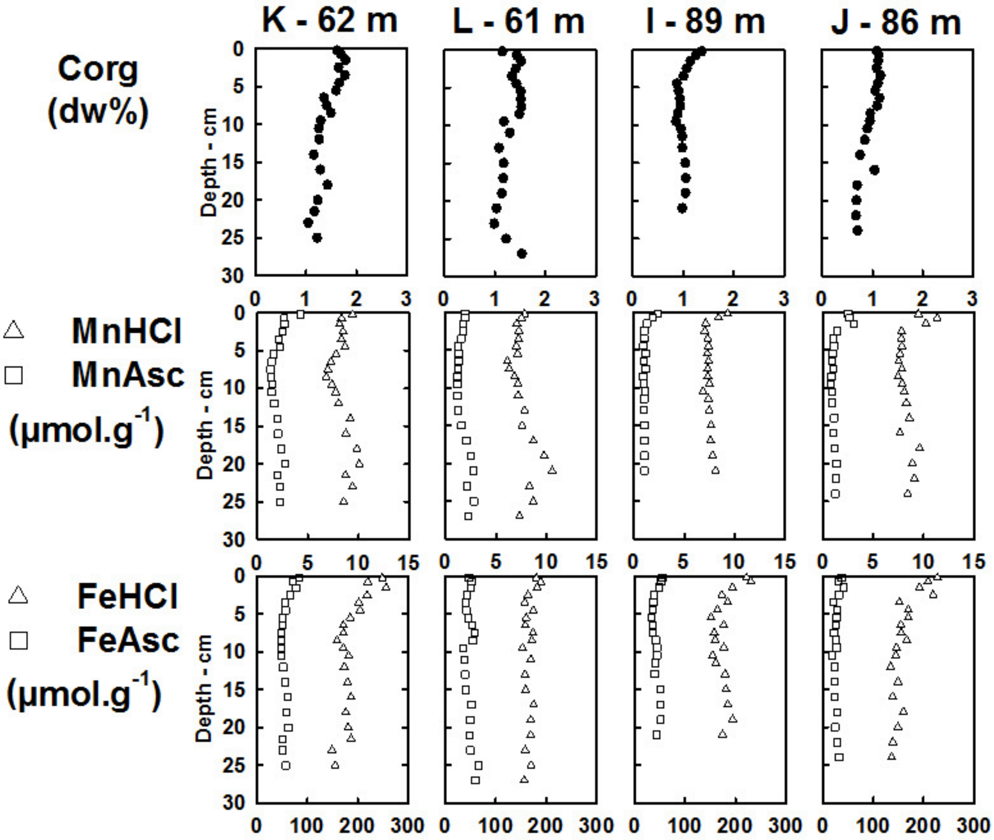

Figure 5 : Measured profiles of solid species in sites K, L, I and J representing the eastern zone.

From the pore water and solid phase profiles interpretation, we can make the principal observations that organic carbon mineralization decrease with depth and distance from the mouth and that precipitation of metal oxides and carbonates seems to play an important role in these sediments. In order to better constrain these observations and identify key processes, we used a modified diagenetic model, OMEXDIA (Soetaert *et al*., 1996a). It allowed us to:

- Calculate the oxic and anoxic mineralization rates and their relative contribution in these sediments; We will then be able to compare them with the organic degradation rates calculated from the oxygen profiles and conclude on the accuracy of this approximation commonly used in different coastal areas
- Estimate carbon deposition flux and carbon degradation rates to link quality and quantity of the organic matter inputs in a single example of coastal area.
- Calculate the precipitation of sulfides and the oxygen demand for reoxidation of reduced species.

5.4.3 Model fit of the experimental data

a) Model parameters

Pore waters and sediment organic carbon profiles were fitted by optimizing the total flux of degradable organic carbon deposited at the surface (Fc), its partitioning over a fast and a slow degraded fraction (Pfast) and their relative first order degradation constant (respectively Rfast and Rslow), the bioturbation coefficient (Db) and the sedimentary deposition rate (w). First priority was given to an accurate description of the in situ oxygen and sediment organic carbon profiles by adjusting the degradable organic carbon flux and the refractory organic carbon (OCburial). Then, nitrate was fitted by adjusting the nitrification rate (Rnit) and denitrification half saturation term ($KsNO_3denit$) and ammonia by adjusting the carbon degradation rates. ODUs were then fitted by adjusting a precipitation term (ODUdepo). For all sites, satisfactory fits were performed (Figure 6; Figure 7). The interface gradient was fitted in priority because some non steady state features may occur at a certain depth in many sites (i.e. site B, 10-15 cm depth, Figure 2).

Sedimentation rates were adjusted in regard to literature. They ranged from 10 cm yr^{-1} at the mouth to 0.1 cm yr^{-1} in site F and J and are coherent with previous studies from Charmasson *et al.* (1998), Miralles *et al.* (2005), Radakovitch *et al.* (1999) and Zuo *et al.* (1997). Bioturbation coefficients were adjusted in regards to literature (Radakovitch *et al.*, 1999;Zuo *et al.*, 1991), sediment profile imagery data (i.e. SPI;(Rosenberg *et al.*, 2003) ; M. Desmalades personal communication) and fauna analyses (data not shown) during the same cruise. They ranged from 0.5 cm^2 yr^{-1} in site A to 10 cm^2 yr^{-1} in sites C, F, I and J. It is likely that the strong disturbance due to the river plume at the mouth causing resuspension, and large anoxic mineralization, make it difficult for benthic organisms to settle. The fauna seems to be more active offshore with deeper water depths where the particulate deposition is less intense. The mixed layer was averaged to 13 cm regarding to the SPI values. N/C values were averaged to 0.14 for the fast fraction and 0.07 for the slow fraction. Diffusivity in water was calculated according to (Boudreau, 1986) and corrected for salinity, temperature and pressure using the marelac package on R (Soetaert, Petzoldt and Meysman, 2009). The bulk sediment diffusion coefficient of solutes was calculated from Rasmussen and Jorgensen (1992) as

$Ds = \frac{Do}{(1 + 3(1 - \Phi))}$ where ϕ is the sediment porosity and D_0 is the diffusion coefficient in water as calculated above. Fixed parameters used in the model are presented in Table 3.

Table 3. Fixed parameters used in the model.

Sites	A	B	N	C	F	K	L	I	J
Fc (gC/m^2/yr)	450	120	70	55	25	100	70	35	35
w (cm/yr)	10	2	1	0.5	0.1	1	1	0.1	0.1
Rfast (/yr)	7	37	37	37	37	22	22	37	37
Rslow (/yr)	0.04	0.37	0.04	0.37	0.004	0.33	0.33	0.004	0.004
Pfast (%)	90	90	90	80	70	90	90	70	80
OC burial (%)	2.00	1.30	1.15	0.98	0.40	1.20	1.20	0.75	0.60
biot (cm^2/yr)	0.5	2	5	10	10	3	8	10	10
ODU depo (%)	99.5	97.5	98	99	99	98	99	99	99
Rnit (/d)	100	100	100	100	100	100	5	100	10
ksNO3denit (/d)	10	10	10	10	10	300	10	200	10

b) Comparison of model outputs with independent data: dissolved species fluxes

To validate the model on our dataset, we compared fluxes calculated from the model to fluxes measured or calculated on our data. This comparison is given in Table 2. After a good visual fit to our profiles is obtained, the model generates consumption or production fluxes of the different dissolved species involved. Here we compare fluxes experimentally achieved to the model outputs. The oxygen fluxes were measured from our profiles using the fick's first law of diffusion and nitrate and ammonium release fluxes were measured with dark cores incubation. The ODU's release fluxes were calculated from the gradient of concentration of Fe^{2+} and Mn^{2+} in our profiles using the Fick's first law of diffusion too and applying the stoechiometry described in 5.3.2e). Oxygen fluxes calculated from the model are in good agreement with our data (Table 1), and are, as observed previously, exponentially decreasing with distance from the mouth (Figure 1). Their relative oxygen penetration depths are also in good agreement with a minimum in site A (1.8 mm) and a maximum in site F (9.7 mm) (Figure 2). Irrigation seems not to be a dominant process in the benthic carbon oxidation since Total Oxygen Uptake and Diffusive Oxygen Uptake rates were not significantly different (Cathalot *et al*, submitted; Pastor *et al*, In prep.; Hulth *et al*., 1994).

Concerning the nutrients fluxes, ammonium release are smaller in the model than the one measured by core incubations but the order of magnitude and the variation is the same (Table 2; values given for sites A, B, K and L). On the contrary, the nitrate release calculated by the model is higher in sites situated at the close vicinity of the Rhône River (i.e. sites B and K). It is possible that the model overestimates ammonium oxidation and nitrate production and release. The coarse resolution for core slicing is clearly a problem when fitting calculated curves to the data and estimating nitrate and ammonium reactions rates close to the sediment-water interface. In those sites, oxygen penetration depth is very shallow and range between 2.2 and 2.6 mm. Nitrate production and ammonium oxidation occurs in this sediment layer which is documented by a single data point on the porewater profile. Thus, the differences of nitrate and ammonium fluxes must be interpreted with caution. Finally, the ODUs reoxydation flux is also in good agreement with our measurement on profiles with modeled fluxes. This comparison thus confirms the overall reliability of the OMEXDIA model to represent our dataset and thus allow us to discuss the following model outputs.

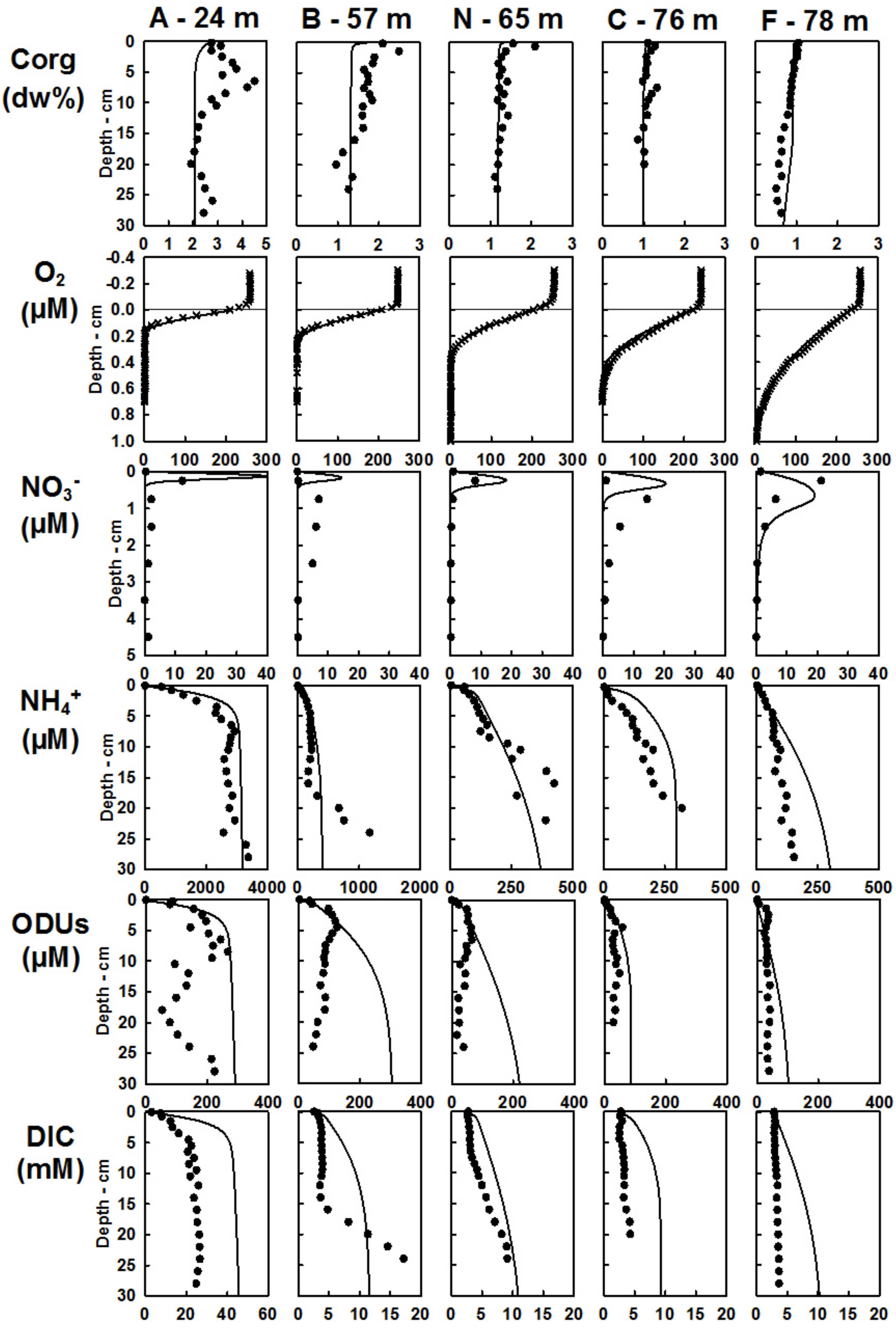

Figure 6. Experimental profiles (symbols) and the best fit using the steady-state version of OMEXDIA, a numerical coupled diagenetic model (lines) in sites A, B, N, C and F. Note that different scales are used for different stations.

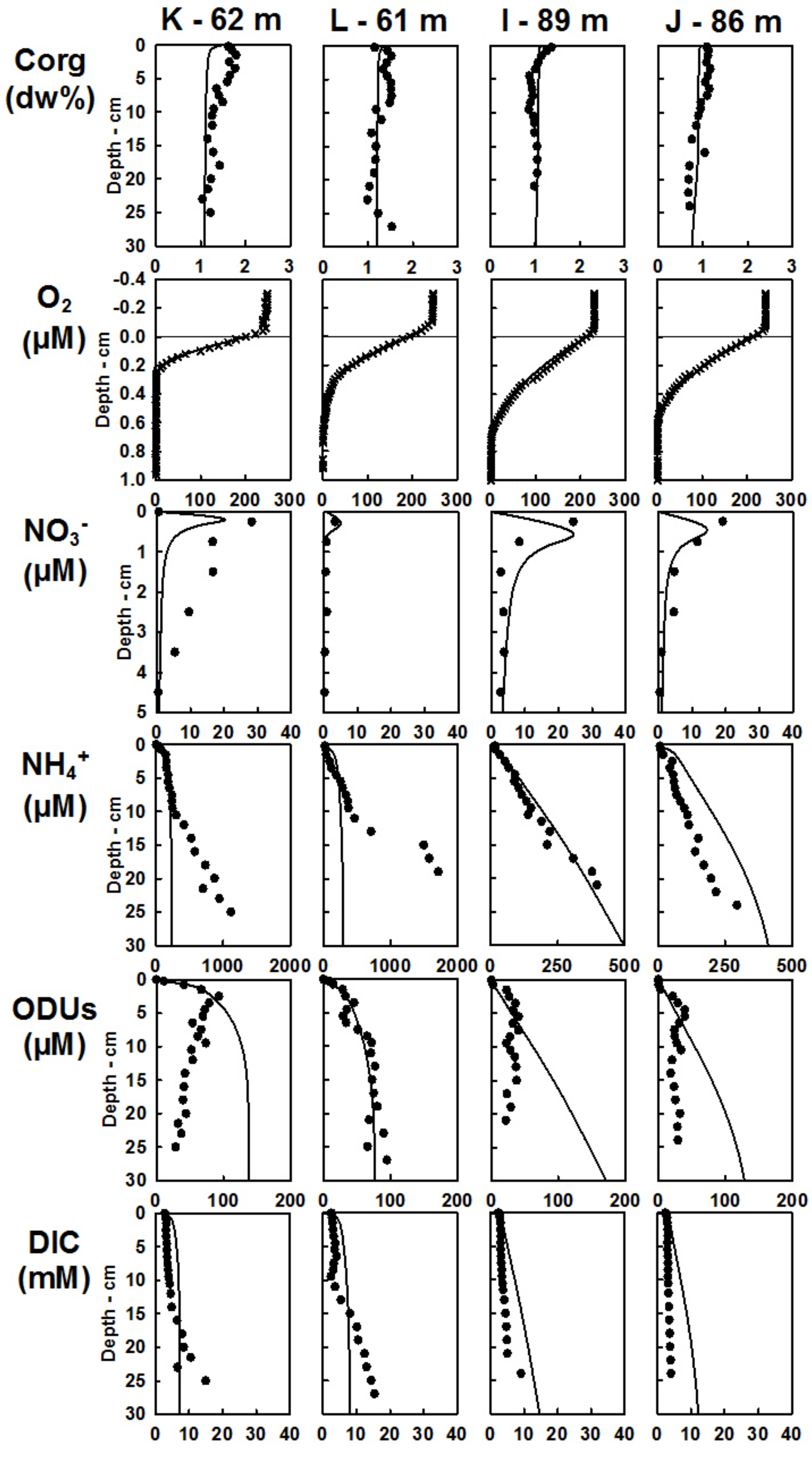

Figure 7 . Experimental profiles (symbols) and the best fit using the steady-state version of OMEXDIA, a numerical coupled diagenetic model (lines) in sites K, L, I and J. Note that different scales are used for different stations.

5.4.4 Organic carbon (OC) deposition and mineralization

The pore water data in the Rhône River delta suggest that both deposition and carbon oxidation vary substantially with distance from the river outlet. Figure 9 shows the model estimated rates of carbon degradation and carbon deposition (i.e. degraded + buried) as a function of distance from the river mouth. The total organic carbon deposition and oxidation rates for the Rhône river delta show a gradual decline offshore that could be described with the following equations (in gC m^{-2} y^{-1}):

Flux of degradable organic carbon $\mathrm{F}_{\mathrm{deg}} = 27.7\, e^{\frac{3.4}{x-0.7}}$

Total organic carbon flux $\mathrm{F}_{\mathrm{tot}} = 49.2\, e^{\frac{3.8}{x-0.9}}$

where x denotes distance from the river outlet (km). Flux of degradable organic carbon to the sediment, F_{deg}, represents the total organic carbon oxidation and represents the sum of aerobic oxidation, denitrification, and anaerobic oxidation, processes. The maximum and minimum rate of total organic carbon degradation (F_{deg}) for all stations differed by a factor of 18. As temperature ranged between 14.2 and 14.9°C (Table 1), such differences in the rates of benthic OC mineralization can not be explained by enhancement or inhibition of bacterial metabolic activity. It is therefore most likely that organic carbon oxidation in the Rhône River prodelta is controlled by other factors.

Table 4. Estimated degradable OC, buried OC and total particulate matter fluxes from the model (Fc, Fb and Ft respectively) expressed in gC m^{-2} yr^{-1}.

Sites	A	B	N	C	F	K	L	I	J
Fc	450	120	70	55	25	100	70	35	35
Fb	2120	276	122	52	4	127	127	8	6
Ft	2570	396	192	107	29	227	197	43	41

The modelled fluxes of degraded OC in the Rhône River delta show a pattern consistent with previous studies: high amounts of organic carbon are mineralized at the vicinity of the river mouth and carbon oxidation decreases offshore. Combined with the high accumulation of ammonium, phosphate and dissolved inorganic carbon as end products of the organic carbon mineralization, these fluxes underline the high OC degradation rates in the close vicinity of the Rhône, and their decrease with distance from the river mouth. This is in agreement with former calculations based on Total Oxygen Uptake measurements (Lansard *et al.*, 2009) who estimated total carbon oxidation in the Rhône River delta: around 170 gC m^{-2} y^{-1} at the immediate outlet, 90 gC m^{-2} y^{-1} in a 3 km radius zone and 70 gC m^{-2} y^{-1} offshore. The oxygen uptake rates calculated by the model in this paper range between 5 and 22 $mmolO_2$ m^{-2} d^{-1} (Figure 8; Table 2). Previous studies used DOU rates as a rough estimation of carbon oxidation in the Rhône delta from and founded values around 20 $mmolO_2$ m^{-2} d^{-1} (Rabouille *et al.*, 2003), 11 $mmolO_2$ m^{-2} d^{-1} (Blackburn and Lomstein, 1989;Denis and Grenz, 2003) further away on the shelf. Moreover, Helder (1989) also measured organic carbon mineralization rates by different electron acceptors on the shelf and estimated it to be 5.2 mmolC m^{-2} d^{-1} i.e. 23 gC m^{-2} y^{-1} which is in agreement with our own estimations for the shelf. These fluxes are moreover in the same range than other carbon degradation fluxes estimated in coastal areas (Canfield *et al.*, 1993a;Canfield *et al.*, 1993c).

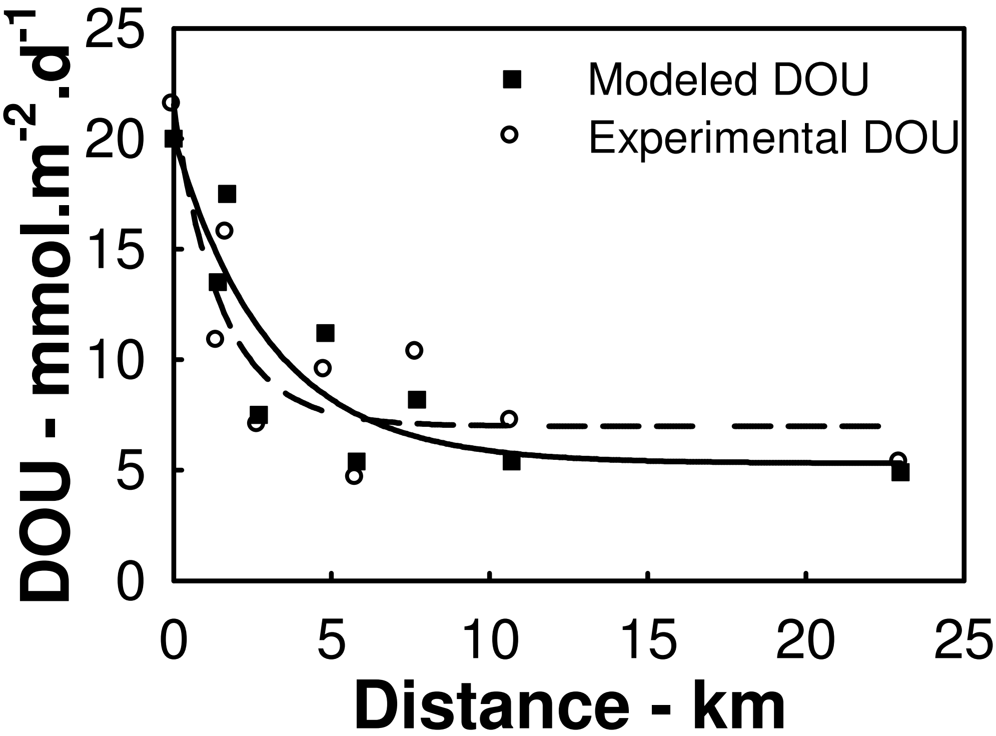

Figure 8 : Experimental versus modeled diffusive oxygen uptakes. The full line represents the model while the dashed line represents the experimental data.

This spatial disctribution of mineralization activity clearly reflects the influence of the Rhône River inputs. High discharge rates of terrestrial OC support high accumulation rates and significant mineralization. The direct influence of the river OC inputs and the benthic degradation rates have been demonstrated in the Rhône River delta (Lansard *et al.*, 2009;Denis and Grenz, 2003;Cathalot *et al.*, submitted) and other river-dominated continental margins (Alongi, 1995;Archer and Devol, 1992;Canfield *et al.*, 1993a;Morse and Rowe, 1999). Briefly, in our system, radionuclides and pollutant measurements combined with organic components and carbon isotopes studies and hydrodynamical modelling showed that the terrestrial organic material mainly settles in front of the Rhône River and that only 10-20% is exported via resuspension events, generally in the south-west direction (Naudin *et al.*, 1997;Ulses *et al.*, 2008;Tesi *et al.*, 2007;Roussiez *et al.*, 2005;Radakovitch *et al.*, 2008). Moreover, recently, Cathalot *et al.* (submitted) showed that the Rhône River delta sediment react strongly to a change in lability of the riverine inputs. This is, for instance similar to the feature in the Changjiang estuary and adjacent continental shelf: terrestrial OC is mainly deposited nearby the outlet and post-depositional diagenetic processes in surface sediments rapidly alter their chemical composition and control the OC preservation (Wang *et al.*, 2008). Therefore our results confirm that the Rhône River delta represents an active biogeochemical and diagenetic system that clearly matches the footprint of riverine inputs, with an enhanced activity of carbon degradation at the immediate vicinity of the river mouth, as indicated by both high carbon degraded and buried fluxes (Table 4). Figure 9 also illustrates the active burial site that the Rhône River prodelta is: the OC degraded in this proximal area accounts for only 20 - 40% of the total OC flux deposited, versus > 80% further away in the adjacent continental shelf. This role of OC preservation and efficient burial centre has already been highlighted in other of river-influenced continental margins systems (Galy *et al.*, 2007;Hedges and Keil, 1995;Ståhl, 2001;Burdige, 2005). This concomitance of high degradation and burial rates again underlines the major role in the global carbon cycle of these river-influenced ecosystems, such as deltas and estuaries (Aller, 1998;Borges *et al.*, 2006).

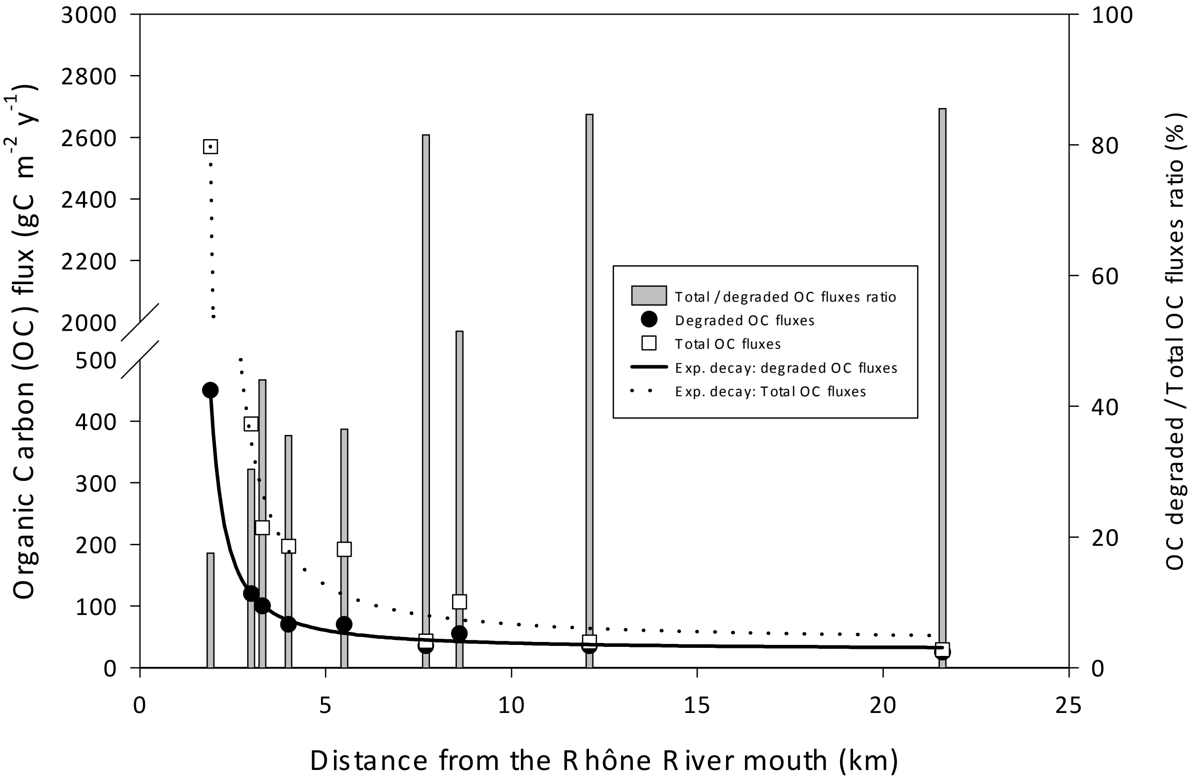

Figure 9. Flux of degraded ● and total ☐ organic carbon (OC) as a function of distance from the Rhône River outlet. Exponential decays reflect the best fit to the dataset.

5.4.5 The reactivity of organic carbon in sediments

As described in Soetaert *et al.* (1996a), the flux of degradable organic carbon deposited at the sediment surface is composed of two distinct fractions: a very labile fraction and a moderatly reactive fraction. These two fractions are represented by a first-order degradation constant characteristic of their lability. The more labile fraction is likely to be degraded at a much faster rate and thus the relative concentration of both fractions changes with time. We fixed the proportion of the more labile fraction depending on the water depth and distance from the mouth.

Pastor *et al.* (*In prep.*) and Cathalot *et al.* (submitted) studied the carbon mineralization activity in the surface sediment of our site in relation with the quality of organic matter deposited. During april 2007, under normal discharge rates conditions, sites close to the mouth receive an important amount of fresh material (with high Chla and bioavailable content) that is likely not degraded in the water column due to a shallow water depth (< 70 m): we thus considered that 90% of the degradable organic carbon was composed of very labile material (Table 3). In sites with a water depth > 70 m, we assumed that 70- 80% of the degradable pool of organic carbon was composed of very labile material. The model is sensitive to a change in the two fractions degradation constants. We then found first-order degradation constants ranging between 7 in site A and 37 yr^{-1} in sites B, N, C, F, I and J for the more labile fraction. These values are in good agreement with a previous study from Westrich and Berner (1984) who used two fractions of degradable organic carbon in his model and found first-order degradation constant around 24 ± 4 yr^{-1} for the more labile fraction. For the moderately-reactive fraction, we found first-order degradation constants ranging between 0.004 in sites F, I and J and 0.37 yr^{-1} in sites B and C (Table 3). The highest values (0.37 and 0.33 yr-1) could correspond to resuspended organic matter (Berner, 1980;Hargrave and Phillips, 1989) while the lower values could be characteristic of a much degraded material (Herman *et al.*, 2001).

These two fractions are likely to be related to the dilution of the Rhône River material previously evidenced (Cathalot *et al.*, submitted;Lansard *et al.*, 2009;Tesi *et al.*, 2007): a mixing of fine continental material, isotopically depleted, rich in OC, relatively rich in lignin and chlorophyll (i.e. labile material) with continental shelf aged resuspended particles, initially originating from marine phytodetritus, which underwent many deposition/degradation/remobilization cycles and characterized by lower OC, “heavier” isotopic composition and the absence of lignin (i.e. moderately reactive fraction). The two modelled carbon fractions are thus most likely to reflect this dual composition and complex origin of the material settling down in the Rhône River delta. As pointed by Holstein *et al*, 2009, the carbon cycle is mainly controlled by organic matter decay, and therefore these two degradable fractions and their respective fractions are likely to influence the OC oxidation pathways occurring in the sedimentary column.

5.4.6 Biogeochemical processes occurring in the prodelta area

a) Oxic versus anoxic

Although there is a clear enhancement of carbon oxidation near the river outlet, the spatial distribution of OC oxidation processes in the Rhône River delta are slightly different. Anaerobic oxidation at station A, the closest station from the river mouth, accounts for more than 90% for the OC oxidation rates, this percentage decreasing quickly to an homogeneous value around 50% in the delta (Table 5; Figure 10). Denitrification is also ~10 times higher at the vicinity of the outlet (stations A, B, K, N) than further offshore in the shelf. Finally, rates of aerobic oxidation of carbon at the outlet were only slightly enhanced (factor 3) compared to further stations in the shelf.

Table 5. Degradation rates of organic carbon by oxic mineralization, denitrification and anoxic mineralization expressed in mmol m^{-2} d^{-1} and the relative percentage of each process

Sites	**Oxic mineralization**		**Denitrification**		**Anoxic mineralization**	
	flux	%	flux	%	flux	%
A	6.9	6	4.2	4	111	90
B	12.0	44	2.7	5	14.0	51
N	8.0	42	1.3	7	9.7	51
C	5.8	37	1.1	7	8.9	56
F	4.0	59	0.4	6	2.3	35
K	10.2	37	0.9	3	16.8	60
L	7.5	38	0.4	2	11.9	60
I	4.6	48	0.4	4	4.5	48
J	5.4	55	0.3	3	4.1	42

Figure 10 shows the model estimated partitioning of degradable organic carbon over aerobic oxidation, denitrification and anaerobic oxidation. Carbon oxidation in the Rhône River delta sediments present a bimodal structure directly linked to the footprint of river inputs (see above): at stations with moderate river influence corresponding to moderate fluxes of degradable carbon (F_{deg}), carbon oxidation appears to be fairly balanced between aerobic and anaerobic oxidation. Anaerobic oxidation becomes dominant with increasing river influence i.e. decreasing distance from the outlet and increasing F_{deg}. The relative contributions of oxidation pathways confirm these ideas (Table 5). In the immediate prodelta, the importance of anaerobic oxidation increases with proximity of the river outlet and accounts for almost 90% of the total carbon oxidation. Since the contribution of denitrification is ~5% over the entire shelf range, the distribution of anaerobic oxidation with distance from the river mouth shows a mirror image of aerobic oxidation. This is consistent several other studies in continental margins: anaerobic oxidation on the shallow shelf in the Iberian Margin and in coastal sediment of Ago Bay (Japan) ranged around 30-40% (Epping *et al.*, 2002;Kasih *et al.*, 2009).

The rates of denitrification seem to be negligible almost everywhere on the shelf except for stations nearby the outlet i.e. at high fluxes of degradable organic carbon. Globally, this partitioning among processes is in good agreement with the empirical relationships derived by Middelburg *et al.* (1997) when calculating total carbon oxidation as the sum of aerobic oxidation, denitrification and sulphate reduction.

Our results highlight the importance of anaerobic pathways in carbon oxidation processes for sediment near the river outlet. In anoxic mineralization, iron is more important than manganese. Indeed, the amount of reactive iron oxide was almost 100 times higher than the pool of reactive manganese oxides and Mn^{2+} pore water content were at least 10 times lower than the iron reduced ones (Figure 2 and Figure 4). Although some manganese reduction may occur and be coupled to reoxidation of reduced iron and sulphur, it is rather unlikely that manganese reduction plays a significant role in the degradation of organic carbon in the Rhône River delta sediment (Canfield *et al.*, 1993a;Canfield *et al.*, 1993c;Glud *et al.*, 2000).

Iron reduction, however, seems to be a quantitatively important degradation pathway all over the prodelta, as indicated by the important stock of iron degradable oxides. Nevertheless, for stations A and B, and to a lower extent, N and C, sulphate reduction is also most likely to play a significant part in anaerobic carbon oxidation as indicated by a significant decrease in sulphate concentration in the lower sedimentary column (Figure 2). The absence of sulphide combined to the observed accumulation of reduced manganese and iron in the pore water may indicate intense cycling of metal oxides and pyrite formation (Berner, 1977).

b) Re oxidation of reduced products

The distribution of modelled oxygen fluxes (Table 2) follows the pattern of total carbon oxidation with distance from distance to the river outlet (Figure 8). Utilisation of oxygen can be attributed to aerobic mineralization, nitrification (as a result of reoxidation of the ammonia produced by denitrification) and reoxidation of reduced compounds generated by sulphate or Mn and Fe oxides reduction.

Table 6. Relative use of oxygen in the different processes

Sites	Aerobic respiration	Nitrification	ODUs reoxydation
A	45.8	52.8	1.4
B	78.1	18.1	3.8
N	76.8	21.8	1.4
C	75.1	23.9	1.0
F	79.1	19.2	1.7
K	78.1	20.2	1.7
L	91.9	6.9	1.2
I	82.6	16.8	0.6
J	88.8	10.6	0.6

Except for station A, 80–90% of the oxygen flux is used for the oxidation of carbon, this fraction being maximum on the eastern part of the Rhône River delta, i.e. the area potentially less impacted by the river inputs. Respectively, around 20% of the oxygen flux is used for nitrification: the production of nitrite and subsequent nitrate generation via the oxidation ammonia seems to be homogeneous over the shelf, with no significant impact of riverine inputs, except at the station A where nitrification accounts for up to 50% of the oxygen fluxes. This enhanced nitrification may be related to the large of concentration of NH_4^+ just below the sediment-water interface that can induce higher nitrification rate (Kemp and Dodds, 2002): this large amount of ammonia available most likely results from the intense carbon oxidation and the major role played by anaerobic pathway at this site.

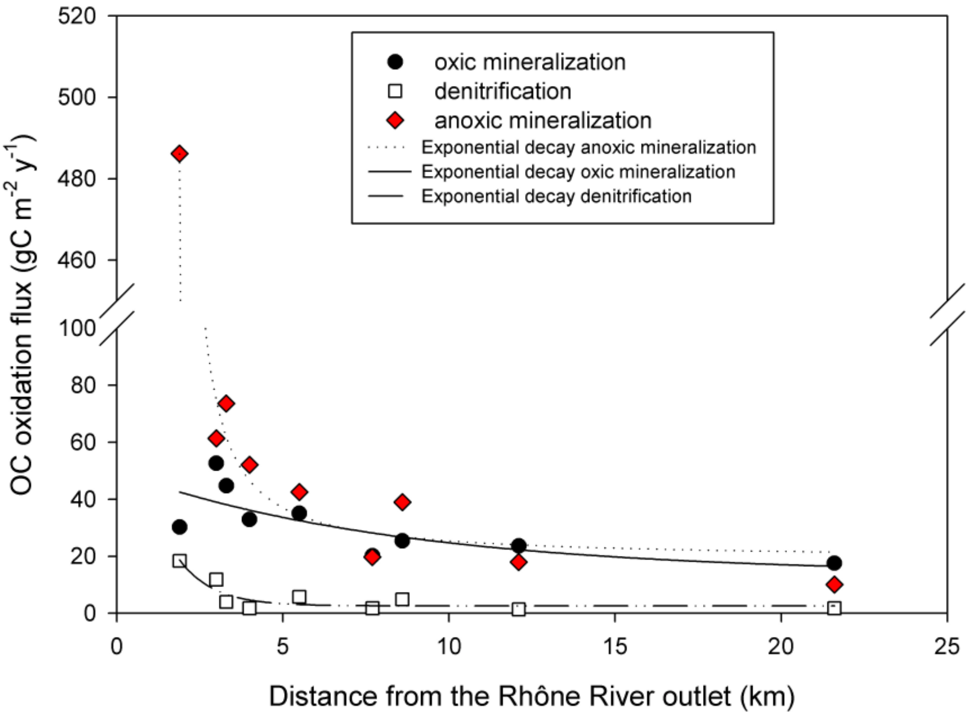

Figure 10. Rates of carbon oxidation estimated by the model showing oxic mineralization ● denitrification □ and anoxic mineralization ◆ Lines represent the exponential fitcurve relating process rate to distance of the outlet.

An interesting feature for our shallow continental margin system is the low fraction of oxygen flux dedicated to reoxidation of reduced chemical species such as Fe^{2+}, Mn^{2+} or sulfides..In the model, precipitation of iron or manganese sulphide is represented by a pDepo term, which corresponds to the amount of ODU leaving the sediment system without consuming oxygen.. In the Rhône River delta, > 95% of the ODU is precipitated in this pDepo term. This term is largely constrained by the low concentration of ODU in porewater compared to the large mineralization rates indicated by DIC or NH4. This large precipitation of reduced phases is consistent with previous observations. Indeed, during diagenesis, sulphide and dissolved iron removal from sediment pore waters are closely coupled through the precipitation of authigenic phases of iron sulphides (Westrich and Berner, 1984). Iron and manganese are also known to cycle rapidly in the sediment (Kasih *et al*, 2009, Canfield *et al.*, 1993). and Mn and Fe reduction may also be coupled to the oxidation of dissolved sulfides. For instance, Kasih *et al* (2009) estimated that around 40% of Fe^{2+} could be used to produce FeS. Since we observed sulphate reduction but no sulphide production, especially near the river outlet, sulphide removal from pore water due to reactions with other elements into the anoxic zone such as pyrite formation is likely to occur in sediment of the Rhône River delta.

A calculation of Fe^{2+} and SO_4^{2-} diffusion fluxes within the core according to Fick's first law allow us a brief insight of the existing coupling between iron and sulphur.

$$J = -\phi\, D \frac{dC}{dz}$$

Where J is the flux, C is the concentration of the species studied (in our case: Fe^{2+}, Mn^{2+} and $SO4^{2-}$), ϕ the sediment porosity and D the molecular diffusion coefficient of the concerned species at in situ temperature. At station A, for instance, it leads to $J\ Fe^{2+} = 0.3$ mmol m^{-2} d^{-1}, $JMn^{2+} = 0.03$ mmol m^{-2} d^{-1}, $JSO4^{2-} = 4$ mmol m^{-2} d^{-1}. Since no sulphides were recorded in the sediment column above 30cm, and assuming sulphate flux as a measure of sulphate reduction linked to OC oxidation, the latter can be considered as equivalent to the sulphide removal from pore water. Fe^{2+} production, although 10 times lower, than the sulphate downward flux, and could account for the formation of mono-sulphide of iron or pyrite. Therefore, it is most likely that the major part of reduced products of anaerobic mineralization escapes the oxygen cycle. In the most proximal stations of the Rhône River delta, sediment oxygen uptake rates only may thus not provide accurate carbon oxidation estimates: caution should therefore be taken in river-dominated continental margins.

5.5 CONCLUSION

In this paper, the cycling of oxygen and carbon in the Rhône River delta sediment was examined through a diagenetic model developed by Soetaert *et al.* (1996a) calibrated on experimental and literature data set and clearly points out the influence of the riverine inputs. Deposition rates of degradable organic carbon directly reflect the dynamics of the Rhône River particulate export. Organic matter bounded with fine particles quickly settles out of the river mouth where they are being efficiently buried, resulting in a high OC accumulation within the proximal delta. High OC degradation rates associated with dominant anoxic mineralization processes characterize this area as a “suboxic reactor”, as defined by Aller (1998) for deltaic environments, and mainly rely on the quantity and quality of the Rhône River inputs. The adjacent continental shelf display a balanced contribution of both aerobic and anaerobic pathways, typical for non river-influenced coastal systems (Blair *et al.*, 2004;Epping *et al.*, 2002).

Re-oxidation of reduced compounds formed during anaerobic carbon oxidation was surprisingly not a major sink for the oxygen flux in the Rhône River prodelta. Major precipitation processes of authigenic phases are likely to occur in river-dominated margins, changing the oxygen budget. Therefore, coupling between carbon and oxygen biogeochemical cycles in these ecosystems isn’t straightforward, and budget assessments should be processed with caution.

5.6 REFERENCES

Aller, R. C.: Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors, Mar. Chem., 61, 143-155, 1998.

Aller, R. C., Hannides, A., Heilbrun, C., and Panzeca, C.: Coupling of early diagenetic processes and sedimentary dynamics in tropical shelf environments: The gulf of papua deltaic complex, Cont. Shelf Res., 24, 2455-2486, 2004.

Aloisi, J. C., Cambon, J. P., Carbonne, J., Cauwet, G., Millot, C., Monaco, A., and Pauc, H.: Origin and role of the bottom nepheloid layer in the tranfer of particles into the marine environment - application to the gulf of lions, Oceanol. Acta, 5, 481-491, 1982.

Alongi, D. M.: Decomposition and recycling of organic matter in muds of the gulf of papua, northern coral sea, Cont. Shelf Res., 15, 1319-1337, 1995.

Anschutz, P., Zhong, S. J., Sundby, B., Mucci, A., and Gobeil, C.: Burial efficiency of phosphorus and the geochemistry of iron in continental margin sediments, Limnol. Oceanogr., 43, 53-64, 1998.

Anschutz, P., Sundby, B., Lefrancois, L., Luther, G. W., and Mucci, A.: Interactions between metal oxides and species of nitrogen and iodine in bioturbated marine sediments, Geochim. Cosmochim. Acta, 64, 2751-2763, 2000.

Antonelli, C., Provansal, M., and Vella, C.: Recent morphological channel changes in a deltaic environment. The case of the rhone river, france, Geomorphology, 57, 385-402, 10.1016/s0169-555x(03)00167-3, 2004.

Archer, D., and Devol, A.: Benthic oxygen fluxes on the washington shelf and slope - a comparison of *in situ* microelectrode and chamber flux measurements, Limnol. Oceanogr., 37, 614-629, 1992.

Berner, R. A.: Stoichiometric models for nutrient regeneration in anoxic sediments, Limnol. Oceanogr., 22, 781-786, 1977.

Berner, R. A.: Early diagenesis: A theoretical approach., Princeton series in geochemistry, edited by: Princeton, N. J., Princeton University Press, Princeton, 241 pp., 1980.

Berner, R. A.: Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over phanerozoic time, Global and Planetary Change, 75, 97-122, 1989.

Blackburn, T. H., and Lomstein, B. A.: Carbon and nitrogen mineralization in gulf of lions sediments., European Commission, 1989.

Blair, N. E., Leithold, E. L., and Aller, R. C.: From bedrock to burial: The evolution of particulate organic carbon across coupled watershed-continental margin systems, Mar. Chem., 92, 141-156, 2004.

Borges, A. V., Schiettecatte, L. S., Abril, G., Delille, B., and Gazeau, E.: Carbon dioxide in european coastal waters, Estuar. Coast. Shelf Sci., 70, 375-387, 2006.

Bottrell, S. H., Mortimer, R. J. G., Davies, I. M., Harvey, S. M., and Krom, M. D.: Sulphur cycling in organic-rich marine sediments from a scottish fjord, Sedimentology, 56, 1159-1173, 10.1111/j.1365-3091.2008.01024.x, 2009.

Boudreau, B.: Diagenetic models and their implementation: Modelling transport and reactions in aquatic

sediments., Springer, 414 pp., 1997.

Boudreau, B. P.: Mathematics of tracer mixing in sediments .1. Spatially-dependent, diffusive mixing, Am. J. Sci., 286, 161-198, 1986.

Burdige, D. J.: Burial of terrestrial organic matter in marine sediments: A re-assessment, Glob. Biogeochem. Cycle, 19, 2005.

Buscail, R., Pocklington, R., and Germain, C.: Seasonal variability of the organic-matter in a sedimentary coastal environment - sources, degradation and accumulation (continental-shelf of the gulf-of-lions, northwestern mediterranean-sea), Cont. Shelf Res., 15, 843-869, 1995.

Canfield, D. E., Jorgensen, B. B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N. B., Thamdrup, B., Hansen, J. W., Nielsen, L. P., and Hall, P. O. J.: Pathways of organic-carbon oxidation in 3 continental-margin sediments, Mar. Geol., 113, 27-40, 1993a.

Canfield, D. E., Jørgensen, B. B., Fossing, H., Glud, R., Gundersen, J., Ramsing, N. B., Thamdrup, B., Hansen, J. W., Nielsen, L. P., and Hall, P. O. J.: Pathways of organic carbon oxidation in three continental margin sediments, Mar. Geol., 113, 27-40, 1993b.

Canfield, D. E., Thamdrup, B., and Hansen, J. W.: The anaerobic degradation of organic-matter in danish coastal sediments - iron reduction, manganese reduction, and sulfate reduction, Geochim. Cosmochim. Acta, 57, 3867-3883, 1993c.

Cathalot, C., Rabouille, C., Pastor, L., Deflandre, B., Viollier, E., Buscail, R., Treignier, C., and Pruski, A.: Seasonal dynamics of carbon recycling in coastal sediments influenced by rivers: Assessing the impact of flood inputs in the rhône river prodelta., Biogeosciences, submitted.

Charmasson, S., Bouisset, P., Radakovitch, O., Pruchon, A. S., and Arnaud, M.: Long-core profiles of cs-137, cs-134, co-60 and pb-210 in sediment near the rhone river (northwestern mediterranean sea), Estuaries, 21, 367-378, 1998.

Copin-Montegut, C.: Alkalinity and carbon budgets in the mediterranean sea, Glob. Biogeochem. Cycle, 7, 915-925, 1993.

De Madron, X. D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J. C., Radakovitch, O., Giresse, P., Buscail, R., and Kerherve, P.: Particulate matter and organic carbon budgets for the gulf of lions (nw mediterranean), Oceanol. Acta, 23, 717-730, 2000.

Denis, L., Grenz, C., Alliot, E., and Rodier, M.: Temporal variability in dissolved inorganic nitrogen fluxes at the sediment-water interface and related annual budget on a continental shelf (nw mediterranean), Oceanol. Acta, 24, 85-97, 2001.

Denis, L., and Grenz, C.: Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the gulf of lions (nw mediterranean), Oceanol. Acta, 26, 373-389, 2003.

Epping, E., van der Zee, C., Soetaert, K., and Helder, W.: On the oxidation and burial of organic carbon in sediments of the iberian margin and nazare canyon (ne atlantic), Progress In Oceanography, 52, 399-431, 2002.

Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V.: Early oxidation of organic-matter in pelagic sediments of the eastern equatorial atlantic - suboxic diagenesis, Geochim. Cosmochim. Acta, 43, 1075-1090, 1979.

Galy, V., France-Lanord, C., Beyssac, O., Faure, P., Kudrass, H., and Palhol, F.: Efficient organic carbon burial in the bengal fan sustained by the himalayan erosional system, Nature, 450, 407-U406, 2007.

Gatti, J., Petrenko, A., Devenon, J.-L., Leredde, Y., and Ulses, C.: The rhone river dilution zone present in the northeastern shelf of the gulf of lion in december 2003, Cont. Shelf Res., 26, 1794-1805, 2006.

Glud, R. N., Risgaard-Petersen, N., Thamdrup, B., Fossing, H., and Rysgaard, S.: Benthic carbon mineralization in a high-arctic sound (young sound, ne greenland), Mar. Ecol.-Prog. Ser., 206, 59-71, 2000.

Grasshoff, K., Ehrhardt, M., and Kremling, K.: Methods of seawater analysis, 419, 1983.

Haese, R. R., Schramm, J., van der Loeff, M. M. R., and Schulz, H. D.: A comparative study of iron and manganese diagenesis in continental slope and deep sea basin sediments off uruguay (sw atlantic), International Journal of Earth Sciences, 88, 619-629, 2000.

Hall, P. O., and Aller, R. C.: Rapid, small-volume, flow injection analysis for sco_2 and nh_4^+ in marine and freshwaters, Limnol. Oceanogr., 37, 1113-1119, 1992.

Hargrave, B. T., and Phillips, G. A.: Decay times of organic-carbon in sedimented detritus in a macrotidal estuary, Mar. Ecol.-Prog. Ser., 56, 271-279, 1989.

Hedges, J. I., and Keil, R. G.: Sedimentary organic-matter preservation - an assessment and speculative synthesis, Mar. Chem., 49, 81-115, 1995.

Hedges, J. I., Keil, R. G., and Benner, R.: What happens to terrestrial organic matter in the ocean?, Organic Geochemistry, 27, 195-212, 1997.

Helder, W.: Early diagenesis and sediment–water exchange in the golfe du lion., European Commission, 1989.

Herman, P. M. J., Soetaert, K., Middelburg, J. J., Heip, C., Lohse, L., Epping, E., Helder, W., Antia, A. N., and Peinert, R.: The seafloor as the ultimate sediment trap-using sediment properties to constrain benthic-pelagic exchange processes at the goban spur, Deep-Sea Research Part Ii-Topical Studies In Oceanography, 48, 3245-3264, 2001.

Heussner, S., Cherry, R. D., and Heyraud, M.: 210po,210pb in sediment trap particles on a mediterranean continental margin, Cont. Shelf Res., 10, 989-1004, 1990.

Huertadiaz, M. A., and Morse, J. W.: A quantitative method for determination of trace-metal concentrations in sedimentary pyrite, Mar. Chem., 29, 119-144, 1990.

Huertadiaz, M. A., and Morse, J. W.: Pyritization of trace metals in anoxic marine sediments, Geochim. Cosmochim. Acta, 56, 2681-2702, 1992.

Hulth, S., Blackburn, T. H., and Hall, P. O. J.: Arctic sediments (svalbard) - consumption and microdistribution of oxygen, Mar. Chem., 46, 293-316, 1994.

Hulth, S., Tengberg, A., Landen, A., and Hall, P. O. J.: Mineralization and burial of organic carbon in sediments of the southern weddell sea (antarctica), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 44, 955-981, 1997.

Kasih, G. A. A., Chiba, S., Yamagata, Y., Shimizu, Y., and Haraguchi, K.: Numerical model on the material circulation for coastal sediment in ago bay, japan, Journal of Marine Systems, 77, 45-60, 10.1016/j.jmarsys.2008.11.006, 2009.

Kostka, J. E., and Luther, G. W.: Partitioning and speciation of solid phase iron in salt-marsh sediments, Geochim. Cosmochim. Acta, 58, 1701-1710, 1994.

Lansard, B., Rabouille, C., Denis, L., and Grenz, C.: In situ oxygen uptake rates by coastal sediments under the influence of the rhone river (nw mediterranean sea), Symposium on

Coastal Ecosystem Responses to Changing Nutrient Inputs from Large Temperate and Sub-Tropical Rivers, Fujian, PEOPLES R CHINA, 2005, ISI:000257620200012, 1501-1510,

Lansard, B., Rabouille, C., Denis, L., and Grenz, C.: Benthic remineralization at the land-ocean interface: A case study of the rhone river (nw mediterranean sea), Estuar. Coast. Shelf Sci., 81, 544-554, 10.1016/j.ecss.2008.11.025, 2009.

McKee, B. A., Aller, R. C., Allison, M. A., Bianchi, T. S., and Kineke, G. C.: Transport and transformation of dissolved and particulate materials on continental margins influenced by major rivers: Benthic boundary layer and seabed processes, Cont. Shelf Res., 24, 899-926, 2004.

Middelburg, J. J., Soetaert, K., and Herman, P. M. J.: Empirical relationships for use in global diagenetic models, Deep-Sea Res. Part I-Oceanogr. Res. Pap., 44, 327-344, 1997.

Miralles, J., Radakovitch, O., and Aloisi, J. C.: Pb-210 sedimentation rates from the northwestern mediterranean margin, Mar. Geol., 216, 155-167, 2005.

Monaco, A., Biscaye, P., Soyer, J., Pocklington, R., and Heussner, S.: Particle fluxes and ecosystem response on a continental margin: The 1985-1988 mediterranean ecomarge experiment, Cont. Shelf Res., 10, 809-839, 1990.

Monaco, A., de Madron, X. D., Radakovitch, O., Heussner, S., and Carbonne, J.: Origin and variability of downward biogeochemical fluxes on the rhone continental margin (nw mediterranean), Deep-Sea Res. Part I-Oceanogr. Res. Pap., 46, 1483-1511, 1999.

Morse, J. W., and Rowe, G. T.: Benthic biogeochemistry beneath the mississippi river plume, Estuaries, 22, 206-214, 1999.

Naudin, J. J., and Cauwet, G.: Transfer mechanisms and biogeochemical implications in the bottom nepheloid layer. A case study of the coastal zone off the rhone river (france), Deep-Sea Research Part Ii-Topical Studies In Oceanography, 44, 551-575, 1997.

Naudin, J. J., Cauwet, G., ChretiennotDinet, M. J., Deniaux, B., Devenon, J. L., and Pauc, H.: River discharge and wind influence upon particulate transfer at the land-ocean interaction: Case study of the rhone river plume, Estuar. Coast. Shelf Sci., 45, 303-316, 1997.

Pastor, L., Deflandre, B., Viollier, E., Cathalot, C., Metzger, E., Escoubeyrou, K., Pruski, A., Buscail, R., Grémare, A., and Rabouille, C.: Influence of the organic matter composition on benthic oxygen demand in a deltaic system: The rhône delta (nw mediterranean sea), In prep.

Pont, D., Simonnet, J. P., and Walter, A. V.: Medium-term changes in suspended sediment delivery to the ocean: Consequences of catchment heterogeneity and river management (rhone river, france), Estuar. Coast. Shelf Sci., 54, 1-18, 2002.

Rabouille, C., Denis, L., Dedieu, K., Stora, G., Lansard, B., and Grenz, C.: Oxygen demand in coastal marine sediments: Comparing in situ microelectrodes and laboratory core incubations, Journal Of Experimental Marine Biology And Ecology, 285, 49-69, 2003.

Radakovitch, O., Charmasson, S., Arnaud, M., and Bouisset, P.: Pb-210 and caesium accumulation in the rhone delta sediments, Estuar. Coast. Shelf Sci., 48, 77-92, 1999.

Radakovitch, O., Roussiez, V., Ollivier, P., Ludwig, W., Grenz, C., and Probst, J. L.: Input of particulate heavy metals from rivers and associated sedimentary deposits on the gulf of lion continental shelf, Estuar. Coast. Shelf Sci., 77, 285-295, 10.1016/j.ecss.2007.09.028, 2008.

Raiswell, R., Canfield, D. E., and Berner, R. A.: A comparison of iron extraction methods for the determination of degree of pyritisation and the recognition of iron-limited pyrite formation, Chemical Geology, 111, 101-110, 1994.

Rapin, F., Tessier, A., Campbell, P. G. C., and Carignan, R.: Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure, Environmental Science & Technology, 20, 836-840, 1986.

Rasmussen, H., and Jorgensen, B. B.: Microelectrode studies of seasonal oxygen-uptake in a coastal sediment - role of molecular diffusion, Mar. Ecol.-Prog. Ser., 81, 289-303, 1992.

Revsbech, N. P.: An oxygen microsensor with a guard cathode, Limnol. Oceanogr., 34, 474-478, 1989.

Rosenberg, R., Nilsson, H. C., Gremare, A., and Amouroux, J. M.: Effects of demersal trawling on marine sedimentary habitats analysed by sediment profile imagery, Journal of Experimental Marine Biology and Ecology, 285, 465-477, 10.1016/s0022-0981(02)00577-4, 2003.

Roussiez, V., Aloisi, J. C., Monaco, A., and Ludwig, W.: Early muddy deposits along the gulf of lions shoreline: A key for a better understanding of land-to-sea transfer of sediments and associated pollutant fluxes, Mar. Geol., 222, 345-358, 2005.

Sempere, R., Charriere, B., Van Wambeke, F., and Cauwet, G.: Carbon inputs of the rhone river to the mediterranean sea: Biogeochemical implications, Glob. Biogeochem. Cycle, 14, 669-681, 2000.

Smith, S. V., and Hollibaugh, J. T.: Coastal metabolism and the oceanic organic-carbon balance, Reviews Of Geophysics, 31, 75-89, 1993.

Soetaert, K., Herman, P. M. J., and Middelburg, J. J.: A model of early diagenetic processes from the shelf to abyssal depths, Geochim. Cosmochim. Acta, 60, 1019-1040, 1996a.

Soetaert, K., Herman, P. M. J., and Middelburg, J. J.: Dynamic response of deep-sea sediments to seasonal variations: A model, Limnol. Oceanogr., 41, 1651-1668, 1996b.

Ståhl, H.: Carbon cycling in deep-sea and contrasting continental margin sediments., PhD, Department of Marine Ecology ; Institutionen för marin ekologi, Göteborg University, Göteborg, 2001.

Tesi, T., Miserocchi, S., Goni, M. A., and Langone, L.: Source, transport and fate of terrestrial organic carbon on the western mediterranean sea, gulf of lions, france, Mar. Chem., 105, 101-117, 2007.

Ulses, C., Estournel, C., de Madron, X. D., and Palanques, A.: Suspended sediment transport in the gulf of lions (nw mediterranean): Impact of extreme storms and floods, Cont. Shelf Res., 28, 2048-2070, 10.1016/j.csr.2008.01.015, 2008.

van der Zee, C., van Raaphorst, W., and Epping, E.: Absorbed mn2+ and mn redox cycling in iberian continental margin sediments (northeast atlantic ocean), Journal of Marine Research, 59, 133-166, 2001.

Wang, X. C., Sun, M. Y., and Lil, A. C.: Contrasting chemical and isotopic compositions of organic matter in changjiang (yangtze river) estuarine and east china sea shelf sediments, Journal of Oceanography, 64, 311-321, 2008.

Westrich, J. T., and Berner, R. A.: The role of sedimentary organic matter in bacterial sulfate reduction - the g model tested, Limnol. Oceanogr., 29, 236-249, 1984.

Zuo, Z., Eisma, D., Gieles, R., and Beks, J.: Accumulation rates and sediment deposition in the northwestern mediterranean, Deep-Sea Research Part Ii-Topical Studies In Oceanography, 44, 597-609, 1997.

Zuo, Z. Z., Eisma, D., and Berger, G. W.: Determination of sediment accumulation and mixing rates in the gulf of lions, mediterranean-sea, Oceanol. Acta, 14, 253-262, 1991.

CHAPITRE 6. SYNTHESE ET CONCLUSION : ASSESSING PARTICULATE ORGANIC CARBON BUDGETS IN THE RHONE RIVER DELTA UNDER DIFFERENT HYDROLOGICAL CONDITIONS

6.1 ABSTRACT

A compilation of recent results from the French national CHACCRA program was performed to investigate the transport and fate of particulate organic carbon (POC) in the Rhône River delta.

Sedimentological and geochemical properties of stations studied during the program were used to define sub-units.POC fluxes through each of these compartments were assessed with the completion of a newly achieved data set and a literature review. Globally, POC fluxes highlight the major role played by the Rhône River, its terrestrial inputs and their massive storage near the outlet, in the local carbon cycle. Indeed, considering the known input and output terms, budgets of POC in the delta are proposed for two hydrologically contrasted years: 2008 with two annual floods, and 2007 with no remarkable flood event. Inputs terms were thus river supply, atmospheric deposition and primary production, whereas outputs were sediment burial, advective export on the slope and POC degradation in the water column and at the sediment–water interface. In 2007, the POC budget was slightly in deficit, whereas in 2008 a significant surplus POC was observed. The 2008 excess in the budget represent around 40% of the riverine discharge, and could have been buried during the large flood such as the one in June 2008. It may also have contributed to export off the shelf during storms which generated resuspension.

These results raise the question of the steady-state of river-dominated systems, the pertinence of carbon budget assessment at a yearly time-scale in this environment, especially in a world affected by climate-change with expected changes in river supply.

6.2 INTRODUCTION

Chapter 7 of the last IPCC report demonstrated the importance of biogeochemical cycles in the global climate system. As nonlinear interactions between the climate and biogeochemical systems could amplify (positive feedbacks) or attenuate (negative feedbacks) the disturbances produced by human activities, IPCC highlighted the need of a good assessment of carbon cycle both at global and regional scale to feed climate models. They pointed out that just under 1 GtC yr^{-1} of carbon is transported from the land to the oceans via rivers either dissolved or as suspended particles. Indeed, river-dominated margins are critical buffer regions between land and open ocean (Denman *et al.*, 2007). Nutrient inputs from land sustain high biological productivity of the coastal waters and the terrigenous inputs of particulate organic matter make these areas high organic matter deposition centres. In addition to this deposition, subsequent physical processes can occur and export organic matter further away or out the continental shelf. Accurate carbon budgets in these river-dominated margins is therefore of critical importance to improve biogeochemical cycles representation in climate models and develop budgets at the world scale (Thomas *et al.*, 2005).

The objective of this paper is to estimate the recent deposition and export of particulate organic carbon (POC) in the Rhône River continental margin. It further aims at POC budgets by considering the delta as a single box system. These budgets use river supply, atmospheric deposition and primary production as inputs, and the sediment deposition, as well as degradation and advective transport of matter on the shelf as outputs. Input and output terms were estimated from the integrated work of the CHACCRA program: recent studies allowed up-to-date estimates of carbon budget of different compartments of the Rhône River prodelta. New data were compared with previous estimates to asses their reliability and missing information was gained through existing sedimentological and particle flux data.

On the basis of Durrieu De Madron *et al.* (2000) who studied the transport and fate of particulate matter in the entire Gulf of Lions, we only focused on the Rhône River delta (proximal and distal parts) and defined units based on our sampling stations network. Characteristics of these units were outlined in Pastor *et al*, *In prep.* and Cathalot *et al* (Chapitre 5) for sedimentary and water column properties and their respective production and degradation rates. We tried to assess accurately the production and degradation term in each compartments to evaluate directly the downward fluxes. Few previous studies estimated the degradation in the whole water column off the Rhône River, focusing more either on the surface 3 top meters and the plume, or the intermediate water column off the shelf (Lefevre *et* *al.*, 1997). The advective export of total POC from the delta to the adjacent shelf was determined from bathymetric and numerical studies of sediment distribution in the delta area. Some additional missing terms and the system stationary state need to be discussed to reach balanced budgets.

In this paper, we define the delta units considered. We then describe the sedimentary POC inputs and outputs, i.e. burial and degradation at the sediment/water interface and in the water column. Finally, we discusse the balance POC budgets in the Rhône River delta under two contrasted discharge rates conditions and their corresponding advective export term.

6.3 SEDIMENTOLOGICAL AND GEOCHEMICAL PROPERTIES OF RHONE RIVER DELTA

6.3.1 Organic carbon

Organic Carbon (OC) content of surficial sediments in the Rhône River prodelta has been extensively studied and, under normal flow discharge rates, show a stable distribution pattern (Cathalot *et al.*, submitted; Lansard *et al.*, 2009; Tesi *et al.*, 2007) . OC content used in this study are the one reported by Cathalot *et al.* (submitted) and measured during the same period (April 07) in the prodelta: they ranged from 0.99 % to 1.99% d.w and decreased exponentially with distance from the river outlet. Stations far away from the river outlet (C, F, I, J) displayed a homogeneous and stable OC content of 1.03 ± 0.08 %. Stations close to the river outlet showed higher content around 1.5 – 2%, station A being the more enriched.

6.3.2 Grain size and porosity

Mean diameter and grain size values reported by Cathalot *et al*, *In prep.*, and Bourgeois *et al*, *In prep.* showed fine grain muddy sediment all over the prodelta with a dominant <63 μm fraction. This is consistent with previous observations from De Madron *et al.* (2000) et Tesi *et al.* (2007).

At all stations, porosity decreases gradually with depth from 0.85 – 0.9 for the top 2 mm to a value ranging around 0.6 – 0.7 at 30 cm (Pastor *et al.*, In prep.-a; Reimers *et al.*, 1992).We therefore considered a porosity of 0.6 for mass accumulation rates calculation.

According to the model results, all OC degradable fractions have been removed at this depth: the buried flux can thus be calculated using the sedimentation rate, the porosity and the OC content at this depth.

6.3.3 Mass accumulation rates

(De Madron *et al.*, 2000) compiled and mapped all the available mass accumulation rates in the Gulf of Lions. Mass accumulation rates were calculated from linear sedimentation rates derived from ^{210}Pb or ^{137}Cs core profiles.

The highest mass accumulation rates were recorded near the river and ranged from a few centimetres per year up to 50 cm y^{-1} (Charmasson *et al.*, 1998). Therefore, considering the wide range of sedimentation rates in the area and in an attempt to stay consistent with the work of (Pastor *et al.*, In prep.-b), we estimated sedimentations rates to be 10 cm y^{-1} at station A (located 1.9 km off the river mouth), 2 cm y^{-1} at station B (3 km) and 1 cm y^{-1} at station K, L and N (respectively, 3.3, 4.0 and 5.5 km) (Charmasson *et al.*, 1998; De Madron *et al.*, 2000; Radakovitch *et al.*, 1999a; Zuo *et al.*, 1997). As our “off-shore” stations mostly represent the distal Rhône river prodelta described by (De Madron *et al.*, 2000), we considered values between 0.1 and 0.5 cm y^{-1} further away in the prodelta (stations C, I, J).

6.3.4 Sedimentary units

De Madron *et al.*, 2000 defined the Rhône River delta in two proximal and distal zones with respective areas of 10 and 600 km². Based on the work of Cathalot *et al* (Chapitre 5) and Pastor *et al*, In Prep, we were able to define a denser stations network in the prodelta with accurate sedimentological parameters. From these stations, we generated Thiessen’s polygons spatial interpolation through an R algorithm: indeed, Thiessen polygons’ boundaries define the area that is closest to each point relative to all other points. We were thus able to associate an effective area to each station and to split the prodelta into separate units (Figure 1). These units are referred by the letters of their corresponding station and their characteristics reported in Table 1. The total area covered was 610 km². Still in a concern of consistency with work of Cathalot *et al* (Chapitre 4), we redefined the vocabulary and designated prodelta as the zone which receives the Rhône River inputs, i.e. the area with accumulation rates ≥ 1 cm y^{-1} which represents an area of 83 km² around the river outlet. We refer to the remaining area as the adjacent continental shelf.

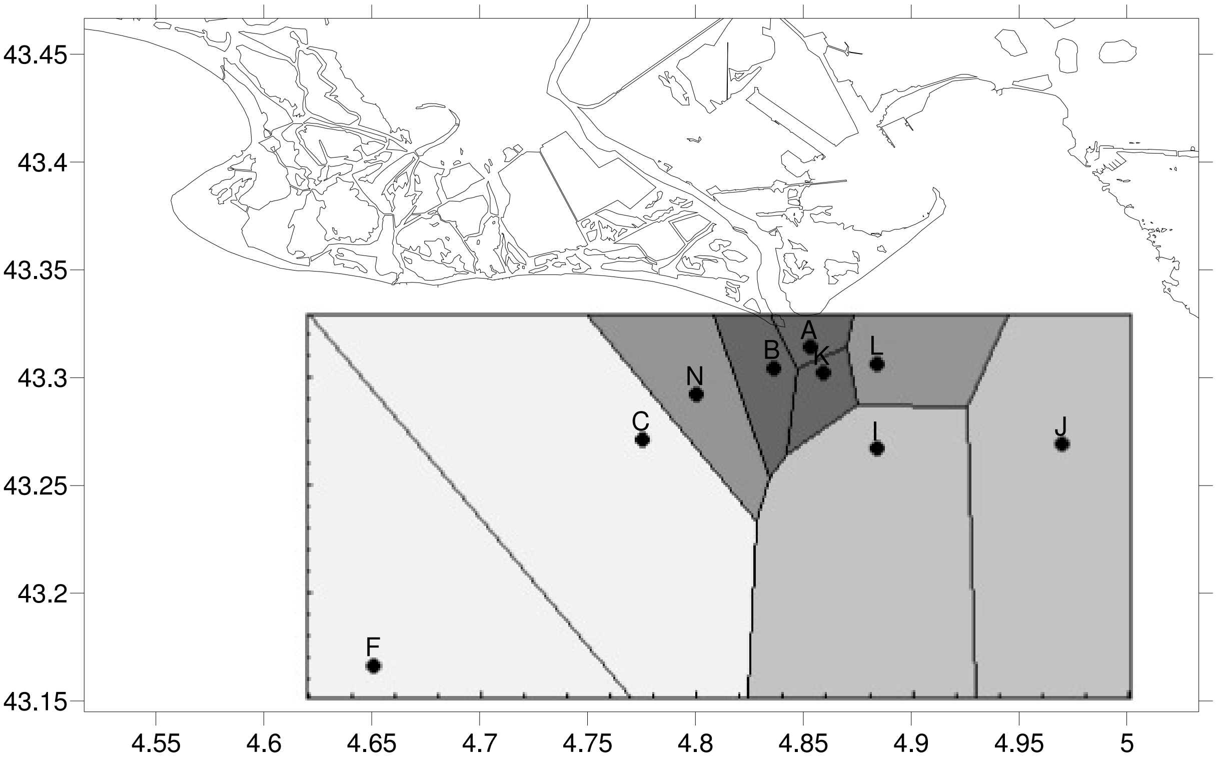

Figure 1. Sedimentary units defined from Thiessen's polygons method.

6.3.5 Error estimation

An important feature in budget assessment is the uncertainty estimate, which ensures the reliability of the conclusions drawn from the budget balance. Therefore, for each unit defined, such as for the integration over the whole Rhône River prodelta, calculate the associated error to each term is crucial.

When no statistical information on the measurements or error estimates were available, the uncertainty on data was arbitrarily fixed to cover most of the range of known or supposed mean values. The confidence interval of composed variables was then calculated by considering the 'worst-case' combination. Its upper limit was calculated by maximizing the input terms and their derived terms, while minimizing the output terms, and vice versa for the lower limit.

As budget evaluation implies calculations upon budget components, fluxes, summing or subtracting terms together, the errors have been propagated using the formula:

$$X = (\sum_i x_i^2)^{\frac{1}{2}}$$

Where X denotes the final combined error and x the partial errors of the i budget terms considered.

6.4 SEDIMENTARY AND ADVECTIVE OUTPUT OF POC

We considered each unit as being uniform and homogeneous. We thus applied the properties of the station to its dependent unit, extrapolated and integrated their values, along with their uncertainties, over the whole unit surface. Therefore for each parameter, the sum of all units gave us an estimate of the average value over the Rhône River prodelta and the adjacent shelf area.

6.4.1 Sedimentary sink

The annual organic carbon accumulation was estimated for the different sedimentary units by the relation: $buried\ \ flux = \omega(1-\phi)\rho * A * \%OC$, where:

ω = sedimentation rate
ϕ = porosity
ρ = sediment dry density (2.65 g cm-3)
A = Surface area of the unit
%OC = Organic Carbon content, for each unit respectively.

The total OC accumulation in the prodelta is about **3.5 ± 0.8 10^4 T y^{-1}**.

This is in the lower range of the previous estimate of POC deposition in the Rhône River prodelta by De Madron *et al.* (2000) around 10.9 ± 6.2 10^4 T y^{-1}. This comes from their definition of the proximal Rhône River delta: they consider an area of 10 km² receiving the riverine inputs with associated deposition rates of 40 gC m^{-2} y^{-1}, corresponding to sedimentation rates of 30 cm y-1. Our accumulation area was more narrow (5 km²) and we only considered sedimentation rates up to 10 cm y^{-1}: indeed we took an intermediate value between estimates from ^{137}Cs profiles (Radakovitch *et al*, 1999) corresponding to maximum rates and values from ^{210}Pb (Zuo *et al*, 1997) which reflect a decadal scale and maybe underestimated at the temporal scale needed for this study.

6.4.2 Degradation at the sediment-water interface

Lansard *et al.* (2009) tried to assess the total carbon oxidation in the Rhône River prodelta based on their Total Oxygen Uptake measurements: brought back to our study area, it leads to a carbon degradation in prodelta sediment of 4.2 ± 0.9 10^4 tC y^{-1}. Similarly, previous studies measured DOU rates in this site and found values of 20 mmolO_2 m^2 d^{-1} (Lansard *et al*, 2008; 2009), 11 mmolO_2 m^2 d^{-1} (Blackburn and Lomstein, 1989; Denis and Grenz, 2003). Helder (1989) also measured organic carbon mineralization rates by different electron acceptors and estimated it to be 5.2 mmolC m^2 d^{-1} i.e. 1.4 10^4 tC y^{-1} for our whole study site.

Pastor *et al*, *In prep.* evaluated the total carbon degradation in the prodelta sediments under normal flow rates conditions (April 07, Q = 825 ± 127 m^3 s^{-1}) . Using OMEXDIA, we modelled sedimentary early diagenetic processes including oxic and anoxic mineralization (Soetaert *et al.*, 1996). Based on Diffusive Oxygen Uptake rates measurements by Cathalot *et al* (submitted) and sediment pore-waters content analysis, they determined the amount of organic carbon mineralized in the sedimentary column: the mineralization rates ranged from 25 gC m^{-2} y^{-1} “out” of the Rhône River influence to 450 gC m^{-2} y^{-1} near the river outlet. Since *in situ* DOU rates were a critical parameter for the model calibration, we considered the same variation coefficient (C.V.) for carbon mineralization than diffusive sediment oxygen uptake rates to estimate the associated error. Integrated over the whole prodelta, we therefore estimated a total degraded carbon of **3.0 ± 0.4 10^4 tC y^{-1}**, consistently with the previous estimates.

6.4.3 Advective export to the continental shelf and the open ocean

Based on bathymetric surveys, Maillet *et al.* (2006) studied the sedimentation distribution dynamics in the Rhône River delta, and, in particular, assessed changes and effects of an important flood. They concluded that the delta area acts as a trap for fluvial inputs, exporting only around 10% of the riverine material. A numerical study confirmed this assessment: a large part of river inputs is stored on the shelf (~ 90%), mostly in the Rhone prodelta (Ulses *et al.*, 2008). Therefore, we assumed that 10% of the Rhône River inputs are exported out of the delta. The relative uncertainty on these estimates is assumed to be about 50 %.

Table 1. Properties of the defined units (sediment and water column).

Cruise	Unit	Area (km²)	Station coordinates		Distance (km)	Water depth (m)	T (°C)	[O$_2$] (µM)	OC (%)	[POC] (µgC l^{-1})
			Long. (°N)	Lat. (°N)						
April 07	A	**5.64**	43° 18' 47"	4° 51' 4"	1.9	24	14.9	259	1.99	262.50
	B	**14.89**	43° 18' 14"	4° 50' 4"	3.0	54	14.6	249	1.61	212.82
	C	**176.30**	43° 16' 17"	4° 46' 33"	8.6	76	14.5	243	1.25	167.04
	F	**121.40**	43° 10' 1"	4° 41' 59"	21.6	78	14.2	257	1.43	144.76
	I	**115.34**	43° 16' 0"	4° 53' 1"	7.7	89	15.1	231	1.03	159.85
	J	**114.59**	43° 16' 7"	4° 58' 6"	12.1	86	14.1	243	0.99	72.86
	K	**8.34**	43° 18' 7"	4° 51' 29"	3.3	62	14.6	249	1.79	174.42
	L	**24.33**	43° 18' 24"	4° 52' 59"	4.0	62	14.3	247	1.51	218.35
	N	**29.40**	43° 17' 33"	4° 47' 59"	5.5	67	14.5	253	1.43	152.07

6.5 INPUTS OF POC TO THE PRODELTA WATER COLUMN

Inputs of POC to the Rhône River prodelta come from primary production, river discharge and atmospheric deposition.

6.5.1 Primary production

Pujo-Pay *et al.* (2006 estimated primary production in the Rhône River plume during 4 cruises from April 2008 to April 2009, and found values between 90 and 400 mgC m^{-2} d^{-1}. This is consistent with various previous values. Leveau *et al.* (1990) found maximum primary production rates of 20 µgC l^{-1} h^{-1} within the first 5 m of the water column at the outlet of the river (depth: 27m i.e. really close to our station A), and about 50 µg l^{-1} h^{-1} in the first ten meters of the water column for stations located further offshore (corresponding to our stations F, I, J).

In an attempt to review all existing production and respiration data in the Gulf of Lions, Lefevre *et al.* (1997) estimated primary production in the Rhône River plume in June 1983 to be around 1-5 mgC m^{-3} d^{-1}, leading to 10 – 50 mgC m^{-2} d^{-1} when integrating the production on 10m. In spring 1990 values in our study area mostly range between 50 and 240 mgC m^{-2} d^{-1}.

Sempere *et al.* (2000) considered a mean value of primary production in the Rhône River dilution area of 408 mgC m^{-2} d^{-1}. We therefore assumed a primary production between 50 and 400 mgC m^{-2} d^{-1} on the total surface of the Rhône River prodelta, which lead to a total production of 1.1 – 8.9 10^4 tC y^{-1} *i.e.* **5.0 ± 3.9 10^4 tC y^{-1}**. This wide range is to be related to variations in river discharge rates and local hydrodynamics: high nutrient inputs associated to stratification enhanced local production, while heavy particulate matter discharges inhibit it by light-limiting the water column and creating strong turbulences.

6.5.2 The Rhône River inputs

Extensive water discharge data for the Rhône River are available from the Compagnie Nationale du Rhône. Particulate organic carbon concentrations were measured all year through in 2007 and 2008: the few daily data missing (9% of total) were filled in by the mean between the previous and following available data. No flood occurred during 2007 and the Rhône River brought **4.9 10^4 tC**, whereas the riverine inputs were **19.5 10^4 tC** in 2008 when 2 annual floods occurred in May and November. The 2008 inputs estimate is consistent with the one from Sempere *et al.* (2000) that evaluated the mean POC discharge from 1987 to 1996 to be about 19.2 ± 6.0 10^4 tC y^{-1}: the longer time scale considered takes into account discharge rates variability and flood events, not reflected by the year 2007.

6.5.3 Atmospheric inputs

(De Madron *et al.*, 2000) estimated atmospheric POC inputs in the Golfe of Lion from an 11 years measurement in Corsica (Löye-Pilot *et al*, 1992) to be about 0.3 gC m^{-2} y^{-1} for an annual particulate matter flux of 12.5 ± 7 g m^{-2} y^{-1}. More recently, Pulido-Villena *et al.* (2008) estimated a particulate matter (PM) flux between 0.3 and 2.58 g m^{-2} y^{-1} in 2006 at the Dyfamed site located between the French southern coast and Corsica. Thus, considering the same OC content (~ 2.4%), the estimate of De Madron *et al.* (2000) may be a bit overestimated. Assuming therefore the PM range given by Pulido-Villena *et al.* (2008), this leads to a POC rain over the Rhône River prodelta of 0 – 0.06 gC m^{-2} y^{-1} , which gives after integration over our study area, **0 - 0.004 10^4 tC y^{-1}** of atmospheric POC inputs, *i.e.* four orders of magnitude lower than the riverine inputs, and thus negligible.

6.6 LOSSES OF POC BY DEGRADATION

6.6.1 Degradation in the first meters of the water column and the Rhône River plume

Over a given oceanic layer, the light stimulated Gross Community Production (GCP) integrates the Gross Primary Production (~ primary production) and the production by the microbial (heterotrophic) community, whereas Dark Community Respiration (DCR) is the result of grazing, viral lysis, settling, and respiration rates. Net Community Production (NCP) is defined as the sum of the GCP and DCR, and can be regarded as equivalent to the export production, i.e. the flux of organic carbon out of the euphotic zone (Brix *et al.*, 2006). (Lefevre *et al.*, 1997) measured DCR and estimated NCP in the Gulf of Lions. In January and July 1989, NCP in the prodelta was respectively about 4 mmolO_2 m^{-3} d^{-1} and -33 mmolO_2 m^{-3} d^{-1} corresponding to 0.3 and - 0.8 10^4 tC y^{-1} when integrated on the first 10 m and taking a respiratory quotient RQ of 1. These two figures underline the high turn-over rates within the plume and the variability in both primary production and respiration within the plume, switching from an autotrophic to a heterotrophic mode. They also indicate that the POC export from the plume is not important. Using a f factor of 0.37, (Conan *et al.*, 1998b) estimated the new production in the Gulf of Lions to be around 42 -56 gC m^{-2} y^{-1}, corresponding to 2.6 – 3.4 10^4 tC y^{-1} for our study site. At the same time, an estimation of the potential new production (Conan *et al.*, 1998a) for the Rhône River of 32.2 - 40.2 10^4 tC y^{-1} was calculated for the entire gulf, which reported to the prodelta leads to a potential export production ranging between 1.8 and 2.2 10^4 tC y^{-1}. We therefore assumed a carbon export leaving the photic layer ranging between 0.3 and 3.4 10^4 tC y^{-1} in the Rhône River prodelta. This carbon export occurs in both DOC and POC form.

Moutin and Raimbault (2002) estimated POC export flux out of the photic zone at the eastern part of the Gulf of Lions: for an integrated Primary Production (PP) of 353 mgC m^{-2} d^{-1} (*i.e.* included into our values range), the POC export was 44.2 mgC m^{-2} d^{-1} which corresponds to 12.5% of the PP. This is close to the 10% estimate of De Madron *et al.* (2000). Therefore, applying this 12.5% ratio to our estimated PP values leads to 0.1 – 1.1 10^4 tC y^{-1} *i.e.* **0.6 ± 0.5 10^4 tC y^{-1}** being exported out of the photic layer in POC form in the Rhône River prodelta. Consistently with De Madron *et al.* (2000), POC represents about 33% of the total carbon export leaving the photic layer (see above).

6.6.2 Degradation in the aphotic water layer

Cathalot *et al*, *In prep.* measured DCR in bottom and intermediate water column in the Rhône River prodelta in April and September 2007: among stations, the values ranged between 1.5 and 25.0 mmolO_2 m^3 d^{-1}. As the values were not statistically different between April and September 2007, we considered them as a whole data pool representative of an average "normal flow rate" condition. Integrated over the whole area, this leads to a carbon consumption of **33.0 ± 6.3 and 51.1 ± 10.3 tC y^{-1}** respectively in the bottom and intermediate waters. This degradation term integrates bacterial respiration, zooplankton grazing. Nevertheless, previous studies reported that microbial respiration is a major component of the community respiration. Indeed, in eutrophic rivers bacteria can account for 11 to 100% of the total respiration (Warkentin *et al*, 2007, Biddanda *et al*, 2001), and in marine environments this fraction is usually around higher than 50% (Robinson *et al*, 2002; Blight *et al*, 1995; La Ferla *et al.*, 2005). For instance, Biddanda *et al.* (1994) reported microbial respiration rates in the Louisiana continental shelf to be 49% of the community respiration. In our area, Cathalot *et al*, In prep underlined the dominance of bacterial respiration during a flood in the Rhône River delta. Given the importance of microbial community, the microbial loop and the carbon degradation it induces mainly rely on DOC (Azam *et al.*, 1983). Although bacteria attached to particles can represent in the most active bacterial community in estuaries and turbid coastal environments (Crump *et al*, 1998), the fraction of community respiration corresponding to POC degradation is poorly known, and varies between 10 to 60% (Azzaro *et al*, 2006; Del Giorgio et Cole, 1998). Lefevre *et al.* (1996) estimated that POC in the aphotic layer of the North Western Mediterranean Sea can support only 20% of the overall organic matter remineralisation. We therefore apply this ratio to our Community Respiration rates: it leads to POC degradation in the bottom and intermediate waters of the Rhône River prodelta and adjacent shelf of **16.8 ± 2.4 10^4 tC y^{-1}**.

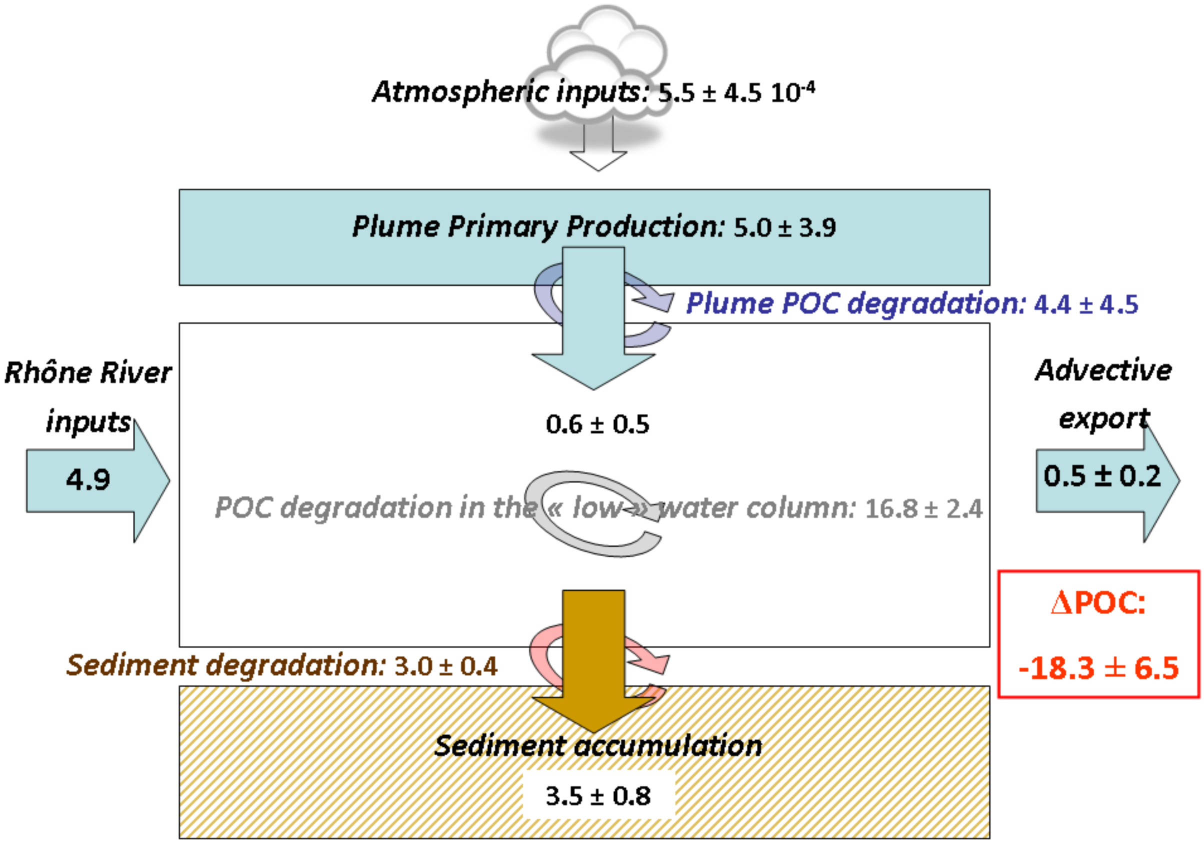

Figure 2. Annual POC budget for the Rhône river delta system during a no flood event year (2007). ΔPOC represent the unbalanced term.

6.7 POC BUDGETS IN THE RHONE RIVER DELTA

We examined the balance of POC budget in the Rhône River deltaic system for two different contrasted scenarios: 2007 year without any flood, and 2008 which experienced two annual floods. Indeed, in June 2008 a flood occurred and brought massive amount of organic carbon depleted particles (3.5 10^6 t SPM corresponding to ~ 78.5 10^3 tC over 10 days, (Cathalot *et al*, submitted) and a second one in early December 2008 brought approximately 12.6 10^3 tC in the same time but associated only with 0.5 10^6 t SPM.

6.7.1 Potential biases to be examined

As De Madron *et al.* (2000) indicated in their own budget, the question concerning the steady state of the system is to be risen, especially since the advective export term is unknown. Indeed, as presented in the description of the Rhône River input terms, on yearly time scales, the system undergoes significant natural variations. Pont *et al.* (2002) showed that, in the past century, the flow of sediment to the Rhône River delta varied as a result of river management practices (e.g. dam erection) but also of climatic shift. Short-term climatic fluctuations thus play an important role in the inter-annual variability of annual solid discharges, and thus in the variability of the major carbon inputs term.

2007 IPCC reports recounts that, based on various global climate modelling studies, "in the Mediterranean area and in central Europe in summer, where reduced mean precipitation is projected, extreme short-term precipitation may either increase (due to the increased water vapour content of a warmer atmosphere) or decrease (due to a decreased number of precipitation days, which if acting alone would also make heavy precipitation less common)." Similarly, Llanes (2008) concluded from a technical study on the future consequences of climate change on the Rhône River hydrological regimes that no straight tendency can be drawn, but more multiple ones, each single one depending on the climatic evolution at a basin or under-basin scale. Thus, even if there is still a lot of quantitative uncertainty in the changes in both mean and extreme precipitation, future changes in the Rhône River POC inputs are to be expected and therefore the carbon budgets should take into account all possibilities.

Another difficulty in this carbon budget assessment comes from the different time scales involved since physical transport processes and particulate fluxes mainly occur on a yearly scale whereas sedimentation rates are evaluated over decades from radionuclides profiles. Concerning benthic recycling in particular, Cathalot *et al.* (submitted), showed a rapid response to flood deposits of benthic mineralization activity in the sediments of the Rhône River delta: acting as a suboxic sediment reactor, they may shorten the relaxation time. At a one year scale, the degradation rate at the sediment-water interface may thus integrate already the hydrological events. In theory, budgets should be assessed for a single and homogeneous time scale among the system units. Indeed, many studies highlighted the changes in the sedimentation dynamics at the Rhône River mouth induced by a large flood event that imply several different transport and deformation processes at different temporal and spatial scales. Annual sedimentation in the deltaic area results from a complex interaction of the sediment supply from the river, the deposition from resuspension, and sediment remobilisation: a representative sedimentation rate is difficult to achieve since the time scale covered by the cores taken to measure them is variable (Charmasson *et al.*, 1998; Maillet *et* *al.*, 2006; Radakovitch *et al.*, 1999a; Radakovitch *et al.*, 1999b; Zuo *et al.*, 1997). This raises the difficulty of assessing entire carbon budgets assuming steady-state conditions.

6.7.2 Carbon budgets under various discharge rates conditions

We assessed carbon budget for two hydrologically contrasted years 2007 and 2008 (Table 2). At the annual time scale considered, POC export fluxes from the Rhône River plume, sustained by local primary production, are low: the major contributor to the Rhône River delta system appears to be the river inputs only. Therefore, one can expect the two carbon budgets to present different features.

Table 2. Interannual Budgets in Organic C Fluxes in the Rhône River delta considering respiration in bottom and intermediate waters relying on 20% on POC

Budget terms	POC fluxes 10^4 tC y^{-1}					
	2007			*2008*		
River fluxes	4.9			19.5		
atmospheric fallout	$5.5\ 10^{-4}$	±	$4.5\ 10^{-4}$	$5.5\ 10^{-4}$	±	$4.5\ 10^{-4}$
primary production	5.0	±	3.9	5.0	±	3.9
Total inputs	**9.9**	**±**	**3.9**	**24.5**	**±**	**3.9**
Sediment burial	3.5	±	0.8	3.5	±	0.8
Water sediment degradation	3.0	±	0.4	3.0	±	0.4
plume degradation	4.4	±	4.5	4.4	±	4.5
"low" water column degradation	16.8	±	2.4	16.8	±	2.4
Advective export	0.5		0.2	2.0		1.0
Total outputs	**28.2**	**±**	**5.2**	**29.6**	**±**	**5.3**
Missing balance term	***-18.3***	***±***	***6.5***	***-5.1***	***±***	***6.6***

For the year 2007, characterized by rather low Rhône River inputs since no flood event occurred, we observed a strong imbalance between the POC, originating from riverine inputs and locally produced and exported, and respiration and burial (Table 2; Figure 2). Indeed, a significant deficit in the POC export flux (defined as the difference between all of the inputs and the sum of the outputs) of -18.3 ± 6.5 10^4 tC y^{-1} was estimated. The imbalance amounts almost 4 times the Rhône River inputs. Respiration in the water column constitutes the major sink term in this budget since it represents alone 340% of the Rhône River inputs, while burial and POC degradation at the sediment-water interface represented both around 65% of the riverine inputs.

On the contrary, for the year 2008, assuming a short-term steady state, the combination of the local primary produced POC, the terrestrial POC delivered by the Rhône River and the negligible atmosphere fallout, leads to a POC input of about 24.5 ± 3.9 10^4 tC (Table 2; Figure 3). About 21.2 ± 5.1 10^4 tC of these inputs are recycled or degraded in the entire water column, 3 10^4 tC are degraded at the sediment–water interface, 3.5 ± 0.8 10^4 tC are buried in the sediment whereas 2.0 ± 1.0 10^4 tC are being exported further away on the continental shelf in the Gulf of Lions. This implies a deficit of about -5.1 ± 6.6 10^4 tC. Given the magnitude of the input and output uncertainties, the year 2008 POC budget cannot be regarded as significantly different from zero. Therefore, the 2008 results contrast sharply with results from the no-flood 2007 year and points out the prodelta as an efficient filter for river inputs: high water column respiration rates coupled to active sediment mineralization and burial minimize the off-shelf export of POC.

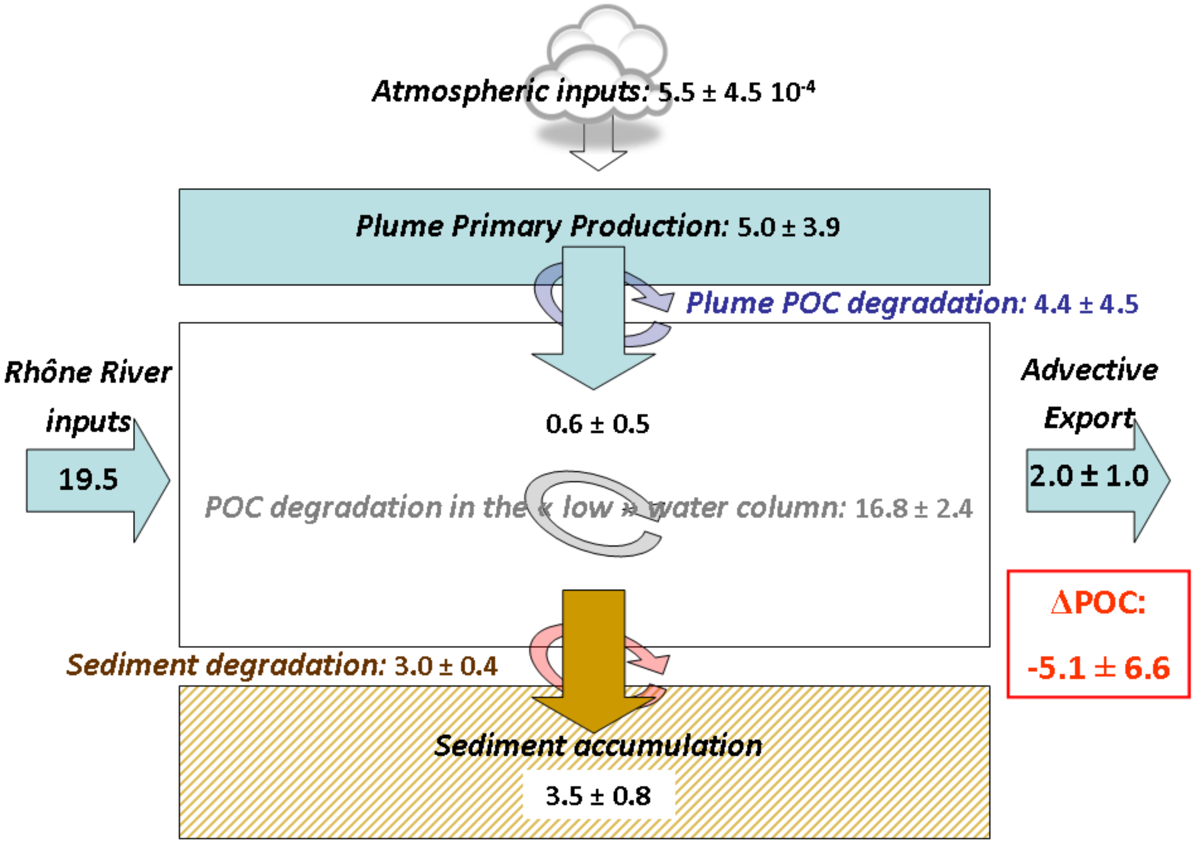

Figure 3. Annual POC budget for the Rhône river delta system for the 2008 year with two annual flood events. ΔPOC represent the unbalanced term.

6.7.3 Water column degradation: a major term of the POC budget?

Degradation of the POC in bottom and intermediate is by far the most important term in our budget. In 2008 respiration in the low water column (i.e. excluding the plume) alone represented around 86% of the Rhône River inputs, whereas the sedimentary sink (benthic mineralization + burial) theoretically corresponded to ~ 33 %. Similarly in 2007, respiration in the water column constitutes the major sink term in this budget since it represents alone 340% of the Rhône River inputs, while burial and POC degradation at the sediment-water interface represented both around 65% of the riverine inputs. These features has already been observed in other coastal environments which display similar retention and recycling capacity such as the Gulf of Riga or the Columbia estuary turning them into seasonally net heterotrophic (Crump *et al.*, 1998; Donali *et al.*, 1999).

We estimated POC degradation of being 20% of the community respiration from literature but this feature is surrounded by large uncertainties. Indeed, the microbial loop depends mainly on DOC and therefore the DOC inputs from the Rhône River (10.2 ± 0.5 10^4 tC in 2007 and 2008; data not shown from the Compagnie Nationale du Rhône) and from the Liguro-Provençal current which DOC inputs have been shown to be ca. 100 times higher (Yoro *et al.*, 1997): these inputs are enough to support the carbon demand and equilibrate the system. Heterotrophy of the system seems therefore rather unlikely. Given the high DOC fluxes involved, one could argue that it has been overestimated which could severely impact the final budget. Indeed, when this value is decreased to 10%, the budgets for 2007 and 2008 are presented in Table 3 and are -9.9 ± 6.2 10^4 tC and 7.6 ± 4.3 10^4 tC respectively. It leads therefore to a slight deficit during the no-flood 2007 year and an exporting system in 2008. Furthermore, Cathalot *et al*, (Chapitre 3) found that community respiration rates significantly decreased during an annual flood event (around 4 times lower) in June 2008. The respiration rates we applied may therefore be overestimated and may not integrate the seasonal variability of the Rhône River delta system. Since several studies pointed out an export of the Rhône River particulate material during flood events (Ferre *et al.*, 2008; Roussiez *et al.*, 2005; Ulses *et al.*, 2008), that is only reflected by the budgets calculated with POC accounting for only 10% of the community respiration, we assessed the fate of the Rhône River POC from these ones: degradation in bottom and intermediate waters is therefore assumed to represent about 170% and 43% of the Rhône River inputs, for 2007 and 2008 respectively, which is similar to the sediment system (burial + benthic mineralization). Therefore, we assume that the POC budget in the Rhône River prodelta presented a slight deficit in 2007 and a surplus in 2008. Different scenario related to hydrological changes can thus be assumed (Table 3).

Table 3. Interannual Budgets of Organic C Fluxes in the Rhône River delta considering respiration in bottom and intermediate waters relying on 10% on POC

Budget terms	POC fluxes 10^4 tC y^{-1}					
	2007			*2008*		
River fluxes	4.9			19.5		
atmospheric fallout	5.5 10^{-4}	±	4.5 10^{-4}	5.5 10^{-4}	±	4.5 10^{-4}
primary production	5.0	±	3.9	5.0	±	3.9
Total inputs	**9.9**	**±**	**3.9**	**24.5**	**±**	**3.9**
Sediment burial	3.5	±	0.8	0.0	±	0.0
Water sediment degradation	3.0	±	0.4	3.0	±	0.0
plume degradation	4.4	±	4.5	0.0	±	0.0
"low" water column degradation	8.4	±	1.2	8.4	±	1.2
Advective export	0.5		0.2	2.0		1.0
Total outputs	**19.8**	**±**	**4.8**	**13.4**	**±**	**1.5**
Missing balance term	***-9.9***	***±***	***6.2***	***11.1***	***±***	***4.2***

6.7.4 Fate of the riverine POC: two scenarios

Cathalot *et al* (Chapitre 3) evidenced the existence of a pool of resuspended shelf particles recirculating over the prodelta area: given the large reservoir pool, this old and poorly degradable shelf material may support the high respiration rates in bottom and intermediate waters observed during low discharge rates period. Therefore the slight deficit term observed in a no-flood year such as 2007 is likely to correspond to inputs of suspended particles originating from resuspension events in the adjacent shelf. Cathalot *et al* (chapitre 2) also evidenced the trapping of the Rhône River particulate material nearby the river outlet. A scenario for a low discharge rates year is thus: all riverine available organic carbon settles down quickly in the bottom, through flocculation and aggregation processes, without being remobilized and is quickly remineralized, whereas resuspension from the shelf induced by the Gulf of Lions hydrodynamic circulation feeds intermediate and bottom waters. This is consistent with previous observations and numerical studies of the sediment dispersal mechanisms in the area showing that the Rhône River delta acts as real deposit centre and that export mainly takes place through resuspension induced by wave and currents from flood and storms (Ferre *et al.*, 2008; Roussiez *et al.*, 2005; Ulses *et al.*, 2008).

The floods that occurred in 2008 brought substantial amounts of river material which, most likely, settled down and underwent various processes. Rapid deposition and efficient burial in the delta are likely to occur and may have been underestimated here since we took average values. Indeed, as stated above, sedimentation rates are highly variable and time-scale dependent, and Cathalot *et al.* (submitted)(chapitre 1) showed that the sediment of the Rhône River delta can react quickly to river inputs and act like an enhanced carbon mineralization reactor. Furthermore, Cathalot *et al.* (submitted) also showed that the layer deposited during the flood in June 2008 persisted through the fall and was buried during a lower flood in November. This certainly highlights the unstationary nature of burial in prodelta sediments which may work on a flood basis rather than on a yearly average.

Some other processes may also be involved. Strong currents or winter storms may have generated resuspension and generated the export of the flood material further away in the shelf (Roussiez *et al.*, 2005; Ulses *et al.*, 2008). Indeed, our estimate of 10% of the Rhône River inputs being exported taken is based on numeric simulations at the entire Gulf of Lion scale: it actually points towards the material exported off the shelf in the open ocean. Indeed, a proportion of resuspended material and river inputs is generally transported towards the southwestern end of the Gulf by the wind-driven cyclonic circulation (Millot, 1990; Ulses *et al.*, 2008).

As stated before, climate change will most likely result in changes in river discharge rates. Several scenarios are possible:

- More frequent extreme short-term precipitation events associated with high liquid and solid discharge rates are likely to increase deposition and burial of carbon in prodelta sediments. It may also contribute to larger export to the shelf because of unconsolidated sediments which are more prone to resuspension. This would change the features that constrain the budget: sedimentation rates, mineralization rates…
- Dryer years are likely to reduce the riverine particulate matter supply to this area, enhancing shelf particulate inputs and degradation rates in the water column, and likely shifting to a deficit system which would mineralize organic carbon rather than be a burial centre.

6.8 REFERENCES

Blackburn, T.H., Lomstein, B.A., 1989. Carbon and nitrogen mineralization in Gulf of Lions sediments. In: Martin, J.-M., Barth, H. (Eds.), EROS 2000 (European River Ocean System) Project. Water Pollution Research Report. European Commission.

Brix, H., Gruber, N., Karl, D.M., Bates, N.R., 2006. On the relationships between primary, net community, and export production in subtropical gyres. Deep Sea Research Part II: Topical Studies in Oceanography 53 (5-7), 698-717.

Cathalot, C., Rabouille, C., Pastor, L., Deflandre, B., Viollier, E., Buscail, R., Treignier, C., Pruski, A., submitted. Seasonal dynamics of carbon recycling in coastal sediments influenced by rivers: assessing the impact of flood inputs in the Rhône River prodelta. Biogeosciences.

Charmasson, S., Bouisset, P., Radakovitch, O., Pruchon, A.S., Arnaud, M., 1998. Long-core profiles of Cs-137, Cs-134, Co-60 and Pb-210 in sediment near the Rhone River (Northwestern Mediterranean Sea). Estuaries 21 (3), 367-378.

Conan, P., Pujo-Pay, M., Raimbault, P., Leveau, M., 1998a. Hydrological and biological variability in the Gulf of Lions. I. Nitrogen fluxes and potential productivity. Oceanologica Acta 21 (6), 751-765.

Conan, P., Pujo-Pay, M., Raimbault, P., Leveau, M., 1998b. Hydrological and biological variability in the Gulf of Lions. II. Productivity on the inner edge of the North Mediterranean Current. Oceanologica Acta 21 (6), 767-782.

Crump, B.C., Baross, J.A., Simenstad, C.A., 1998. Dominance of particle-attached bacteria in the Columbia River estuary, USA. Aquatic Microbial Ecology 14 (1), 7-18.

De Madron, X.D., Abassi, A., Heussner, S., Monaco, A., Aloisi, J.C., Radakovitch, O., Giresse, P., Buscail, R., Kerherve, P., 2000. Particulate matter and organic carbon budgets for the Gulf of Lions (NW Mediterranean). Oceanologica Acta 23 (6), 717-730.

Denis, L., Grenz, C., 2003. Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean). Oceanologica Acta 26 (4), 373-389.

Denman, K.L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P.M., Dickinson, R.E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., Dias, P.L.d.S., Wofsy, S.C., Zhang, X., 2007. Couplings Between Changes in the Climate System and Biogeochemistry. In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K.B., M.Tignor, Miller, H.L. (Eds.), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, United Kingdom

New York, NY, USA.

Donali, E., Olli, K., Heiskanen, A.S., Andersen, T., 1999. Carbon flow patterns in the planktonic food web of the Gulf of Riga, the Baltic Sea: a reconstruction by the inverse method. Journal of Marine Systems 23 (1-3), 251-268.

Durrieu De Madron, X., Abassi, A., Heussner, S., Monaco, A., Aloisi, J.C., Radakovitch, O., Giresse, P., Buscail, R., Kerherve, P., 2000. Particulate matter and organic carbon budgets for the Gulf of Lions (NW Mediterranean). Oceanologica Acta 23 (6), 717-730.

Ferre, B., de Madron, X.D., Estournel, C., Ulses, C., Le Corre, G., 2008. Impact of natural (waves and currents) and anthropogenic (trawl) resuspension on the export of particulate matter to the open ocean Application to the Gulf of Lion (NW Mediterranean). Continental Shelf Research 28 (15), 2071-2091.

Helder, W., 1989. Early diagenesis and sediment–water exchange in the Golfe du Lion. In: Martin, J.-M., Barth, H. (Eds.), EROS 2000 (European River Ocean System) Project. Water Pollution Research Report. European Commission.

Lansard, B., Rabouille, C., Denis, L., Grenz, C., 2009. Benthic remineralization at the land-ocean interface: A case study of the Rhone River (NW Mediterranean Sea). Estuarine Coastal and Shelf Science 81 (4), 544-554.

Lefevre, D., Minas, H.J., Minas, M., Robinson, C., Williams, P.J.L., Woodward, E.M.S., 1997. Review of gross community production, primary production, net community production and dark community respiration in the Gulf of Lions. Deep-Sea Research Part Ii-Topical Studies in Oceanography 44 (3-4), 801-&.

Leveau, M., Lochet, F., Goutx, M., Blanc, F., 1990. Effects of a plume front on the distribution of inorganic and organic matter off the Rhône River. Hydrobiologia 207, 87-93.

Llanes, A., 2008. Climate change incidence on the Rhone Ruver hydrology. AgroParisTech, Institut des sciences et industries du vivant et de l'environnement, Montpellier, p. 19.

Maillet, G.M., Vella, C., Berne, S., Friend, P.L., Amos, C.L., Fleury, T.J., Normand, A., 2006. Morphological changes and sedimentary processes induced by the December 2003 flood event at the present mouth of the Grand Rhone River (southern France). Marine Geology 234 (1-4), 159-177.

Millot, C., 1990. The Gulf Of Lions Hydrodynamics. Continental Shelf Research 10 (9-11), 885-894.

Moutin, T., Raimbault, P., 2002. Primary production, carbon export and nutrients availability in western and eastern Mediterranean Sea in early summer 1996 (MINOS cruise). Journal of Marine Systems 33, 273-288.

Pastor, L., Cathalot, C., Deflandre, B., Viollier, E., Soetaert, K., Buscail, R., Grémare, A., Ulses, C., Rabouille, C., In prep.-a. Biogeochemical processes in sediments from the Rhône River prodelta (France): A model of carbon mineralization.

Pastor, L., Deflandre, B., Viollier, E., Cathalot, C., Metzger, E., Escoubeyrou, K., Pruski, A., Buscail, R., Grémare, A., Rabouille, C., In prep.-b. Influence of the organic matter composition on benthic oxygen demand in a deltaic system: The Rhône delta (NW Mediterranean Sea).

Pont, D., Simonnet, J.P., Walter, A.V., 2002. Medium-term changes in suspended sediment delivery to the ocean: Consequences of catchment heterogeneity and river management (Rhone River, France). Estuarine Coastal and Shelf Science 54 (1), 1-18.

Pujo-Pay, M., Conan, P., Joux, F., Oriol, L., Naudin, J.J., Cauwet, G., 2006. Impact of phytoplankton and bacterial production on nutrient and DOM uptake in the Rhone river plume (NW Mediterranean). Marine Ecology-Progress Series 315, 43-54.

Pulido-Villena, E., Wagener, T., Guieu, C., 2008. Bacterial response to dust pulses in the western Mediterranean: Implications for carbon cycling in the oligotrophic ocean. Global Biogeochemical Cycles 22 (1).

Radakovitch, O., Charmasson, S., Arnaud, M., Bouisset, P., 1999a. Pb-210 and caesium accumulation in the Rhone delta sediments. Estuarine Coastal and Shelf Science 48 (1), 77-92.

Radakovitch, O., Cherry, R.D., Heussner, S., 1999b. Pb-210 and Po-210: tracers of particle transfer on the Rhone continental margin (NW Mediterranean). Deep-Sea Research Part I-Oceanographic Research Papers 46 (9), 1539-1563.

Reimers, C.E., Jahnke, R.A., McCorkle, D.C., 1992. Carbon Fluxes and Burial Rates Over The Continental Slope and Rise Off Central California with Implications for the Global Carbon Cycle. Global Biogeochem. Cycles 6.

Roussiez, V., Aloisi, J.C., Monaco, A., Ludwig, W., 2005. Early muddy deposits along the Gulf of Lions shoreline: A key for a better understanding of land-to-sea transfer of sediments and associated pollutant fluxes. Marine Geology 222, 345-358.

Sempere, R., Charriere, B., Van Wambeke, F., Cauwet, G., 2000. Carbon inputs of the Rhone River to the Mediterranean Sea: Biogeochemical implications. Global Biogeochemical Cycles 14 (2), 669-681.

Soetaert, K., Herman, P.M.J., Middelburg, J.J., 1996. A model of early diagenetic processes from the shelf to abyssal depths. Geochimica Et Cosmochimica Acta 60 (6), 1019-1040.

Tesi, T., Miserocchi, S., Goni, M.A., Langone, L., 2007. Source, transport and fate of terrestrial organic carbon on the western Mediterranean Sea, Gulf of Lions, France. Marine Chemistry 105 (1-2), 101-117.

Thomas, H., Bozec, Y., de Baar, H.J.W., Elkalay, K., Frankignoulle, M., Schiettecatte, L.S., Kattner, G., Borges, A.V., 2005. The carbon budget of the North Sea. Biogeosciences 2 (1), 87-96.

Ulses, C., Estournel, C., de Madron, X.D., Palanques, A., 2008. Suspended sediment transport in the Gulf of Lions (NW Mediterranean): Impact of extreme storms and floods. Continental Shelf Research 28 (15), 2048-2070.

Yoro, S.C., Sempere, R., Turley, C., Unanue, M.A., de Madron, X.D., Bianchi, M., 1997. Cross-slope variations of organic carbon and bacteria in the Gulf of Lions in relation to water dynamics (northwestern Mediterranean). Marine Ecology-Progress Series 161, 255-264.

Zuo, Z., Eisma, D., Gieles, R., Beks, J., 1997. Accumulation rates and sediment deposition in the northwestern Mediterranean. Deep-Sea Research Part Ii-Topical Studies in Oceanography 44 (3-4), 597-609.

CONCLUSION GÉNÉRALE

Ce travail a permis de mieux contraindre le cycle du carbone dans le prodelta du Rhône et le plateau continental adjacent en s'intéressant notamment au devenir des particules organiques du Rhône, leur modification et les processus d'export en jeu. Il a ainsi souligné l'étroite interaction entre le système sédimentaire du prodelta et la dynamique des apports rhodaniens. En effet, l'étude couplée, expérimentale et numérique, du cycle de l'oxygène et des processus diagénétiques dans les sédiments ont souligné l'intensité des processus de dégradation et d'enfouissement de la matière organique terrigène à l'immédiate embouchure. L'importance de la minéralisation anoxique dans cette zone a ainsi été mise en évidence soulignant les limites de l'étude de la seule dynamique de l'oxygène pour quantifier l'activité de dégradation de la matière organique dans les sédiments côtiers sous influence fluviale. Ce travail a ainsi caractérisé les sédiments du prodelta du Rhône comme une zone réactive d'accumulation de carbone organique d'origine terrigène.

Au-delà de l'étude du compartiment sédimentaire, l'utilisation de marqueurs isotopiques du carbone (^{13}C et ^{14}C) ont également permis d'affiner la compréhension des mécanismes particulaires dans le prodelta en révélant le lien étroit entre les conditions hydrodynamiques locale et l'export des particules rhodaniennes. Contrastant avec l'ancienne perception d'un système gouverné par le couplage apports du Rhône/production primaire et donc la dilution des deux pools terrigènes et marins (Lansard *et al.*, 2009; Tesi *et al.*, 2007), ce travail a permis de faire valoir l'importance des processus de resuspension et de recirculation du plateau continental du Golfe du Lion comme source de particules et support de la respiration dans les eaux de fond et intermédiaires pour la zone du delta rhodanien. Cette étude a ainsi montré que le rôle du Rhône comme source de carbone organique particulaire pour le plateau continental et donc potentiellement pour la mer Méditerranée est dépendant des phénomènes de crue. Les événements hydrologiques de forte intensité apportent une grande quantité de matière dont une part importante est enfouie mais pourraient également avoir pour conséquence la modification qualitative et quantitative des apports organiques particulaires du Rhône. Ceux-ci génèrent un régime transitoire dans les différents compartiments du cycle du carbone et influent sur son bilan intégré.

Ce travail réalisé dans le cadre du projet national CHACCRA (Climate and Human-induced Alterations in Carbon Cycling at the River-seA connection) est le fruit d'une collaboration avec les différents partenaires : la question de la labilité et de la dynamique des apports particulaire du Rhône adressée dans cette étude s'intègre dans un contexte plus large du projet qui prévoit la compréhension du système intégré rivière-panache-plateau.

REFERENCES

Lansard, B., Rabouille, C., Denis, L., Grenz, C., 2009. Benthic remineralization at the land-ocean interface: A case study of the Rhone River (NW Mediterranean Sea). Estuarine Coastal and Shelf Science 81 (4), 544-554.
Tesi, T., Miserocchi, S., Goni, M.A., Langone, L., 2007. Source, transport and fate of terrestrial organic carbon on the western Mediterranean Sea, Gulf of Lions, France. Marine Chemistry 105 (1-2), 101-117.

PERSPECTIVES

Ce travail de thèse, et le programme CHACCRA dans laquelle il s'intègre, contribue à améliorer notre compréhension et la quantification de la contribution des marges continentales aux bilans de carbone et des éléments associés. Cette réflexion a été initiée dès les années 1990 à l'échelle internationale par les programmes JGOFS (Joint Global Ocean Flux Study) et LOICZ (Land-Ocean Interactions in the Coastal Zone) et reprise par les programmes européens Eros (European River Ocean Systems) et français ECOMarge (ECOSystèmes de Marge continentale) et PNEC (Programme National d'Environnement Côtier). Ce travail de thèse sur le devenir des particules organiques du Rhône, et notamment la dynamique du recyclage sédimentaire qui y est associé, a ainsi apporté de nombreuses informations mais il a également soulevé de nouveaux questionnements scientifiques d'ordre fondamental : importance relative de la respiration benthique et planctonique dans les deltas, quantification des processus de précipitation des sulfures de fer dans les sédiments du prodelta du Rhône, appréhension des effets du changement climatique sur le cycle du carbone local...

En proposant un modèle calibré du recyclage sédimentaire dans le delta du Rhône, ce travail de thèse apporte sa contribution au développement d'un modèle numérique, réaliste du delta du Rhône, couplant processus biogéochimique et hydrodynamisme, finalité première du programme CHACCRA. Néanmoins l'intégration et le couplage des différents compartiments (circulation, biogéochimie dans les sédiments et la colonne d'eau) restent une étape cruciale à réaliser. Associé à de nouvelles mesures expérimentales, ce modèle numérique intégré compléterait les précédentes études du programme PNEC en quantifiant notamment, à l'échelle du plateau continental du Golfe du Lion, les exports vers la pente et donc l'impact du matériel rhodanien sur le cycle du carbone de la Mer Méditerranée.

En effet, l'utilisation de tels modèles intégrés constitue un outil puissant permettant de tester l'impact du changement climatique, au travers de la variabilité hydrologique et de la variation connexe des apports fluviaux, ce qui constitue une des problématiques centrales du Chantier Méditerranée. Dans ce contexte, il est nécessaire que de tels modèles numériques intègrent une composante transitoire permettant de décrire les processus non-stationnaires et les mécanismes de relaxation du système. En effet, bien que le modèle numérique OMEXDIA ait permis de quantifier les processus biogéochimiques majeurs participant à la dégradation de la matière organique dans les sédiments deltaïques à l'état stationnaire, la modélisation d’événements transitoires tels que les dépôts de crue permettrait de mieux quantifier la variabilité des flux de carbone au sein de ce compartiment. De plus, afin de quantifier les processus de minéralisation benthique de la matière organique, la dynamique de l’oxygène associée et de contraindre le cycle du carbone dans les sédiments côtiers influencés par les apports de rivières, à l’état stationnaire comme transitoire, il serait judicieux d’utiliser d’autres modèles décrivant plus en détails la minéralisation anoxique de la matière organique, la sulfato-réduction et le cycle des oxydes métalliques.

La qualité et les résultats de cette activité de modélisation reposent bien évidemment sur la capacité à calibrer ces modèles numériques par un jeu de données conséquent et représentatif. Un autre challenge expérimental important réside dans l’acquisition de données pendant les états transitoires qui représentent bien souvent des périodes peu propices à l’échantillonnage (crues ou étiages trop sévères). Ainsi ce travail de thèse a également servi de support à l’élaboration d’une station benthique permanente située à l’embouchure du Rhône. Cette station, équipée de microélectrodes à oxygène, réalise un suivi à haute résolution spatiale et temporelle de la dynamique de l’oxygène dans les sédiments du prodelta : un échantillonnage à haute fréquence pendant des événements temporaires permet d’acquérir un jeu de données et de comprendre la séquence diagénétique en régime transitoire.

De plus, des mesures complémentaires dans les différents compartiments permettront d’affiner les bilans en carbone et les différents mécanismes en jeu. Des mesures de respiration communautaire et bactérienne dans la colonne d’eau, la quantification des contributions respectives du POC et du DOC à la boucle bactérienne (par des incubations et suivi temporel de l’évolution des concentrations par exemple) permettraient de lever l’incertitude sur les processus de dégradation des apports particulaires du Rhône.

Devenir et impact des apports fluviaux sur les marges continentales : importance biogéochimique et environnementale du recyclage dans les sédiments du prodelta du Rhône

Résumé : L'objectif principal de ce travail était d'étudier le devenir biogéochimique du matériel organique particulaire du Rhône, et les mécanismes impliqués dans le cycle du carbone au niveau de son delta. L'utilisation de microélectrodes in situ a permis l'obtention de profils haute résolution d'oxygène dans les sédiments et l'estimation du recyclage sédimentaire. Il apparait que la variabilité saisonnière des apports rhodaniens tant qualitative que quantitative influence l'activité de minéralisation benthique dans le delta du Rhône. Cependant, l'impact de ces apports pulsés est limité dans le temps, les sédiments deltaïques constituant un centre actif de dégradation du carbone organique pérenne.

Des mesures isotopiques ($\Delta^{14}C$ et $\delta^{13}C$) ont confirmé que le prodelta en plus d'une zone prépondérante de minéralisation est le siège d'un enfouissement massif du matériel organique particulaire du Rhône. L'utilisation d'un modèle numérique stationnaire diagénétique a permis de quantifier les termes d'enfouissement et de dégradation, et souligné l'importance de la minéralisation anoxique. Un pool important de matières en suspension du plateau continental en constante recirculation alimentant le prodelta a été identifié: des particules terrigènes et marines déjà dégradées, ayant subi plusieurs cycles de déposition/resuspension, diluent les particules rhodaniennes, diminuant ainsi la labilité du matériel atteignant le sédiment. Enfin, des mesures de respiration dans la colonne d'eau ont souligné l'effet des variations du régime hydrologique du Rhône qui modifient distinctement les termes d'export de carbone du delta vers la marge continentale.

Mots clés : oxygène, minéralisation benthique, apports fluviaux, bilan carbone, océans côtiers

Fate and impact of fluvial inputs on continental margins: biogeochemical and environmental importance of the recycling in the sediments of the Rhône River prodelta

Abstract: The main purpose of this work was to study the biogeochemical fate of the Rhône River particulate organic matter, and investigate the mechanisms involved in the carbon cycle of its delta. In situ microsensors measurements allowed us to perform high resolution oxygen profiles in the sediment and estimate thus the sediment recycling. It appears that the seasonal variability of the Rhône River inputs, both in quality and in quantity, impacts the benthic mineralization activity in the Rhône River delta. Nevertheless, the influence of these pulsed inputs is limited in time: deltaic sediments are a stable centre of organic carbon degradation.

More than just a major mineralization area, isotopic analyses ($\Delta^{14}C$ and $\delta^{13}C$) showed that the prodelta also acts as a massive burial centre for organic particulate matter of the Rhône River. Using a stationary diagenetic numerical model, we were able to quantify these burial and degradation terms, and highlighted the importance of anoxic mineralization processes. Moreover, an important pool of suspended matter particles feeding the prodelta and originating from the adjacent continental shelf was identified: terrigeneous and marine particles, already degraded and that have encountered many deposition/resuspension cycles, dilute the riverine particles and decrease thus the lability of the material reaching the sea floor. Finally, respiration measurements in the water column underlined the impact of hydrological variations of the Rhône River that change distinctly the carbon export terms from the delta towards the continental margin.

Keywords: oxygen, benthic mineralization, fluvial inputs, carbon budget, coastal ocean