Métabolisme des écosystèmes côtiers : de l'échelle locale (fjord de Randers, baie de Palma et estuaire de l'Escaut) à l'échelle européenne

Thèse présentée par:

Frédéric Gazeau

en vue de l'obtention
du grade de docteur en Sciences
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Travaux co-dirigés par
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Résumé

L'océan côtier, la zone de transition entre le continent et l'océan ouvert, reçoit des apports considérables d'eau douce, de sels nutritifs ainsi que de matière organique dissoute et particulaire en provenance du continent. Ces apports font que la zone côtière est une région très active du point de vue biogéochimique. Le statut trophique de l'océan côtier, distinction entre l'autotrophie et l'hétérotrophie) est un sujet encore très discuté. L'étude présentée ici a trois objectifs: (1) de compiler et analyser une base de données bibliographique concernant la production primaire brute (GPP) et la respiration communautaire (CR) benthiques et planctoniques, mesurées par des incubations et par l'approche budgétaire Land-Ocean Interaction in the Coastal Zone (LOICZ) au niveau de la zone côtière européenne. (2) de tester différentes méthodes d'estimation du métabolisme de trois sites côtiers européens. Ces méthodes sont la méthode classique d'incubations O_2, la méthode LOICZ et d'autres méthodes en système ouvert telles que la méthode Response Surface Difference (RSD) et l'utilisation de cycles journaliers de carbone inorganique dissous et d'O_2. De plus, étant donné que l'estimation du coefficient d'échange de gaz à l'interface air-mer (*k*) est critique lors de l'utilisation de méthodes en système ouvert, ce paramètre et sa relation avec la vitesse du vent ont été étudiés dans deux des sites (Fjord de Randers et estuaire de l'Escaut). (3) d'étudier la relation existant entre les paramètres métaboliques tels que GPP ou CR dans les compartiments benthiques et planctoniques.

Plus de 190 publications ont été analysées dont 129 ont été intégrées à une base de données consultable sur Internet (http://www.obs-vlfr.fr/eurotroph/index.php). L'analyse de cette base de données a permis de mettre en avant un sévère manque mesures dans de nombreuses régions telles que le bassin Est de la mer Méditerranée, le nord de la Baltique et le nord de la mer du Nord. Une estimation de la production nette (NEP = GPP+ CR) de la zone côtière européenne n'a pas été possible dans cette étude. En effet, des estimations fiables de paramètres tels que la minéralisation de matière organique dans la colonne d'eau, la diminution de la production et respiration benthique avec la profondeur et la distribution des macrophytes, font cruellement défaut.

Les différentes méthodes testées ont fourni des résultats le plus souvent similaires, bien que chacune d'elles soit associée à une marge d'erreur significative qui limite son utilisation à des sites et conditions bien particuliers. La méthode LOICZ basée sur le phosphore inorganique dissous (DIP) n'a pu fournir un résultat réaliste dans l'estuaire de l'Escaut. Ceci est dû à un fort impact de processus abiotiques sur le flux non-conservatif de DIP, tels que l'adsorption/désorption sur ou à partir de particules en suspension et/ou du sédiment, dans ce système très turbide. Les méthodes en milieu ouvert souffrent de la difficulté d'estimer de façon fiable le coefficient d'échange de gaz à l'interface air-mer (O_2 ou CO_2). Bien qu'il ait été montré que la relation liant ce paramètre à la vitesse du vent dépendait du site étudié, la relation établie pour l'estuaire de l'Escaut n'a pu être validée en utilisant la méthode LOICZ appliquée au DIC en raison des fortes erreurs associées. Finalement, les différences significatives observées entre les estimations de GPP et CR à partir des incubations et des méthodes en système ouvert confirment les résultats de travaux antérieurs et mériteraient une attention particulière à l'avenir.

Les trois sites étudiés sont bien contrastés: du turbide et eutrophisé estuaire de l'Escaut à la baie oligotrophe dominée par les macrophyte (Palma). De relations significatives entre les paramètres métaboliques et les conditions environnementales ont été montrées. En effet, les plus fortes CR ont été mesurées dans l'Escaut tandis que la GPP y était très sévèrement limitée par la disponibilité en lumière. Les plus fortes GPP ont été mesurées dans le fjord de Randers où les concentrations en sels nutritifs ainsi que la stratification de la colonne d'eau et la faible turbidité permettent au phytoplancton en provenance de la rivière de continuer à produire dans la zone estuarienne. Tandis que l'estuaire de l'Escaut est clairement le site le plus hétérotrophe, il a été impossible de différencier les métabolismes de la baie de Palma et du fjord de Randers sur une échelle annuelle.

Abstract

The coastal zone, the transition area between land and the open ocean, receives considerable amounts of freshwater, nutrients as well as dissolved and particulate organic matter. These inputs make the coastal zone a very biogeochemically active area. The trophic status of the coastal zone, that is whether it is autotrophic or heterotrophic, is still a matter of debate. The present work had three main objectives: (1) to compile and analyse a bibliographic database of benthic and planktonic primary production (GPP) and community respiration (CR) measured by incubation methods and by the Land-Ocean Interaction in the Coastal Zone (LOICZ) budgeting approach in the European coastal zone, (2) to test different methods to estimate the functioning of three European coastal sites (Randers Fjord, Palma Bay and Scheldt Estuary). These methods are the classical O_2 incubation technique, the LOICZ budgeting procedure and other open-system techniques such as the Response Surface Difference (RSD) method and daily cycles of dissolved inorganic carbon (DIC) and O_2. Moreover, as the estimation of the gas exchange coefficient at the air-sea interface (k) is critical when applying open-system methods, this parameter and its relationship with wind speed were studied in two of the sites (Randers Fjord and Scheldt estuary) and (3) to study how the metabolic parameters such as GPP or CR both in the benthic and planktonic compartment are controlled by environmental conditions.

More than 190 papers have been analysed among which 129 were integrated in a database available on the Internet (http://www.obs-vlfr.fr/eurotroph/index.php). The analysis of the bibliographic database allowed pinpointing a severe lack of knowledge in many areas of Europe such as the Eastern Mediterranean Sea, the Northern Baltic Sea and the Northern North Sea. An assessment of the net ecosystem production (NEP = GPP + CR) of the European coastal zone was not possible based on this study. Indeed, several confident estimates of parameters such as the mineralization of organic matter in the water column, the decrease of benthic production and respiration with depth and the distribution of macrophytes are lacking.

The different methods tested during this study generally provided consistent results although each of these is associated with significant errors and uncertainties which limit their use to specific sites and conditions. Particularly, the LOICZ procedure applied to dissolved inorganic phosphorus (DIP) failed to provide a realistic estimate of the trophic status in the Scheldt estuary. This is due to a strong impact of abiotic processes such a sorption and desorption to and from suspended matter and sediments on the non-conservative DIP flux in this highly turbid system. Open-system methods suffer from the difficulty to estimate with accuracy the gas exchange coefficient. Although the relation linking this parameter to the wind speed was shown to be site-specific, the validation of thisµ relationship in the Scheldt estuary using the LOICZ approach applied to DIC was not possible due to strong associated errors and uncertainties. Finally, significant differences observed between GPP and CR estimated by incubation and open-system methods confirmed previous results and suggest that future works should focus on this matter.

The three sites investigated were well contrasted: from the nutrient-rich and turbid Scheldt estuary to the oligotrophic seagrass-dominated Bay of Palma. The metabolic parameters were well related to these environmental differences. Indeed, the highest CR rates were measured in the Scheldt estuary while GPP was strongly limited by light availability. The highest GPP was measured in the Randers Fjord where nutrient concentrations as well as water column stratification and a relatively low turbidity allowed the riverine phytoplankton to remain very active in the estuarine zone. While the Scheldt estuary was clearly the most heterotrophic site in this study, it was not possible to conclude whether the Randers Fjord or the Bay of Palma is the most productive ecosystem on an annual scale.

Plan

Chapitre 1

Introduction

L'émission de dioxyde de carbone (CO_2) par les activités humaines (utilisation de combustibles fossiles et déforestation) est à l'heure actuelle (année 2000) de 725 Tmol C an^{-1} (Sources: Houghton & Hackler 2002 ; Marland *et al.* 2003). Pour une émission de 525 Tmol C an^{-1} dans les années 1990, l'augmentation observée de la concentration en CO_2 dans l'atmosphère n'était "que" de 270 Tmol C an^{-1} (IPCC 2001). Cette différence est due à la capacité des autres réservoirs actifs au niveau du cycle du carbone à puiser une partie des émissions d'origine anthropique, à savoir le réservoir océanique et le réservoir terrestre.

La Terre contient environ 83×10^6 Tmol C, dont 3.3×10^3 Tmol C dans les réservoirs actifs près de sa surface et environ 0.3×10^3 Tmol C dans les combustibles fossiles (Schlesinger 1997). Parmi ces réservoirs actifs, l'océan est de très loin le plus important site de stockage du carbone et contient environ 3.2×10^3 Tmol C (soit environ 95% du total).

La biosphère (terrestre et océanique) possède la capacité de puiser le CO_2 pour créer de la matière organique à partir de la photosynthèse (dépendante de l'énergie lumineuse). Bien que d'autres processus de production primaire non dépendant de la lumière existent (chémoautotrophie), ceux-ci sont négligeables à l'échelle globale. Cette assimilation de CO_2 s'accompagne d'une production d'oxygène (O_2) selon la réaction simplifiée:

$$CO_2 + H_2O \rightarrow CH_2O + O_2 \qquad (1)$$

Tous les organismes vivants ont besoin de matière organique d'une part pour produire leurs propres tissus et d'autre part pour satisfaire leurs besoins énergétiques (respiration) selon la réaction inverse de l'équation (1). Ce processus de reminéralisation de la matière organique s'accompagne donc de la consommation d'O_2 et de la production de CO_2.

Nous devons dans un premier temps définir quelques termes qui seront employés dans la suite du texte:

(1) la production primaire brute (*gross primary production*: GPP) est le taux de production de matière organique par les organismes autotrophes (i.e. capables de synthétiser par eux-mêmes les matières organiques qui les composent à partir d'éléments minéraux et d'énergie lumineuse).

(2) La production primaire nette (*net primary production*: NPP) est le taux de production de matière organique par les organismes autotrophes après oxydation (respiration) des composés nécessaires à combler leurs besoins énergétiques.

$$NPP = GPP + R_a$$

Où R_a est le taux de respiration des organismes autotrophes (exprimée en valeur négative). Contrairement à GPP, NPP peut être négative si $|R_a| > GPP$.

(3) La respiration communautaire (*community respiration*: CR) est la minéralisation de matière organique par tous les organismes de la communauté, qu'ils soient autotrophes ou hétérotrophes.

$$CR = R_a + R_h$$

Où R_h est le taux de respiration des organismes hétérotrophes (exprimée en valeur négative).

(4) La production communautaire nette (*net community production*: NCP) est le taux de production de matière organique après consommation de celle-ci par tous les organismes du système considéré (autotrophes + hétérotrophes). Un organisme hétérotrophe ne peut tirer son énergie que de la décomposition de matière organique préexistante.

$$NCP = GPP + CR$$

Le terme production nette de l'écosystème (*net escosystem production*: NEP) sera souvent utilisé par la suite. Il s'agit de la somme des NCP de toutes les communautés (compartiment planctonique, microphytobenthos, macrophytes…) constituant un écosystème.

Une communauté ou un écosystème est dit autotrophe (NCP ou NEP > 0) lorsque GPP > |CR|. La production de matière organique en surplus est soit stockée, soit exportée vers les communautés ou les écosystèmes adjacents. Ce type de fonctionnement implique généralement une production nette d'O_2 et une consommation nette de CO_2. Ce processus a été appelé la pompe biologique. Ce n'est toutefois pas toujours le cas. En effet, les upwellings et les estuaires peuvent être autotrophes et pourtant des sources de CO_2 pour l'atmosphère, lorsqu'ils reçoivent des apports d'eaux riches en CO_2 (eaux profondes pour les upwellings et eaux continentales pour les estuaires). De plus, des effets strictement thermodynamiques peuvent modifier la pression partielle en CO_2 (pCO_2) tels ceux liés à des variations de température ou au mélange de masses d’eau de caractéristiques chimiques contrastées.

Une communauté ou un écosystème est dit hétérotrophe (NCP ou NEP < 0) lorsque GPP $<$ |CR|. Ces systèmes ont besoin d'un apport externe de matière organique (matière allochtone) pour se maintenir et sont des sources de CO_2 atmosphérique avec la même remarque que ci-dessus à savoir que la direction du flux dépend de la valeur de pCO_2 initiale.

Bien que sujette à une grande incertitude, la NPP terrestre a été estimée à environ 4500-5000 Tmol C an^{-1} à partir de mesures *in situ* (Saugier & Roy 2001 in IPCC 2001) et à partir de données de télédétection et de CO_2 atmosphérique (Ruimy *et al.* 1994 ; Knorr & Heimann 1995 in IPCC 2001 ; Field *et al.* 1998). Le réservoir terrestre serait autotrophe dans sa globalité et sa capacité à puiser le CO_2 atmosphérique a été estimée à 17 et 117 Tmol C an^{-1} dans les années 1980 et 1990, respectivement (IPCC 2001).

La capacité des océans à puiser le CO_2 atmosphérique a été estimée à 142 ± 42 Tmol C an^{-1} dans les années 90 (IPCC 2001), basée sur des mesures de pCO_2 (Takahashi 2002) et d'O_2 (Keeling & Shertz 1992 ; Bender *et al.* 1998), des modèles de circulation globale calibrés sur la distribution du ^{14}C (Sarmiento *et al.* 1992 ; Murnane *et al.* 1997), des mesures isotopiques (C^{13}) atmosphériques et océaniques (Quay *et al.* 1992) et des mesures atmosphériques de O_2/N (Battle *et al.* 2000). Il convient de noter que, d'une part ces méthodes prennent rarement en compte l'océan côtier et que, d'autre part les estimations faites à partir du gradient de pCO_2 entre l'air et l'eau souffrent de la difficulté d'estimer de façon fiable la vitesse d'échange de gaz entre ces deux milieux (Liss & Merlivat 1986 ; Wanninkhof 1992).

Le cas de l'océan est un peu plus complexe que celui du réservoir terrestre, car en plus de la pompe biologique décrite précédemment, la capacité de l'océan à puiser le CO_2 atmosphérique est caractérisée par deux autres processus: la pompe chimique et la pompe physique. Le carbone inorganique dissous (DIC) est présent dans l'eau sous trois formes: le bicarbonate (HCO_3^-), le carbonate (CO_3^{2-}) et le CO_2 dissous ($CO_2 + H_2CO_3$). Pour des valeurs de pH de 7.5 à 8.6 (gamme de variation du pH dans l'eau de mer), la majorité du DIC (91%) se trouve sous forme bicarbonate (Fig. 1). Le CO_2 atmosphérique puisé par l'océan, interagit avec le système des carbonates, pour former principalement du bicarbonate (pompe chimique). D'autre part, les eaux de surface équilibrées avec l'atmosphère peuvent être entraînées en profondeur (pompe physique) et, du fait des échelles de temps de la circulation thermohaline, seront soustraites à tout contact atmosphérique pour des durées de l'ordre du millier d'années.

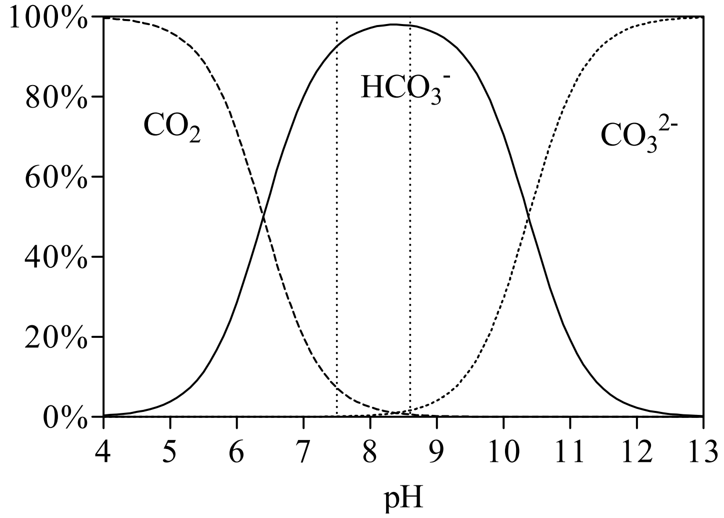

Figure 1 Variation en fonction du pH de la contribution des différentes espèces du système des carbonates à la concentration en carbone inorganique dissous.

L'efficacité de la pompe biologique océanique est difficile à quantifier à l'heure actuelle. Une des premières estimations globales de production primaire est attribuée à Riley (1939) basée sur quelques mesures avec la méthode de l'O_2 ; il s'agissait donc d'une estimation de la GPP. L'apparition de la méthode basée sur le ^{14}C (Steemann-Nielsen 1952) a engendré une augmentation considérable des mesures *in situ* et de nombreuses estimations de la production primaire globale sont apparues par la suite (Tableau 1). Un point très important à souligner est que malgré le nombre important de mesures effectuées et la perdurance de cette méthode à l'heure actuelle, cette dernière a fait l'objet de nombreuses critiques. Premièrement, Fitzwater *et al.* (1982) ont mis en évidence que les premières estimations basées sur le ^{14}C pouvaient être sous-estimées du fait de la contamination des stocks de ^{14}C utilisés. Depuis 1985, les précautions nécessaires ont été prises de telle sorte que cette méthode fournit des résultats fiables (Martin *et al.* 1987 ; Knauer 1993), mais on ne sait pas exactement ce qu'estime cette méthode: GPP ou NPP (Peterson 1980) ? Selon le temps d'incubation choisit, il est possible qu'une partie du ^{14}C incorporé à partir de la réaction de photosynthèse soit réoxydé en CO_2 par la respiration. Une incubation longue fournira donc un taux de production plus proche de NPP que de GPP. Un autre inconvénient de cette approche par rapport à la méthode basée sur l'O_2 est qu'il est impossible de quantifier la respiration. De plus, la majorité des expériences se cantonnent à mesurer uniquement la production de matière organique particulaire (*particulate organic carbon*: POC). Il est maintenant admis qu'une part significative de la production par la photosynthèse est relarguée sous forme dissoute (*dissolved organic carbon*; DOC), particulièrement dans les régions oligotrophes (Baines & Pace 1991 ; Morán *et al.* 2002). Par exemple, Karl *et al.* (1998) ont estimé que les estimations de production primaire à l'aide du ^{14}C à la station ALOHA (Pacifique Nord) pourraient être sous-estimées de 30 à 50% du fait de la non prise en compte de cette production dissoute. Ces possibles sous-estimations (GPP ou NPP ; production particulaire vs. production dissoute) sont également vraies pour les méthodes basée sur l'utilisation d'images satellitales calibrées sur des données acquises avec la méthode du ^{14}C (Longhurst *et al.* 1995 ; Antoine & Morel 1996 ; Field *et al.* 1998). Il est à noter également que cette méthode se limite généralement à l'océan ouvert car (1) la turbidité qui caractérise une partie des eaux côtières fausse les estimations basées sur les images satellitales et (2) la gamme de concentration en chlorophylle *a* typiquement rencontrée en milieu côtier est le plus souvent bien au dessus de la gamme de valeurs utilisée pour le développement des algorithmes de calibration des images. Dans le Tableau 1, le terme GPP s'applique uniquement aux estimations faites à partir de l'O_2 alors que le terme "NPP ou GPP" correspond aux estimations basées soit directement, soit indirectement sur le ^{14}C.

La respiration dans l'océan est très certainement le paramètre le moins bien documenté. Récemment, Robinson & Williams (sous presse) ont estimé une respiration de l'océan ouvert global de l'ordre de 9000 à 12000 Tmol C an^{-1}. Ces valeurs sont largement supérieures aux dernières estimations de production. En considérant, d'une part que les estimations basées directement ou indirectement sur la méthode du ^{14}C fournissent des données de NPP et, d'autre part que la NPP représente 60% de la GPP (soit 40% de la GPP respirée par les organismes autotrophes), del Giorgio & Williams (sous presse) ramènent les valeurs de NPP de Longhurst *et al.* (1995), Antoine & Morel (1996) et Field *et al.* (1998) à des GPP de l'ordre de 5000-7000 Tmol C an^{-1}. Deuxièmement, del Giorgio & Williams (sous presse) ajoutent une production potentielle de DOC de l'ordre de 15% amenant les estimations de GPP à 6000-8000 Tmol C an^{-1}, toujours significativement inférieures aux estimations de respiration. L'océan ouvert serait-il hétérotrophe (Smith & Mackenzie 1987) ?

Tableau 1 Estimations de production primaire (GPP et "NPP ou GPP"), production nette (NEP) et exportation vers l'océan profond. Les valeurs sont exprimées en Tmol C an^{-1}.

Références	GPP	"NPP ou GPP"	NEP	Export
Riley (1939)	10500			
Steemann-Nielsen & Jensen (1957)				
Fleming (1957)		1670		
Ryther (1969)		1670		
Koblentz-Mishke (1970)		1920		
Garrels & Mackenzie (1972)			-30	
Platt & Subba Rao (1975)		2580		
Eppley & Peterson (1979)		2000		
Martin *et al.* (1987)		4250		500
Smith & Mackenzie (1987)		3750	-20	636
Smith & Hollibaugh (1993)		4000	-20	500
Longhurst *et al.* (1995)		4170		
Antoine & Morel (1996)		2750		
Field *et al.* (1998)		4080		
Falkowski *et al.* (1998)				1330
Wollast (1998)		4170		350
Laws *et al.* (2000)				920
Schlitzer (2000)				920
Ducklow & McCallister (sous presse)			-200	

L'idée est tentante mais malheureusement impossible à vérifier à l'heure actuelle. Cette hypothèse a été avancée par certains auteurs avec des NEP allant de -17 à -500 Tmol C an^{-1}, nettement inférieure à la différence observée plus haut. Toutefois, Karl *et al.* (2003), ont utilisé des mesures continues d'O_2 à la station ALOHA (Pacifique nord) pour montrer que l'autotrophie pouvait être un phénomène particulièrement épisodique et suggéré que les programmes actuels d'observation de l'océan ont une résolution temporelle trop faible, et par conséquent sous-estiment grandement la production océanique.

Un océan ouvert hétérotrophe signifierait un océan dépendant des apports de matière organique en provenance de la zone côtière, car : (1) les apports potentiels en provenance de l'atmosphère seraient beaucoup trop faibles pour supporter une hétérotrophie prononcée

(Willey *et al.* 2002) et (2) la matière organique dissoute (DOC) contenue dans l'océan profond est considérée comme principalement réfractaire (Bauer *et al.* 1992).

Il faut toutefois noter qu'un océan hétérotrophe ne signifie pas forcément une source de CO_2 pour l'atmosphère. Bien au contraire, la couche euphotique (zone de pénétration de la lumière) peut être autotrophe et ainsi un puits de CO_2, exportant de la matière organique vers l'océan profond où l'activité hétérotrophique reminéralise cette matière organique ainsi que celle en provenance de la zone côtière. C'est pourquoi certains auteurs se sont intéressés à la production d'export de la zone euphotique océanique. Falkowski *et al.* (1998) ont calculé, à partir d'estimation de production nette dérivées de mesures satellitales et d'une relation production totale vs. production d'export (Eppley & Peterson 1979) qu'environ 30% de la NPP (1330 Tmol C an^{-1}) étaient transférés et reminéralisés dans l'océan profond et ainsi échapperaient à tout contact avec l'atmosphère pendant des centaines voir des milliers d'années. Cette valeur d'export a été revue à la baisse (920 Tmol C an^{-1}) par les modèles de Laws *et al.* (2000) et de Schlitzer (2000).

Un autre processus à prendre en considération au niveau du cycle du carbone océanique est la calcification. En effet, certains organismes marins qu'ils soient benthiques ou pélagiques, animaux ou végétaux, sont capables de précipiter du carbonate de calcium ($CaCO_3$) selon la réaction:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + H_2O \qquad (2)$$

Le processus de précipitation de carbonate de calcium consomme du bicarbonate mais relargue du CO_2 dans l'eau qui, si à proximité de l'interface air-mer, pourra être dégazé vers l'atmosphère. La formation de $CaCO_3$ agit donc sur le CO_2 en sens inverse de la formation de matière organique. Etant donné de rôle tampon de l'eau, le quotient CO_2 produit/$CaCO_3$ précipité (Ψ) est, à l'heure actuelle, proche de 1 en eau douce et environ 0.6 en eau salée (Frankignoulle *et al.* 1995). Toutefois, une augmentation de la pCO_2 atmosphérique implique une diminution du pouvoir tampon de l'eau au niveau de la dynamique des carbonates. Ainsi, pour un doublement de la pCO_2 atmosphérique préindustrielle (i.e. 580 ppm), Ψ devrait augmenter et atteindre une valeur de 0.76 (Frankignoulle *et al.* 1994), agissant par conséquent comme un "feedback" positif à cette augmentation de CO_2 atmosphérique. Milliman (1993) a estimé la production globale de $CaCO_3$ à 60 Tmol C an^{-1} dont 50% proviendrait de la zone côtière. Environ 40% de cette production ne s'accumule pas et est dissoute soit dans la colonne d'eau soit au niveau du sédiment. D'après Milliman (1993), la production nette de CO_2 en surface par la calcification serait de 50 Tmol C an^{-1}.

Le budget présenté dans le Tableau 2, concernant les années 1990 (IPCC 2001) semble être balancé : annuellement, sur les 525 Tmol C émis par la combustion d'énergies fossiles, 140 Tmol C seraient puisés par les océans, 120 Tmol C seraient puisés par la biosphère terrestre et 270 Tmol C resteraient dans l'atmosphère. Toutefois, et comme nous l'avons vu plus haut, ces valeurs restent approximatives et associées à des marges d'erreur conséquentes malgré les progrès des connaissances sur le cycle de carbone et de la capacité des réservoirs actifs de la planète à puiser le CO_2 atmosphérique produit par les activités humaines. Il est à noter également que l'océan côtier n'est que rarement incorporé dans les budgets globaux de flux de carbone du fait de (1) la faible quantité de mesures de pCO_2 disponibles (2) l'hétérogénéité et la diversité des écosystèmes côtiers (3) l'intense variabilité spatiale et temporelle des processus biogéochimiques au sein d'un écosystème côtier donné et (4) la difficulté d'intégration dans des modèles de circulation générale. La capacité de l'océan à puiser le CO_2 atmosphérique dépend pourtant également de la quantité de carbone apporté dans l'océan en provenance du continent. L'océan côtier, la zone de transition entre le compartiment terrestre et océanique, ne se comporte pas comme un simple réservoir mais est le site d'intenses processus physiques et biogéochimiques qui transforment, transportent et séquestrent le carbone en provenance des rivières (Liu *et al.* 2000). Il est donc primordial de l'intégrer dans un budget global de carbone océanique.

Tableau 2 Budgets de CO_2 globaux (en Tmol C an^{-1}; IPCC 2001)

	Années 1980	Années 1990
Emissions (combustibles fossiles, production de ciment)	450 ± 25	525 ± 33
Flux océan-atmosphère	-160 ± 50	-140 ± 50
Flux réservoir terrestre-atmosphère	-17 ± 60	-120 ± 70
Augmentation atmosphérique	275 ± 8	270 ± 8

La zone côtière, de profondeur entre 0 et 200 m, couvre une surface de 26 x 10^6 km^2 et représente 7% de l'océan global. Malgré cette faible superficie, la zone côtière semble avoir un rôle considérable au niveau des cycles biogéochimiques (Gattuso *et al.* 1998). De plus, de par sa proximité avec le compartiment terrestre, elle est fortement influencée par les activités humaines. L'eutrophisation a été définie par Nixon (1995) comme étant une augmentation du taux d'apport de matière organique vers un écosystème. Les activités humaines provoquent le déversement dans les rivières et les régions côtières de matière organique particulaire et dissoute ainsi que de la matière inorganique dissoute et particulaire. D'après Meybeck (1993), en plus des 31 Tmol C an^{-1} de carbone organique (TOC: particulaire + dissous) transportés naturellement par les rivières vers la zone côtière, 8 Tmol C an^{-1} sont ajoutés par les activités humaines. Les apports d'azote et de phosphore ont été récemment estimé à 1350 et 74 Gmol an^{-1} respectivement (Smith *et al.* 2003). Ces apports anthropiques de sels nutritifs sont causés par l'utilisation d'engrais agricoles, le défrichage des sols, les déchets domestiques etc.. L'augmentation des apports de sels nutritifs et la modification des rapports élémentaires (par exemple, N:P:Si) ont provoqué dans certaines régions une augmentation de la production phytoplanctonique (Radach *et al.* 1990 ; Wasmund *et al.* 2001 ; Cadée & Hegeman 2002), des modifications de la composition et du fonctionnement du réseau trophique, l'apparition de floraisons toxiques, la disparition d'espèces macroalgales etc… (Ducrotoy 1999 ; Kautsky & Kautsky 2000 ; Ærtebjerg 2001). L'eutrophisation peut avoir un effet non négligeable sur le cycle du carbone au niveau de la zone côtière et ainsi sur le cycle du carbone océanique. L'augmentation de l'apport en sels nutritifs peut en effet stimuler la croissance phytoplanctonique et augmenter ainsi le pompage de CO_2 atmosphérique par ce processus. Inversement, l'augmentation de l'apport de matière organique et de particules sédimentaires peut stimuler la respiration hétérotrophe et limiter la quantité de lumière disponible pour la photosynthèse, produisant ainsi du CO_2 en excès. Par exemple, Frankignoulle *et al.* (1998) ont montré que neuf estuaires européens émettaient de 5 à 10% du CO_2 produit par les activités anthropiques en europe de l'ouest. Toutefois, l'impact de l'homme sur le cycle du carbone côtier est à l'heure actuelle difficile à quantifier car la diversité des écosystèmes rend l'extrapolation au niveau global plus difficile que dans l'océan ouvert.

Tsunogai *et al.* (1999) ont mesuré des flux de CO_2 à l'interface air-mer en mer de Chine de l'ordre de -8 mmol C m^{-2} d^{-1}. Par convention, un flux négatif signifie un flux vers l'océan. Extrapolé à toute la zone côtière, cela revient à 80 Tmol C an^{-1} puisé par l'océan côtier (contre 140 Tmol C an^{-1} pour l'océan ouvert, voir plus haut). Ces auteurs ont avancé le terme de "continental shelf pump", à savoir la pompe du plateau continental. Depuis, Frankignoulle & Borges (2001), DeGrandpré *et al.* (2002) et Thomas *et al.* (2004) ont mesuré des valeurs légèrement inférieures mais toujours nettement significatives de l'ordre de -2 à -8 mmol C m^{-2} d^{-1} dans le Golfe de Gascogne, la côte est nord américaine (*Middle Atlantic Bight*) et la mer du nord, respectivement. Toutefois, ces études ne concernent que des pentes continentales dans des régions tempérées. En effet, le récent travail de Cai *et al.* (2003) au large des côtes de la Géorgie suggère que les plateaux continentaux situés à des latitudes sub-tropicales seraient des sources de CO_2 vers l'atmosphère. La diversité des écosystèmes côtiers citée plus haut implique des mesures dans des systèmes variés:

- upwellings (Goyet *et al.* 1998 ; Borges & Frankignoulle 2002 ; Friederich *et al.* 2002)
- estuaires (Cai & Wang 1998 ; Frankignoulle et al. 1998 ; Raymond et al. 2000 ; Abril & Borges 2004)
- plumes de dilution (Borges & Frankignoulle 2002 ; Körtzinger 2003)
- récifs coralliens (Gattuso et al. 1993 ; Frankignoulle et al. 1996 ; Gattuso et al. 1997 ; Ohde & van Woesik 1999 ; Bates et al. 2001)
- mangroves (Borges et al. 2003)
- marais salants (Wang & Cai 2004), etc…

A l'heure actuelle, du fait du faible nombre de mesures disponibles et de la grande diversité des écosystèmes côtiers, il n'est pas possible de donner une valeur globale du flux net de CO_2 entre l'atmosphère et l'océan côtier. De plus, et comme nous l'avons mentionné précédemment, l'estimation du flux de CO_2 à l'interface air-mer requiert d'estimer le coefficient d'échange (k).

Une grande part de l'incertitude de l'estimation du flux de CO_2 est attribuée au calcul de ce coefficient. Il dépend principalement de l'état de turbulence de l'interface air-mer, et que ce soit en océan ouvert ou en zone côtière, il a été paramétrisé en fonction de la vitesse du vent considéré comme le principal générateur de turbulence à la surface. Toutefois, Raymond & Cole (2001) ont mis en évidence que cette paramétrisation du coefficient d'échange pouvait varier en fonction de la géomorphologie du site concerné (système ouvert ou fermé). Afin de fournir des estimations de flux de CO_2 fiables au niveau de la zone côtière, il devient impératif de diminuer la marge d'erreur due à l'estimation du coefficient d'échange.

De plus, pour réaliser ces budgets de CO_2, il est nécessaire de connaître la quantité de carbone inorganique dissous (DIC) transporté par les rivières et susceptible d'être dégazé au niveau de l'océan côtier (estuaires principalement, voir plus haut). Cette quantité a été estimée à 50 Tmol C an^{-1} (Sarmiento & Sundquist 1992).

Le Tableau 3 présente les estimations de NPP, "NPP ou GPP" (basées sur le ^{14}C), NEP et production exportée de la zone côtière. Il faut souligner que ces auteurs n'ont pas utilisé la même valeur de surface pour la zone côtière, les valeurs allant de 26 à 58 x 10^6 km^2. Pour faciliter les comparaisons, nous avons choisi ici de rapporter les valeurs obtenues par ces différentes études à une même surface, à savoir 26 x 10^6 km^2 (Gattuso *et al.* 1998). Les estimations de NPP de Longhurst *et al.* (1995) basées sur l'analyse d'image satellitales sont d'une part nettement plus élevées que les estimations basées sur les méthodes d'incubation classiques et d'autre part contiennent une marge d'erreur très importante du fait de la difficulté d'analyser les signaux dans les régions turbides. Comme dans la section précédente (océan global), les valeurs diffèrent beaucoup en fonction des auteurs (270 – 830 Tmol C an^{-1}).

Tableau 3 Estimations de production primaire (GPP et "NPP ou GPP"), production nette (NEP) et production d'export au niveau de l'océan côtier. Les valeurs sont exprimées en Tmol C an^{-1}.

Référence	GPP	"NPP ou GPP"	NEP	Export
Platt & Subba Rao (1975)		270		
Whittle (1977)		350		
Eppley & Peterson (1979)		270		
Wollast & Billen (1981)		475		
Martin *et al.* (1987)		540		
Smith & Mackenzie (1987)		600	-27	0
Walsh (1988)		275		
Berger (1989)		390		
Wollast (1991)		500		75
Walsh (1991)				83
Smith & Hollibaugh (1993)	500		-7	18
Longhurst *et al.* (1995)		520-830		
Rabouille (1997)	423		12	37
Wollast (1998)	500		200	183
Gattuso *et al.* (1998)	790		230	
Liu *et al.* (2000)		470		58
Rabouille et al. (2001)			13	

Peu d'estimations de la production brute côtière ont été effectuées jusqu'à présent, Gattuso *et al.* (1998) avancent une valeur de 790 Tmol C an^{-1}, ce qui amène les auteurs à conclure que la production organique côtière représenterait 23% de la production océanique globale. Toutefois, il convient de préciser que la valeur de production de l'océan ouvert utilisée pour ce calcul est celle de Wollast (1998), i.e. 3400 Tmol C an^{-1} et correspondrait plus à une valeur de NPP que de GPP (voir section précédente). Les estimations de NEP et d'export de matière organique de la zone côtière vers l'océan ouvert (la pompe biologique côtière) diffèrent elles aussi grandement entre les auteurs. Tandis que Smith & Hollibaugh (1993) estiment que la zone côtière serait hétérotrophe et que l'export de matière organique vers l'océan profond correspondrait à environ la moitié des apports organiques continentaux, Gattuso *et al.* (1998) et Wollast (1998) suggèrent que l'océan côtier serait autotrophe et une source nette de carbone organique pour l'océan ouvert. Par ailleurs, nous avons vu dans la section précédente que la calcification pouvait avoir un rôle non négligeable au niveau du cycle du carbone, particulièrement en zone côtière. En effet, d'après Milliman (1993), la production et l'accumulation de $CaCO_3$ en zone côtière seraient de 25 et 17 Tmol C an^{-1}. Comparées aux valeurs d'exportation de matière organique (voir Tableau 3), la production nette de CO_2 due à l'accumulation et à l'exportation de $CaCO_3$ n'est pas négligeable et doit être prise en considération dans les budgets de carbone au niveau de la zone côtière. Cependant, du fait du faible nombre de mesures à l'échelle globale, les marges d'erreurs associées à l'estimation de ces paramètres sont malheureusement encore trop élevées.

En conclusion, que ce soit à partir de mesures directes de pCO_2 ou d'extrapolation des paramètres métaboliques (production/respiration, précipitation/dissolution de carbonate de calcium) gouvernant le flux net biologique entre l'atmosphère et l'océan côtier, il est très difficile de quantifier le rôle de la zone côtière dans le cycle global du carbone. Plusieurs approches peuvent être utilisées pour préciser ce rôle : (1) augmenter les mesures de pCO_2 dans le domaine côtier et calculer les flux tout en affinant l'estimation du coefficient d'échange, (2) augmenter les mesures de production/respiration de matière organique au moyen des méthodes d'incubation classiques, (3) utiliser de nouvelles méthodes permettant d'estimer la production nette des écosystèmes côtiers à de plus grandes échelles spatiales et temporelles et (4) quantifier de façon plus fiable le rôle de la calcification au niveau du cycle du carbone côtier.

L'étude présentée ici a été réalisée dans le cadre du programme européen EUROTROPH (Contrat: EVK3-CT-2000-00040 http://www.ulg.ac.be/oceanbio/eurotroph/) qui a débuté en 2001. Les objectifs étaient (1) d'étudier, par le biais d'une compilation bibliographique de mesures de paramètres métaboliques (GPP, CR et NEP), le statut trophique des écosystèmes côtiers à l'échelle européenne et (2) de quantifier le statut trophique de trois systèmes côtiers en utilisant différentes méthodes à différentes échelles de temps (échelle locale).

Les trois systèmes côtiers étudiés sont la baie de Palma, le fjord de Randers et l'estuaire de l'Escaut. Ces sites ont été choisis en fonction des différences existant au niveau des paramètres environnementaux gouvernant la balance métabolique (Fig. 2).

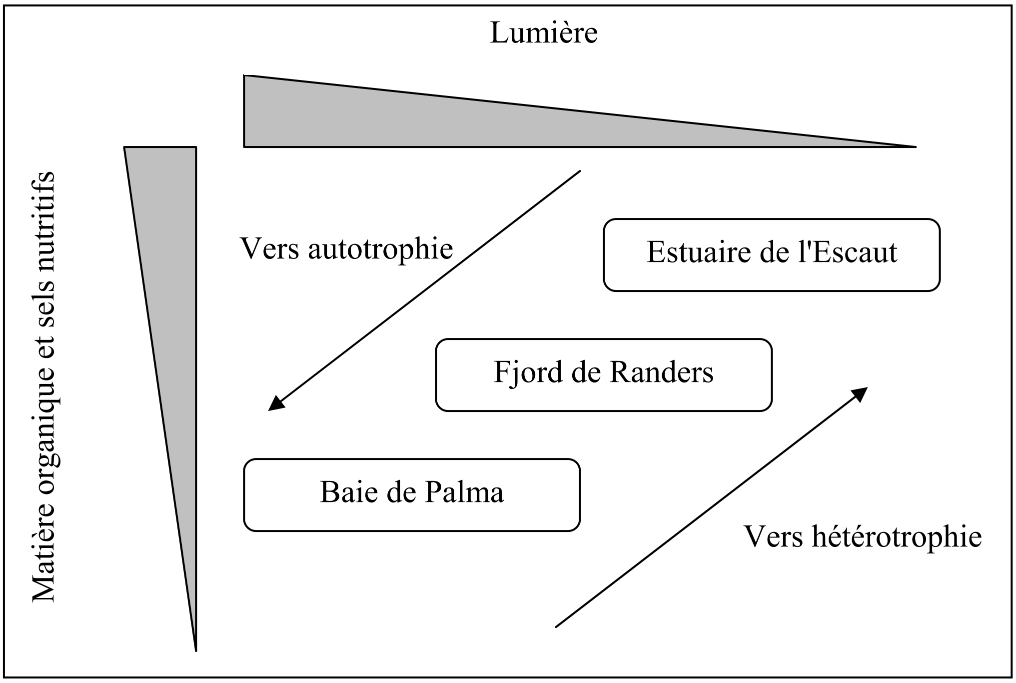

Figure 2 Paramètres environnementaux supposés gouverner la balance métabolique des 3 sites étudiés dans le cadre du programme EUROTROPH

L'estuaire de l'Escaut est considéré comme l'un des estuaires les plus pollués d'europe de l'ouest en terme d'apport de sels nutritifs et de matière organique (Wollast 1988). Situé en Belgique et aux Pays-Bas (Fig. 3), il draine les eaux d'un bassin très peuplé et industrialisé. Dans cet estuaire macrotidal, la colonne d'eau est bien mélangée et la turbidité est forte dans tout l'estuaire, limitant la production phytoplanctonique (van Spaendonk *et al.* 1993 ; Kromkamp *et al.* 1995). Un temps de résidence de l'eau douce élevé (Soetaert & Herman

1995) et une activité hétérotrophe très importante (Goosen *et al.* 1995) sont les causes de fortes concentrations en CO_2 (Frankignoulle *et al.* 1998).

Le fjord de Randers est un estuaire microtidal stratifié situé sur la côte est du Danemark. Les apports en sels nutritifs et matière organique ainsi que la turbidité et le temps de résidence de l'eau douce sont nettement moins important que dans l'estuaire de l'Escaut.

Enfin, la baie de Palma située en Méditerranée occidentale (Baléares, Mallorque) est un écosystème peu turbide dominé par un herbier de phanérogames marines (*Posidonia oceanica*) qui occupe environ 30% de la surface de la baie. L'activité touristique entraîne pendant l'été une augmentation de l'apport de sels nutritifs en provenance de la ville de Palma. L'augmentation de ces apports a été identifiée comme une des causes principales de la régression de l'herbier de *posidonies* dans ce système. Une description plus détaillée de chaque site est donnée dans les chapitres correspondants.

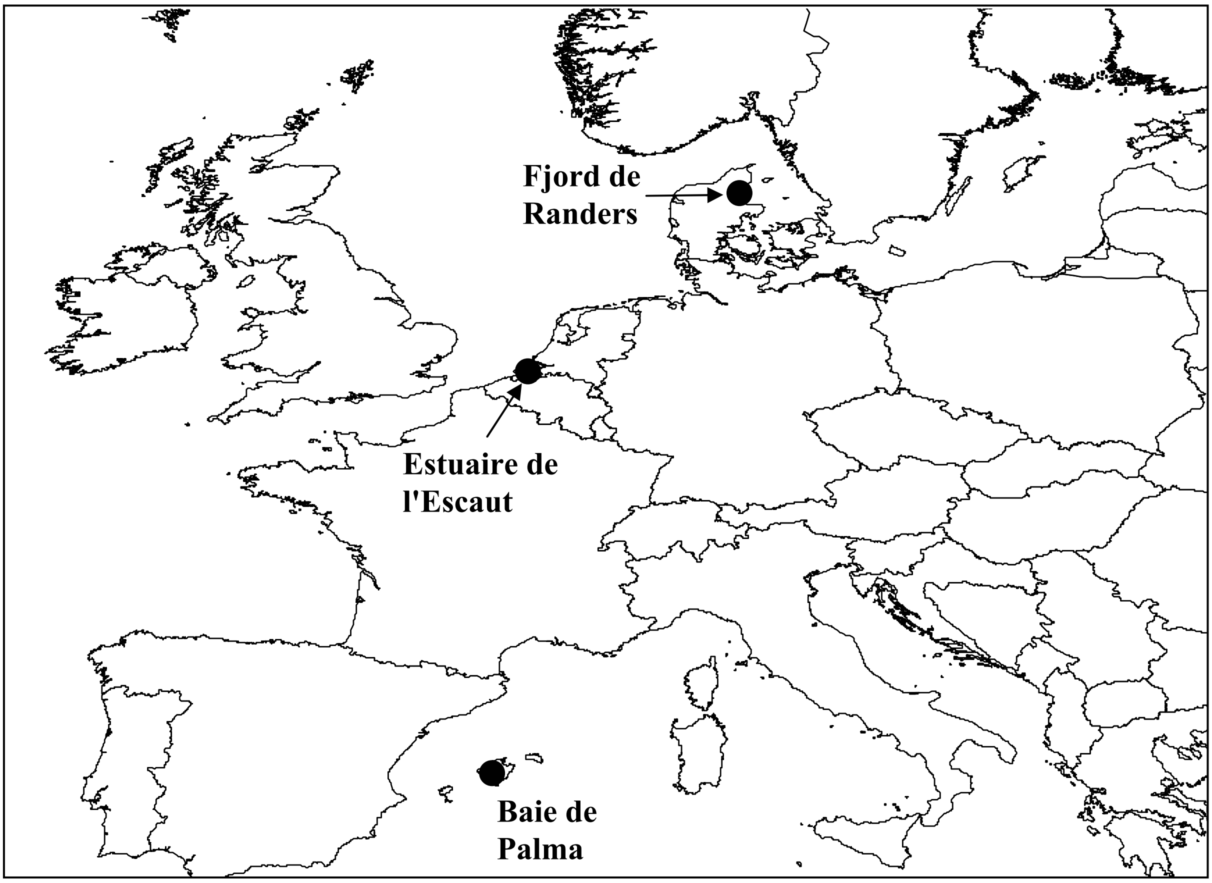

Figure 3 Localisation des sites étudiés dans le cadre du programme EUROTROPH

Deux campagnes dans chaque système ont été effectuées:

- avril et août 2001: fjord de Randers
- mars et juin 2002: baie de Palma
- novembre 2002 et avril 2003: estuaire de l'Escaut

De plus, l'estuaire de l'Escaut a été visité avec une fréquence mensuelle de janvier à décembre 2003.

Les méthodes utilisées dans cette étude pour déterminer le statut trophique sont:

1. la méthode d'incubation classique (mesure de la variation de la concentration en oxygène à la lumière et à l'obscurité) planctonique et benthique de façon discrète à plusieurs stations et extrapolation spatiale des résultats au moyen de cartes bathymétriques établies pour les trois sites.

2. la méthode RSD (*Response Surface Difference*) développée par Swaney *et al.* (1999). Cette méthode intégrative, dérivée de la méthode *multistation averaging* de Howarth *et al.* (1992) consiste en des profils d'oxygène à diverses stations d'un système et à différentes périodes de la journée (*open-system method* ou méthode en système ouvert). Cette méthode a été appliquée uniquement au fjord de Randers. Contrairement à la méthode *multistation averaging*, cette technique considère que dans des systèmes partiellement mélangés, la concentration en oxygène ne dépend pas que des processus biologiques et des échanges avec l'atmosphère, mais également de la profondeur et de la salinité. Il convient d'ajouter que d'autres méthodes basées sur des cycles journaliers (O_2 et DIC) ont été utilisées localement dans le fjord de Randers et la baie de Palma.

3. La méthode LOICZ (*Land-Ocean Interaction in the Coastal Zone*; Gordon *et al.* 1996). Il s'agit d'une procédure de budgétisation d'un système à partir des données de flux d'eau douce, de salinité et de concentration en phosphore, azote et carbone inorganiques dissous (DIP, DIN et DIC). Le volume du système est supposé constant et la salinité (paramètre conservatif) est utilisée pour estimer les flux d'échange entre les différents compartiments du système considéré ainsi qu'entre le système et l'environnement externe. La concentration des différents éléments (DIP, DIN et DIC) est elle aussi supposée constante, la déviation par rapport à la conservativité permettant d'estimer:

    i. La NEP (p-r dans la terminologie LOICZ) du système en considérant que d'une part seuls les processus biologiques (production/minéralisation de matière organique, NEP) ont un effet sur la variation non-conservative du DIP et d'autre part que les flux non-conservatifs de DIC sont attribués à

la production/minéralisation de matière organique (NEP), aux échanges de CO_2 avec l'atmosphère ainsi qu'à la précipitation/dissolution de carbonate de calcium.
Il s'agit donc de deux estimations indépendantes de la NEP, un rapport C:P de la matière organique particulaire permettant de convertir les flux non conservatifs de DIP en carbone.

ii. la différence entre la fixation et la dénitrification ($N_{fix-denit}$ dans la terminologie LOICZ) en considérant que, outre la balance entre la production/minéralisation de matière organique (NEP), seuls ces deux processus interviennent au niveau de la variation non-conservative du DIN. Comme précédemment, un rapport $(N:C)_{part}$ est nécessaire pour transformer l'unité de la NEP de carbone en azote.

Cette méthode n'a pu être appliquée à la baie de Palma car elle requière, pour être fiable, une différence significative de salinité entre le système étudié et l'extérieur, ce qui n'est pas le cas pour la baie de Palma.

Comme nous l'avons vu, les méthodes *open-system* (RSD, cycles journaliers) ainsi que la méthode LOICZ appliquée au DIC nécessitent l'estimation du flux d'O_2 et/ou de CO_2 entre l'eau et l'atmosphère. Nous avons discuté plus haut que le coefficient d’échange (*k*) est un paramètre critique dans l'estimation de ces flux. Celui-ci a été étudié dans les trois sites où ces méthodes ont été appliquées.

Le manuscrit se présente selon le plan suivant:

- L'étude bibliographique permettant de faire un état des lieux de nos connaissances concernant le métabolisme de la zone côtière européenne sera présentée dans le **chapitre 2**. Ce travail a fait l'objet de la publication suivante:

  Gazeau F., Gentili B., Frankignoulle M., Smith S. V. & Gattuso J.-P. The European coastal zone: characterization and first assessment of ecosystem metabolism (2004) Estuarine, Coastal and Shelf Science 60(4): 673-694.

- L'étude du métabolisme de la baie de Palma au moyen de l'intégration de données d'incubation oxygène ainsi que par l'intermédiaire de budgets DIC et O_2 sera présentée dans le **chapitre 3.1.** Ce travail fait l'objet de la publication suivante:

  Gazeau F, Duarte C. M., Gattuso J. -P., Barrón C., Navarro N., Ruíz S., Prairie Y. T., Calleja M., Delille B., Frankignoulle M. and Borges A. V. Whole system metabolism and CO_2 fluxes in the Bay of Palma (NW Mediterranean) (en preparation, soumission mi-août) Biogeosciences issue spéciale *Coastal Biogeochemistry co-editée par H. Thomas et A. V. Borges.*

- L'étude concernant l'estimation du coefficient d'échange dans les estuaires de Randers et de l'Escaut sera présentée dans le **chapitre 3.2**. Ce travail a fait l'objet de la publication suivante:

  Borges A. V., Delille B., Schiettecatte L. -S., Gazeau F., Abril G. & Frankignoulle M. Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt and Thames) (sous presse) Limnology and Oceanography 49(5).

- L'étude du métabolisme du fjord de Randers au moyen de diverses méthodes ainsi que l'utilisation de la méthode LOICZ, à partir de données historiques acquises dans l'estuaire, sur une échelle de temps d'une dizaine d'années sera présentée dans le **chapitre 3.3**. Ce travail fait l'objet de la publication suivante:

  Gazeau F., Borges A. V., Barrón C., Duarte C. M., Iversen N., Middelburg J. J., Pizay M. -D., Frankignoulle M. & Gattuso J. -P. Net ecosystem metabolism in a micro-tidal estuary (Randers Fjord, Denmark): evaluation of methods and interannual variability (soumis) Marine Ecology Progress Series.

- L'étude du métabolisme de l'estuaire de l'Escaut à partir des données de métabolisme acquises in situ pendant l'année 2002-2003, ainsi qu'à partir de la méthode LOICZ sera présentée dans le **chapitre 3.4**. Ce travail fait l'objet de la publication suivante:

  Gazeau F., Gattuso J. -P., Middelburg J. J., Barrón C., Duarte C. M., Schiettecatte L. -S., Brion N., Pizay M. -D., Frankignoulle M. & Borges A. V. Planktonic and whole system metabolism in a nutrient-rich estuary (The Scheldt Estuary) (soumis) Limnology and Oceanography.

- Enfin, la synthèse sera présentée dans le **chapitre 4** et la conclusion et les perspectives dans le **chapitre 5.**

Chapitre 2

L'échelle Européenne

Gazeau F., Gentili B., Frankignoulle M., Smith S. V. & Gattuso J. -P., (2004)
The European coastal zone: characterization and first assessment of ecosystem metabolism. *Estuarine, Coastal and Shelf Science*. 60(4): 673-694.

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The European coastal zone: characterization and first assessment of ecosystem metabolism

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Abstract

The geomorphic, oceanographic, terrestrial and anthropogenic attributes of the European coastal zone are described and published data on ecosystem function (primary production and respiration) are reviewed. Four regions are considered: the Baltic Sea, Mediterranean Sea, Black Sea and the European Atlantic coast including the North Sea. The metabolic database (194 papers) suffers from a non-homogeneous geographical coverage with no usable data for the Black Sea which was therefore excluded from this part of our study. Pelagic gross primary production in European open shelves is, by far, the most documented parameter with an estimated mean of 41 mmol C $m^{-2} d^{-1}$, the lowest value is reported in the Mediterranean Sea (21 mmol C $m^{-2} d^{-1}$) and the highest one in the Atlantic/North Sea area (51 mmol C $m^{-2} d^{-1}$). Microphytobenthic primary production, mostly measured in shallow areas, is extrapolated to the entire 0–200 m depth range. Its contribution to total primary production is low in all regions (mean: 1.5 mmol C $m^{-2} d^{-1}$). Although macrophyte beds are very productive, a regional production estimate is not provided in this study because their geographical distribution along the European coastline remains unknown. Measurements of pelagic community respiration are clearly too sparse, especially below the euphotic zone, to yield an accurate picture of the fate of organic matter produced in the water column. With a mean value of 17 mmol C $m^{-2} d^{-1}$, benthic community respiration consumes approximately 40% of the pelagic organic matter production. Estuaries generally exhibit high metabolic rates and a large range of variation in all parameters, except microphytobenthic primary production. Finally, the problem of eutrophication in Europe is discussed and the metabolic data obtained in the framework of the Land–Ocean Interactions in the Coastal Zone (LOICZ) project are compared with available direct measurements of net ecosystem production.

Keywords: ecosystems; global; metabolism; shelf; estuaries; primary production; respiration; Europe

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1. Introduction

The coastal zone is a transition area between land and the open ocean. It receives considerable amounts of freshwater, nutrients, dissolved and particulate organic matter, sediment and contaminants. It also exchanges matter and energy with the open ocean. The coastal zone is, by definition, relatively shallow. This has two consequences: (1) light penetrates a significant portion of the water column, even reaching the bottom in some areas; and (2) there is a strong coupling between pelagic and benthic processes. These inputs, together with its shallowness, make the coastal zone very active in terms of primary production and respiration. Coastal metabolism has been reviewed in a number of relatively recent papers (Smith and Hollibaugh, 1993; Alongi, 1998; Gattuso et al., 1998; Wollast, 1998).

The European coastal zone has geomorphic and metabolic characteristics similar to those of other coastal areas. Although these attributes have never been fully reviewed, local and thematic studies have received strong support and attention in the European research

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programs. A major reason is that the European Union (EU) has promoted inclusion of socio-economic aspects in the research projects reflecting the increasing significance of the coastal ocean in the EU and elsewhere in terms of fishing, aquaculture and recreation. The European Commission launched ELOISE (European Land–Ocean Interaction Studies) as a loose network of reasonably small coastal research projects. ELOISE is the European contribution to LOICZ (Land–Ocean Interaction in the Coastal Zone), a program element of the International Geosphere Biosphere program (IGBP).

Two of the initial goals of ELOISE (Cadée et al., 1994) were related to ecosystem function: (1) to determine the role of coastal seas in land-ocean interactions (including shelf-deep sea interactions along the shelf break) in the context of global change; and (2) to determine the regional and global consequences of human impact through pollution, eutrophication and physical disturbance on land-ocean interactions in the coastal zone.

This paper has two aims. First, to review the geomorphic, oceanographic, terrestrial and anthropogenic attributes of the EU coastal zone using global databases recently accessible. Second, to review, synthesize and analyse published data on ecosystem function, essentially primary production and respiration.

2. Characterization of the European coastal zone

The continental shelf, continental margin, coastal ocean and coastal zone are fuzzy concepts for which various definitions have been proposed. It is outside the scope of this paper to review these definitions. The definition of the terms as commonly used was adopted and the operational definition applied here was explicitly mentioned.

The continental shelf is the area extending from the coast to the shelf break, which is usually defined by the 200 m depth isobath. The continental margin is the transition zone between the continental crust and the oceanic crust, including the coastal plain, continental shelf, slope and rise (Kennett, 1982). The coastal ocean is the portion of the global ocean where physical, biological and biogeochemical processes are directly affected by land. It is either defined as the part of the global ocean covering the continental shelf or the continental margin. The coastal zone usually includes the coastal ocean as well as the portion of the land adjacent to the coast that influences coastal waters. It can readily be appreciated that none of these concepts has a clear operational definition. The marine portion of the coastal zone was defined as the area with a depth of 200 m or less or, when the data are gridded with a large cell size, with at least one depth sounding of 200 m or less. The land portion of the coastal zone is the land area located in the 0.5° × 0.5° cell enclosing the coastline (see below).

Two major sources of information were used: the ETOPO2 data set for the depth attributes and the LOICZ environmental database for most other attributes. The gridded ETOPO2 data set was downloaded from the Data Support Section of the National Center for Atmospheric Research (http://dss.ucar.edu/datasets/ds759.3/data/) on 9 December, 2002. It blends satellite altimetry with ocean soundings and new land data to provide a global elevation and bathymetry on a $2' \times 2'$ grid. The UNIX version of the Generic Mapping Tool (gmt 3.4.2-3), with its full resolution coastline, was used to calculate surface area, volume, as well as median and average depths.

The international program LOICZ has compiled atmospheric, geomorphic, terrestrial, oceanic, biogeochemical and human-related variables, and produced a gridded database freely accessible (http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm) on the World Wide Web. The grid size (0.5° or about 55 km at the equator) is coarse for coastal areas, which exhibit major gradients in their environmental and ecological attributes at scales of 1 km or less. Importantly, data for many of the variables present in the LOICZ database are simply not available on a global scale and with a better geographical resolution. The choice of the grid size was then a compromise between the existing data and the objective of using the same grid size for all variables. This database is a very powerful tool: (1) to describe the attributes of the coastal ocean at a global scale, more specifically its geomorphology, environmental setting and biogeochemical properties; and (2) to explore how the coastal zone is influenced by inputs from land and the atmosphere, as well as by human activities.

Here, four regions are examined (Fig. 1): the Baltic Sea (including the Kattegat), the Mediterranean Sea, the Black Sea (including the Sea of Azov) and the European Atlantic coast (including the English Channel, the North Sea and the Skagerrak). While the Caspian Sea is often included as an EU sea (Mamaev, 2002), this area was not considered because it is not connected to an open ocean or marginal sea. Similarly, freshwater bodies were not considered.

2.1. Geomorphic attributes

2.1.1. Surface area and hypsometry

The European coastal zone covers 8.4% of the world coastal zone surface area (2.18 vs. 25.84×10^6 km^2; Table 1), with a similar median depth (60 vs. 46 m). The European Atlantic coast is the largest region (56% of the EU coastal zone) reflecting the large area of the North Sea and the extended shelf that surrounds the United Kingdom. The next largest region is the Mediterranean (21%). It has a relatively narrow shelf, except in the northern Adriatic Sea, representing only 18% of the total surface area. The coastal zones of the Baltic Sea and the

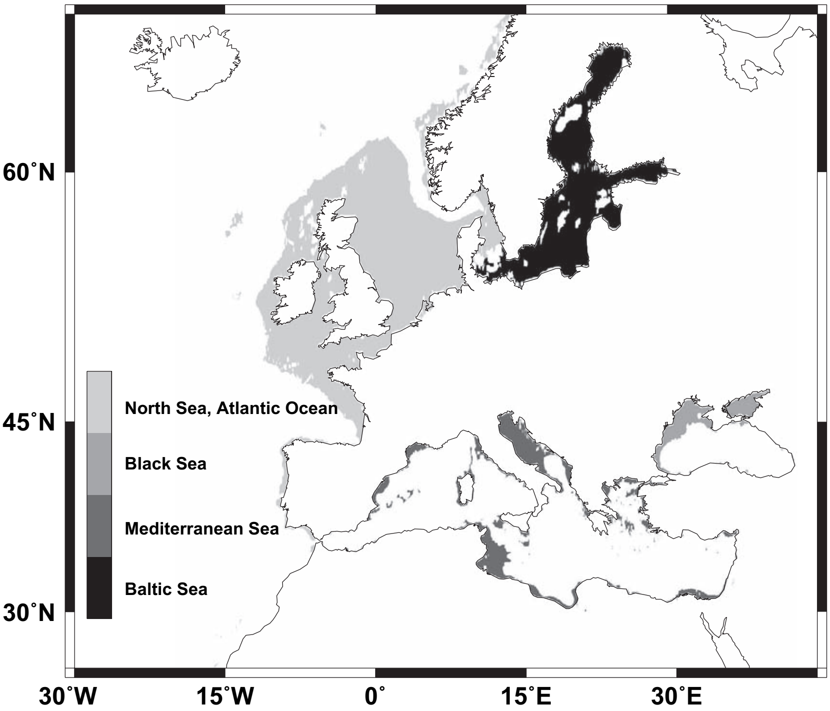

Fig. 1. Map of the European coastal zone with considered sub-regions.

Black Sea (97% and 28% of their total surface area) represent 17% and 6% of the EU coastal zone; they are the shallowest regions (median depth of 35 and 40 m). The European Atlantic region is the deepest (median depth: 73 m). Note that part of the Baltic Sea (Gulf of Bothnia and eastern part of Gulf of Finland) has a seasonal ice cover for up to half a year; the maximum annual ice cover ranges from 12% to 100% of the surface area (Gronvall and Seina, 1999).

The hypsometric curves (Fig. 2) show that the European Atlantic region has a much steeper slope than all other regions of the European coastal zone and is steeper than the mean value for the global coastal zone. About 34% of the Baltic Sea area is shallower than 20 m, 23% of the Black Sea, 19% of the Mediterranean Sea and only 11% of the European Atlantic Ocean, compared with a mean value of 26% for the global coastal zone.

Table 1
Geomorphic attributes of the European coastal zone

Geographical zone	Area (10^6 km^2)	Volume (10^6 km^3)	Mean depth±SD (m)	Median depth (m)
Baltic Sea	0.37	18.17	46±43	35
Mediterranean Sea	0.45	29.07	67±54	56
Black Sea	0.13	7.25	56±49	40
Atlantic, European	1.23	95.59	78±53	73
Total, mean and median depth (Europe)	2.18	150.06	69±53	60

2.1.2. Attributes of the land adjacent to the coastal zone

Nearly 50% of total length of the European coastline (calculated at a nominal scale of 1:250 000) is in the Atlantic domain, 27% in the Baltic Sea, 20% in the Mediterranean Sea and less than 5% in the Black Sea (Table 2). The median elevation of land adjacent to the coast, that is comprised in the LOICZ coastal cells described above, is higher in the Mediterranean (194 m) than elsewhere in Europe (grand median, 112 m). The surface area of the coastal cells covered by crop land

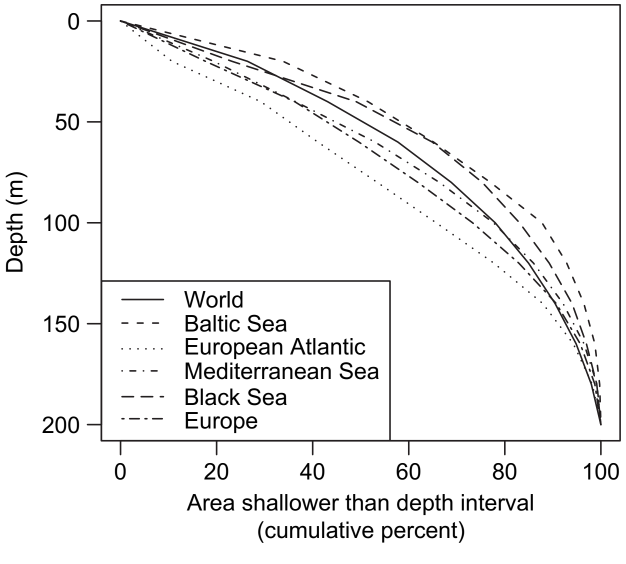

Fig. 2. Hypsometry of the European coastal ocean.

Table 2
Geomorphic attributes of the LOICZ database coastal cells

Variable	Baltic Sea	Mediterranean Sea	Black Sea	European Atlantic	Whole of Europe
Coastline length (km) [1]	77802	56650	10738	133357	278547
Median of mean land elevation (m) [2]	27	194	79	123	112
Median maximum elevation (m) [3]	68	650	227	380	331
Median of SD of elevation (m) [4]	14	138	46	80	68

Numbers in brackets refer to data sources listed in the appendix available at: http://www.obs-vlfr.fr/~gattuso/ECSS_app.htm.

ranges from 15% in the European Atlantic region to 42% in the Black Sea region (Fig. 3).

2.2. *Atmospheric attributes*

Some but not all atmospheric environmental parameters vary greatly depending on the zone considered. The median wind speed is higher in the European Atlantic region than in the Mediterranean region, with a difference of less than 2 m s^{-1} (Table 3). The median air temperature is 10.5 °C for all of Europe; the median, minimum and maximum monthly air temperatures range widely from −15.4 to 31.9 °C. The median annual precipitation is similar in the Baltic, Mediterranean and Black Sea regions (range, 671–720 mm yr^{-1}) but is significantly higher in the European Atlantic region (1022 mm yr^{-1}). The largest range of mean monthly precipitation is found in the Mediterranean region (0–484 mm month^{-1}).

2.3. *Oceanic attributes*

The median mean monthly sea surface temperature (SST) varies almost 3-fold between the geographical regions (7.7 °C in the Baltic Sea and 19.5 °C in the Mediterranean; Table 4). The range of mean monthly SST is >20 °C in the four regions. Sea surface salinity (SSS) is reported but some EU coastal areas are seasonally or permanently stratified. For example, according to Kautsky and Kautsky (2000) the central Baltic Proper is permanently stratified (salinities of 6–8 in the upper layer and 10–14 in the deeper layer). The median SSS differs considerably between geographical regions (6.4 in the Baltic Sea and 38.1 in the Mediterranean Sea). The median wave height is 3–4 times smaller in the Black Sea than in the other three regions; it is highest in the European Atlantic region. The median tidal range also differs largely between regions with values close to 0 m in the Baltic Sea and the Mediterranean Sea regions, and between 2 and 4 m in the European Atlantic region.

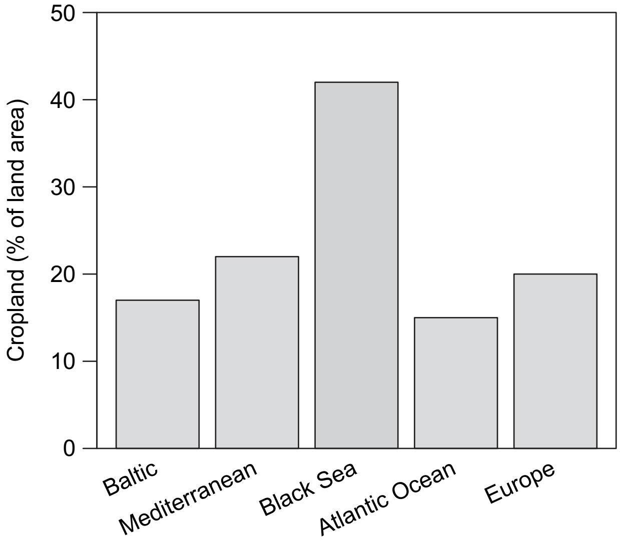

Fig. 3. Relative surface area (%) of cropland in the coastal cells. Data from the University of Maryland's 1 km global land cover product (Hansen et al., 2000) extracted from the LOICZ database.

2.4. *River basin and coastal population attributes*

In Europe, 58% of the total annual runoff comes from 35 large river basins (Fig. 4); individual runoff values range from 13.1 to 329 km^3 yr^{-1}. The calculated combined runoff is similar to that reported by Dai and Trenberth (2002). The European Atlantic region receives about the same total runoff as the Mediterranean Sea (Table 5), but the yield (runoff per unit of river basin area) is 3-times greater. The very large river basin area for the Mediterranean region is due to the Nile basin, which extends over 10 African countries and covers about 3×10^6 km^2. As a result, the total basin population is equally large with more than 360×10^6 inhabitants. European basins drain an area 7-times larger than the surface of the EU coastal zone (15.2 vs. 2.2×10^6 km^2). The rivers that drain Europe are small and carry little sediment (Milliman and Meade, 1983; Milliman and Syvitski, 1992). Only the Rhône, Po and Danube Rivers appear to have annual sediment discharge rates $>10\times10^6$ t. The Danube River, by far the largest in terms of its drainage area and water discharge volume, has a sediment discharge rate of 67×10^6 t yr^{-1}. The total sediment discharge from Europe is 230×10^6 t yr^{-1}. Estimates of nutrient loads, nitrogen (DIN) and phosphorus (DIP), from European drainage basins are based on the model of Smith et al. (2003). Nutrient yield from the European Atlantic river basin is about twice the average and more than 3 times the Mediterranean Sea value. The Baltic and Black Seas are each near the

Table 3
Atmospheric attributes of all cells with at least one depth <200 m

Variable	Baltic Sea	Mediterranean Sea	Black Sea	European Atlantic	Whole of Europe
Median wind speed (m s^{-1}) [5]	7.4	6.5	–	8.3	7.2
Median of air temperature (°C) [6]	3.4	16.0	10.3	8.0	10.5
Minimum and maximum monthly averaged air temperature (°C) [7]	−11; 21.6	−8.5; 31.9	−7.4; 24.5	−15.4; 26.6	−15.4; 31.9
Median CV of 12 months average air temperature (°C) [8]	2.8	1.9	2.7	1.5	1.9
Median annual precipitation (mm yr^{-1}) [9]	720	679	671	1022	794
Minimum and maximum monthly averaged precipitation (mm) [10]	16; 222	0; 484	18; 277	0.1; 342	0; 484

Numbers in brackets refer data sources listed in the appendix available at: http://www.obs-vlfr.fr/~gattuso/ECSS_app.htm.

average. The human attributes of the coastal cells are shown in Table 6. The population density is the highest in the Mediterranean coastal area (58.5 inhabitants km^{-2}), and minimal along the Baltic coast with a value of 13.1 inhabitants km^{-2}.

3. Metabolic performances of European coastal ecosystems

3.1. Construction, content and characteristics of the database

A database was constructed using references from the Aquatic Science and Fisheries Abstracts (ASFA) database and from review papers (Charpy-Roubaud and Sournia, 1990; Smith and Hollibaugh, 1993; Heip et al., 1995; Gattuso et al., 1998; Cahoon, 1999; Cebrián, 2002; Middelburg et al., 2004). This database is available from the authors or on the World Wide Web (http://www.obs-vlfr.fr/eurotroph/). One of the striking outcomes of the literature search was that, while several hundred papers were returned for each search, a relatively small number of them could be used. Indeed, a large number of studies focused on the metabolism of single species rather than of the community. Such data were not considered here. Although budgets of air-sea CO_2 fluxes can be a reliable estimate of the trophic status of an ecosystem (Frankignoulle et al., 1998; Thomas and Schneider, 1999; Frankignoulle and Borges, 2001), this study only focuses on measured processes and LOICZ budgets. The following information has been compiled when available: latitude and longitude of the study site, time of the year, depth of the site and of sampling, salinity, temperature, nutrient concentrations, community primary production (net or gross), community respiration and the methods used to measure these processes. The database presently comprises 194 references. The database is certainly not exhaustive, but it is regularly updated. It also has a significant bias against papers published before 1978 because the ASFA database only lists references published after that date. However, our database is believed to be a relatively unbiased sample of the literature published after 1978.

The number of studies of EU coastal ecosystem function has steadily increased during the past decades (Fig. 5). The present rate of publication is about 10–15 papers per year. However, only some of these studies

Table 4
Oceanic attributes of all cells with at least one depth sounding <200 m

Variable	Baltic Sea	Mediterranean Sea	Black Sea	European Atlantic	Whole of Europe
Median of monthly averaged sea surface temperature [11]	7.7	19.5	14.7	10.6	15.3
Minimum and maximum monthly sea surface temperature [12]	−1.8; 21	6.5; 29.3	3.6; 27.2	−1.8; 24.8	−1.8; 29.3
Median of monthly averaged sea surface salinity [13]	6.4	38.1	18.0	34.9	35.2
Minimum and maximum monthly averaged sea surface salinity [14,15]	3.3; 23.1	17.7; 39.7	15; 19.1	3.3; 37	3.3; 39.7
Median wave height (scaled discrete classes) [15]	3	3	1	4	3
Median tidal range (scaled discrete classes) [16]	0	0	1	3	1

Classes for wave height are: 0 = permanent sea ice, 1 = 0–2.5 m, 3 = 2.5–3.5 m, 4 = 3.5–4.5 m, 6 = 4.5–6.5 m, 7 = >6.5 m. Classes for tidal range are: 0 = tideless, 1 = <2 m, 3 = 2–4 m, 6 = 4–8 m, 10 = >8 m. Numbers in brackets refer data sources listed in the appendix available at: http://www.obs-vlfr.fr/~gattuso/ECSS_app.htm.

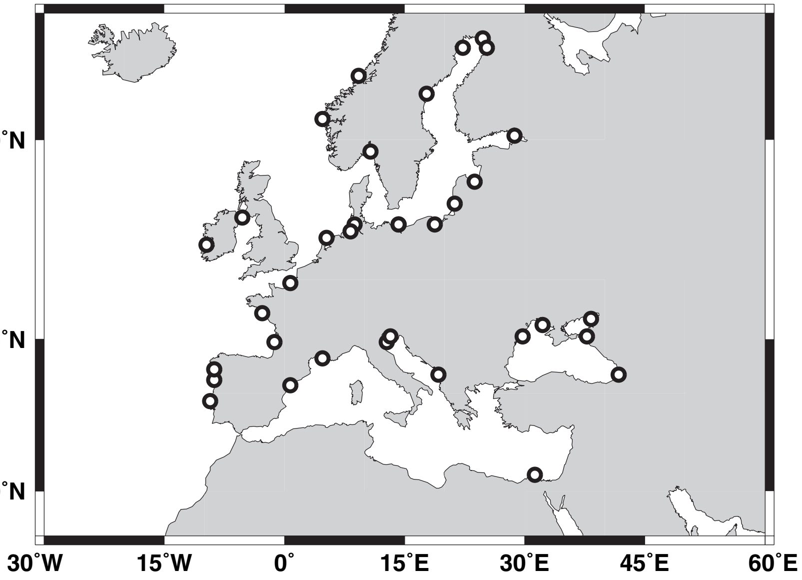

Fig. 4. Location of the 35 coastal cells that contribute most to coastal runoff.

report yearly estimates of the processes, which limits their usefulness to derive the global properties of ecosystem function.

3.1.1. Methods and collection of data

The data were obtained using a wide range of techniques: change in the concentration of a tracer (^{14}C, CO_2 or O_2) during incubations carried out in situ or under in situ simulated conditions, or using large-scale budgeting (Gordon et al., 1996), but all are expressed in mmol C $m^{-2}\,d^{-1}$. The metabolic process measurements originally reported in oxygen units were transformed into carbon units assuming that the photosynthetic and respiratory quotients equal 1. Although PQ seems to be higher than 1 in phytoplankton (Hedges et al., 2002), the paucity of available data and the general lack of recorded environmental conditions (including nutrient sources for photosynthesis) in the publications prevent assessment of the sensitivity of PQ in our evaluation.

Some papers report metabolic rates measured at only one depth and expressed in μmol C $l^{-1}\,d^{-1}$. These references were excluded from our assessment that considered only rates normalized per unit surface area, with the exception of pelagic community respiration data (see next section). A significant number of papers report hourly rates of primary production and/or respiration. Hourly pelagic and benthic respiration rates were converted into daily rates assuming constant values over 24 h. This neglects the fact that respiration can be higher in the light than in the dark in many photosynthetic organisms as reported recently for an algal-dominated reef maintained in a mesocosm (Langdon et al., 2003).

Incubations with the ^{14}C-tracer method were generally carried out around noon; multiplying these rates by the day length averaged over an annual period (12 h) can lead to an overestimation. The procedure of Cahoon (1999) was followed and a factor of 10 was used to convert hourly to daily rates for microphytobenthic gross primary production (GPP). The same approach was used for pelagic GPP estimates.

A large proportion of the annual primary production data (90% in the pelagos and 30% in the benthos) were measured using the ^{14}C technique during incubations ranging from 1 to 24 h. It is well recognized that the ^{14}C

Table 5
River basin attributes of the European coastal zone

Variable	Baltic Sea	Mediterranean Sea	Black Sea	European Atlantic	Whole of Europe
Total river basin area (10^6 km^2) [17]	1.86	8.68	2.49	2.19	15.22
Total runoff (km^3 yr^{-1}) [18]	429	788	413	793	2424
Total river basin population (10^6 inhabitants) [19]	92.6	360.8	187.2	251.8	892.4
Median river basin population density (inhabitants km^{-2}) [20]	19.14	45.44	42.0	34.1	34.3
DIN yield (10^3 mol m^{-2} yr^{-1})	10.2	6.1	11.2	20.1	9.5
DIP yield (10^3 mol m^{-2} yr^{-1})	0.5	0.3	0.6	1.1	0.5

Numbers in brackets refer data sources listed in the appendix available at: http://www.obs-vlfr.fr/~gattuso/ECSS_app.htm.

Table 6
Human attributes of coastal cells

Variable	Baltic Sea	Mediterranean Sea	Black Sea	European Atlantic	Whole of Europe
Total coastal population (million inhabitants) [21]	14.9	133.0	20.5	74.7	243.1
Coastal population density (inhabitants per km^2 land area) [22]	13.1	58.5	30.9	19.4	30.0
Cell road density (road area divided by land area in %) [23]	0.12	0.16	0.17	0.13	0.14

Numbers in brackets refer data sources listed in the appendix available at: http://www.obs-vlfr.fr/~gattuso/ECSS_app.htm.

technique measures something between gross and net primary production (Peterson, 1980), depending on the incubation time: short incubation times are closer to GPP whereas long incubation times are closer to net primary production (NPP). Only the rates of ^{14}C uptake measured over an incubation period ≤ 6 h (90% of the total number of papers reporting ^{14}C primary production) have been considered. It was assumed that they yield rates comparable to GPP estimated by the oxygen technique.

Benthic and pelagic community respiration (CR) were mainly measured by the oxygen method. In coastal areas, and especially within sediments, the oxygen concentration is sometimes too low to allow a complete aerobic mineralization of the organic matter and alternative oxidants are used through anoxic metabolic pathways (Thamdrup and Canfield, 2000). When there is no net accumulation of reduced metabolites, i.e. when anaerobic respiration products are completely reoxidized when they reach the sediment surface, the oxygen method is a reliable estimate of total mineralization processes, both aerobic and anaerobic.

Another oxygen consuming process can occur in coastal ecosystems receiving high loads of ammonium. Nitrification, the conversion of ammonium to nitrate, is the process by which chemoautotrophic bacteria obtain their energy to fix carbon. Even though this process demands significant amounts of oxygen and may lead to suboxic conditions, especially in eutrophic estuaries, it is an inefficient autotrophic process (Heip et al., 1995) and was not considered in our study. As oxygen consumption (OC) values reported in eutrophic estuaries often include both respiration and nitrification processes, OC therefore can overestimate CR.

Sub-annual rather than annual values of processes are reported in about 30% of the studies; these were excluded from our analysis (see Figs. 5 and 6).

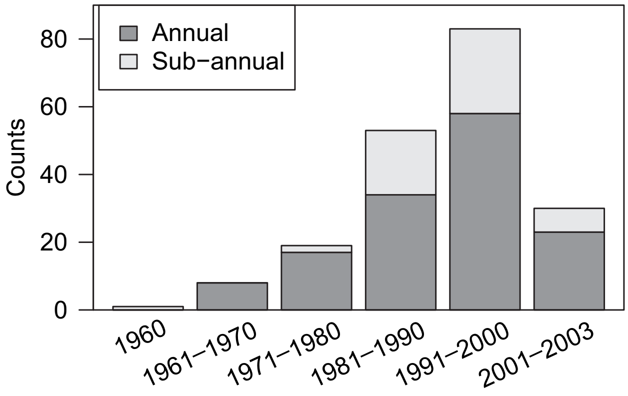

Fig. 5. Number of papers present in the database and year of publication.

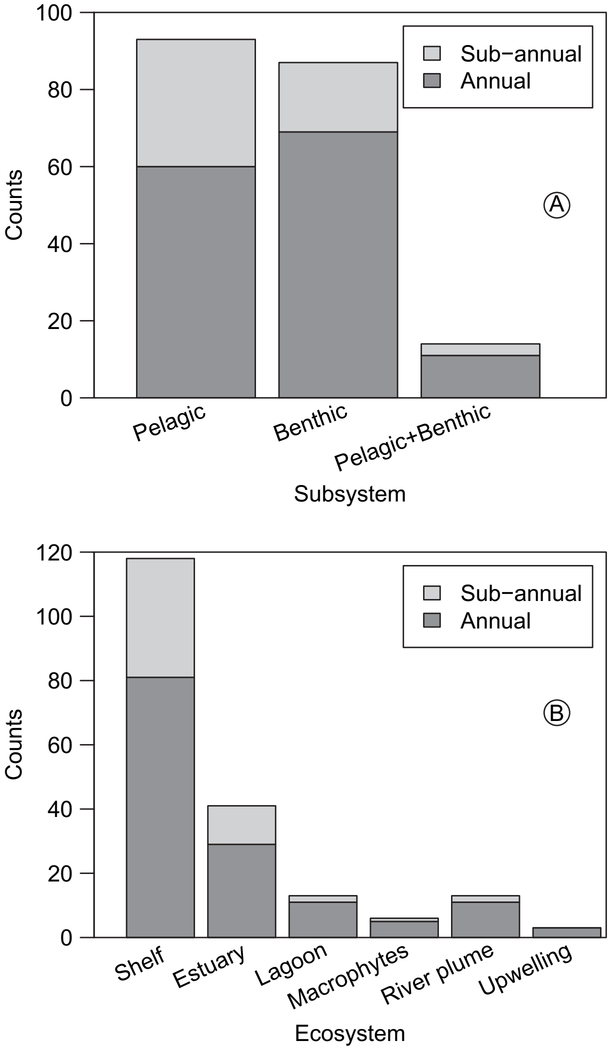

Fig. 6. (A) Number of papers according to ecosystem types. (B) Number of papers reporting annual or sub-annual metabolic data in the pelagos, benthos or both.

Use of the criteria set forth above reduced the number of usable references from 194 to 129. Additional data for pelagic GPP in the North and Baltic Seas ($n = 73$) were obtained from MADS (Den National Database for Marine Data, National Environmental Research Institute, Denmark, http://www.dmu.dk/forside_en.asp) and BIOMAD (Database on Marine Biological Monitoring Data, Department of Systems Ecology, Stockholm University, Sweden, http://www2.ecology.su.se/dbbm/index.shtml) databases.

3.1.2. Geographical location of the data and systems considered

Not surprisingly, the study sites are not evenly distributed in the EU coastal zone (Fig. 7); many more measurements are available from the North Sea and the Kattegat than elsewhere. The database has relatively few data from the Mediterranean region. Most data are concentrated on specific areas, such are river plumes; there is only one site from the northern African coast and none from the Black Sea region. About the same number of data are available for the pelagos (93 references) and for the benthos (87 references; Fig. 6A), while more importantly, relatively few studies report processes from both the water column and the benthos (14 references). The study sites were distributed across different coastal ecosystems or physiographic zones, including: estuary, river plume and macrophyte-dominated ecosystems. Study sites that could not be assigned to one of these categories were grouped in a 'shelf' category which, for our analysis, also included coastal lagoons and upwelling areas. Most data were collected from the shelf (118) and estuaries (41), with few studies from other categories (3—13; Fig. 6B).

3.2. Coastal zone systems other than estuaries

Metabolic data for the European coastal zone were considered in three regions: the Baltic Sea, Atlantic Ocean/North Sea area and the Mediterranean Sea. Each of these regions was divided into sub-regions in order to group areas sharing similar environmental settings or metabolic properties. The Kattegat was grouped with the Baltic Sea, rather than with the North Sea as was done in Section 2, to enable comparison with previous regional estimates (Wasmund et al., 2001). The surface area of the Baltic Sea sub-regions were taken from HELCOM (1996). The Black Sea was not considered because none of the publications considered met the set of criteria described above. Estuaries are considered in a separate section because they exhibit a range of variation and a magnitude of metabolic parameters much larger than other coastal systems.

3.2.1. Pelagic gross primary production

The Baltic Sea is, by far, the most documented area in term of pelagic GPP rates in our database with 83 values including 28 in published papers and 55 extracted from the MADS and BIOMAD databases. Pelagic GPP is lowest in the Belt Sea (7.9 mmol C $m^{-2} d^{-1}$; MADS database) and highest in the plume of the Oder river (96 mmol C $m^{-2} d^{-1}$; Wasmund et al., 2001). Following the procedure of Wasmund et al. (2001), the Baltic was divided into five sub-regions (see Table 7) and the main river plumes (Vistula, Daugava and Oder river plumes) were considered separately. Our database does not include data for the Bothnian Bay and Bothnian Sea, both of which are said to be the least productive areas of the Baltic Sea (Elmgren, 1984; Kautsky and Kautsky,

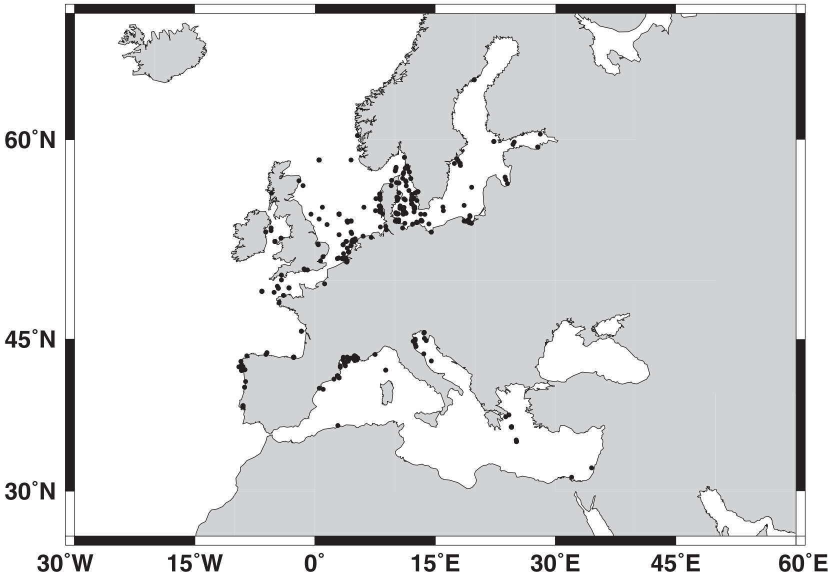

Fig. 7. Location of sites with one or more entry in the database.

Table 7
Annual pelagic gross primary production (GPP) in European coastal regions

	Annual pelagic GPP (mmol C m^{-2} d^{-1})			Area (km^2)	Ref. no.
	Mean	SD	*N*		
Baltic Sea					
Sub-regions					
Kattegat/Belt Sea	37	14	55	42508	1–7
Baltic proper	43	13	15	211069	1, 8–15
Gulf of Finland	25	5	3	29600	16–18
Bothnian Sea	12	–	1	79256	14
Bothnian Bay	4	–	1	36260	14
River plumes				–	
Vistula plume	64	4	4	–	14, 19–21
Daugava plume	68	11	3	–	14, 22
Oder plume	96	–	1	–	14
Weighted average and total Baltic Sea region	31	–	83	398693	
European Atlantic and North Sea					
Sub-regions					
North Sea	48	13	28	454832	1, 23–30
English Channel	40	18	5	71175	31–34
Irish Sea	25	7	4	107051	35–38
Atlantic coast	60	12	5	594642	39–41
Upwelling					
Ría of Vigo	110	6	2	–	42, 43
Weighted average and total European Atlantic and North Sea regions	51	–	44	1227700	
Mediterranean Sea					
Sub-regions					
Western region	20	5	8	198163	44–51
Northern Adriatic Sea	48	–	1	72536	52
Eastern region	11	5	5	172871	53–57
River plumes					
Rhône river plume	160	70	2	–	58, 59
Po river plume	134	–	1	–	52
Coastal lagoons					
Gulf of Fos	150	–	1	–	60
Berre Lagoon	59	10	2	–	51, 61
Weighted average and total Mediterranean region	21	–	20	443570	
Weighted average and total European coastal zone	41		147	2069963	

The list of references is available at http://www.obs-vlfr.fr/~gattuso/ECSS_ref.htm.

2000; Wasmund et al., 2001). Therefore, the same values as Wasmund et al. (2001) were used for the Bothnian Sea (12 mmol C m^{-2} d^{-1}) and the Bothnian Bay (4 mmol C m^{-2} d^{-1}). The highest values of GPP were found in river plume areas. Due to their relative small surface area, these ecosystems will not be included in our estimation. Indeed, Wasmund et al. (2001) reported that a separate treatment of river plumes is not necessary for whole Baltic Sea primary production estimates. Pelagic GPP of the Kattegat and Belt Sea areas, based on 55 values, reaches 37 (±14) mmol C m^{-2} d^{-1}, a value slightly lower than the one used by Wasmund et al. (2001) which was based on only one reference (43 mmol C m^{-2} d^{-1}; Heilman et al., 1994). The mean GPP of the Baltic proper (15 values; 43±13 mmol C m^{-2} d^{-1}) is higher than that of the Kattegat and Belt Sea areas and consistent with the value used by Wasmund et al. (2001) in their global estimate, and with the estimate of Shaffer (1987). The mean value found for the Gulf of Finland, based on only 3 references, is about 25 (±5) mmol C m^{-2} d^{-1}. Our database does not include data from the Neva River plume entering the Gulf of Finland which was therefore excluded from our study. Considering the surface area and GPP values for each of these sub-regions, a weighted average of the whole Baltic Sea pelagic GPP of 31 mmol C m^{-2} d^{-1} is proposed. Wasmund et al. (2001) proposed a pelagic GPP of 34 mmol C m^{-2} d^{-1} for the whole Baltic Sea, based on their measurements between 1993 and 1997 in the south-eastern Baltic Sea as well as data from literature. The pelagic GPP values reported by Elmgren (1984) are also consistent with our estimate.

In the Atlantic/North Sea region, 44 values were found including 18 extracted from the MADS database. The lowest value was reported for western Scotland (16 mmol C m^{-2} d^{-1}; Wood et al., 1973) and the highest for Ría de Vigo, an upwelling area in north-western Spain (114 mmol C m^{-2} d^{-1}; Moncoiffé et al., 2000). This region was divided in 4 areas: North Sea, English Channel, Irish Sea and Atlantic coast. The North Sea is the most documented area in this region (28 measurements) but no data were found for the northern part; its mean GPP is 48 (±13) mmol C m^{-2} d^{-1} (Table 7). The mean GPP of the English Channel is about 40 (±18) mmol C m^{-2} d^{-1} (5 values). The Irish Sea is the least productive area in north-western Europe with a mean value of 25 (±7) mmol C m^{-2} d^{-1} based on four annual measurements. Upwelling areas should be considered separately but this is not possible at this stage because of the lack of data and also the unknown surface area covered by upwellings in European waters. Data from the Ría of Vigo were therefore excluded from the analysis in order to avoid a bias. The average annual value for the Atlantic coast is about 60 (±12) mmol C m^{-2} d^{-1}. A surface-weighted average pelagic GPP for the Atlantic/North Sea region of 51 mmol C m^{-2} d^{-1} was estimated. To the best of our knowledge, this is the first global estimate of pelagic GPP available for the region. In their review, Reid et al. (1990) estimated 40, 57 and 46 mmol C m^{-2} d^{-1}, respectively in the northern, central and southern North Sea. Also, Joint and Pomroy (1993) gave regional estimates based on the

ICES sub-divisions of the North Sea, but their measurements (from 24 h incubations) were closer to NPP than GPP and thus, are not comparable with our estimate.

The Mediterranean Sea was divided into three basins: western (excluding the Rhône River plume), northern Adriatic Sea (excluding the Po River plume) and eastern basins. Pelagic GPP in the region is low, especially in the eastern basin which was characterized by Azov (1991) as a 'marine desert' resulting from phosphorus deficiency (Krom et al., 1991). The lowest value was found near the Israeli coast (4.3 mmol C $m^{-2} d^{-1}$; Berman and Townsend, 1984) and the highest in the Cretan Sea (18 mmol C $m^{-2} d^{-1}$; Psarra et al., 2000). The mean GPP for this area is based on 5 references and reaches a value of 11 (±5) mmol C $m^{-2} d^{-1}$ (see Table 7). The northern Adriatic Sea is one of the most productive areas in the Mediterranean (Sournia, 1973), with a production rate of about 48 mmol C $m^{-2} d^{-1}$. It receives the discharge from the Po River and phosphorus recycling is supposed to be very fast, decreasing the phosphorus limitation in this part of the Mediterranean Sea (Ivancic and Degobbis, 1987). The plume of the Po River has a very high production rate (134 mmol C $m^{-2} d^{-1}$; Puddu et al., 1998). The north-western basin is the most documented in our database, with the lowest GPP reported along the Spanish coast (16 mmol C $m^{-2} d^{-1}$; Margalef and Ballester, 1967; San Feliu and Muñoz, 1970) and the highest in the Rhône dilution plume (205 mmol C $m^{-2} d^{-1}$; Lefèvre et al., 1997). In their recent review, Lefèvre et al. (1997) made an extensive compilation of available primary production data in the Gulf of Lions, dividing the coastal zone of this sub-region into three provinces based on hydrological features: (1) the Gulf of Marseille with a GPP of 20 mmol C $m^{-2} d^{-1}$, (2) the Rhône River plume with very high values (70–340 mmol C $m^{-2} d^{-1}$) and (3) the 'Rhône River dilution zone' with intermediate rates (26 mmol C $m^{-2} d^{-1}$). Furthermore, these authors reported no significant increase in GPP over the last 30 years, indicating that this part of the Mediterranean Sea is less influenced by catchment-based human activities than other coastal areas of Europe. The mean GPP (excluding the Rhône River plume) estimated from our database for this area is based on eight references and reaches a value of 20 (±5) mmol C $m^{-2} d^{-1}$ (see Table 7). Coastal lagoons in this region exhibit higher production rates, i.e. 150 and 59 mmol C $m^{-2} d^{-1}$ for the Gulf of Fos and the Berre lagoon, respectively (Minas, 1976; Kim, 1983; Barranguet et al., 1996), and considering their small area, are not considered in our global estimate. A wider study of the metabolic performance of coastal lagoons adjacent to the Mediterranean Sea is in progress using the LOICZ approach; see the LaguNet web site at http://www.dsa.unipr.it/lagunet/. The present version of the database does not include any data from the south-western basin. One data point was found (46 mmol C $m^{-2} d^{-1}$; Tellaï, 1969) but it was not included in the database because the original paper is not available to us and the data, obtained from a secondary source, could not be checked. Weighing these rates according to the surface areas represented by each sub-region, yielded a first estimation of pelagic GPP (21 mmol C $m^{-2} d^{-1}$) for the coastal Mediterranean Sea, confirming its oligotrophic status (Nixon, 1995).

Thus, a pelagic GPP in European coastal waters of about 41 mmol C $m^{-2} d^{-1}$ was estimated (see Table 7 and Fig. 8A for frequency distribution). Smith and Hollibaugh (1993), Wollast (1998) and Gattuso et al. (1998) estimated the global GPP of continental shelves as 37, 46 and 49 mmol C $m^{-2} d^{-1}$ respectively. Our estimate for European open coastal waters is consistent with these global estimates.

Most of the primary production values used in this review were estimated by the ^{14}C-tracer method and the difficulties for interpreting these data were discussed above. Moreover, almost all studies dealt only with particulate primary production. It is now well accepted that dissolved compounds released by phytoplankton can represent a significant portion of the produced organic matter. Indeed, Holligan (1989), Morán et al. (2002), Witek et al. (1999), and Larsson and Hagström (1982) reported dissolved primary production values of 10%, 16%, 5% and 14% of the total primary production in the North Sea, the north-western Mediterranean Sea, Gulf of Gdánsk and Baltic proper, while very high rates (up to 30%) were recorded in summer in the Gulf of Finland (Kuparinen, 1987). Dissolved production by phytoplankton on a global scale remains poorly known, but Morán et al. (2002) found a significant inverse relationship between PER (percent extracellular release) and total system productivity whereby there is higher PER in oligotrophic environments, confirming earlier results from Fogg (1983). Data on the relative contributions of dissolved and particulate production to GPP are too scarce to attempt an estimation of the importance of dissolved production in our value of GPP. However, our estimates clearly underestimate GPP, especially in low productivity waters, such as the eastern Mediterranean and Baltic Seas regions.

3.2.2. *Microphytobenthic gross primary production*

Fewer annual studies of benthic GPP in coastal areas of Europe were found in the literature compared with pelagic GPP. The database presently comprises 40 annual measurements (both in shallow and deep areas), but study sites are not well distributed within the region of interest. For instance, as already reported by Cahoon (1999), no data were found for the entire eastern Mediterranean Sea nor for the eastern Baltic Sea. Presumably these two regions have low GPP values due to light limitation in the eastern Baltic and nutrient limitation in the eastern Mediterranean Sea. Such lack of information

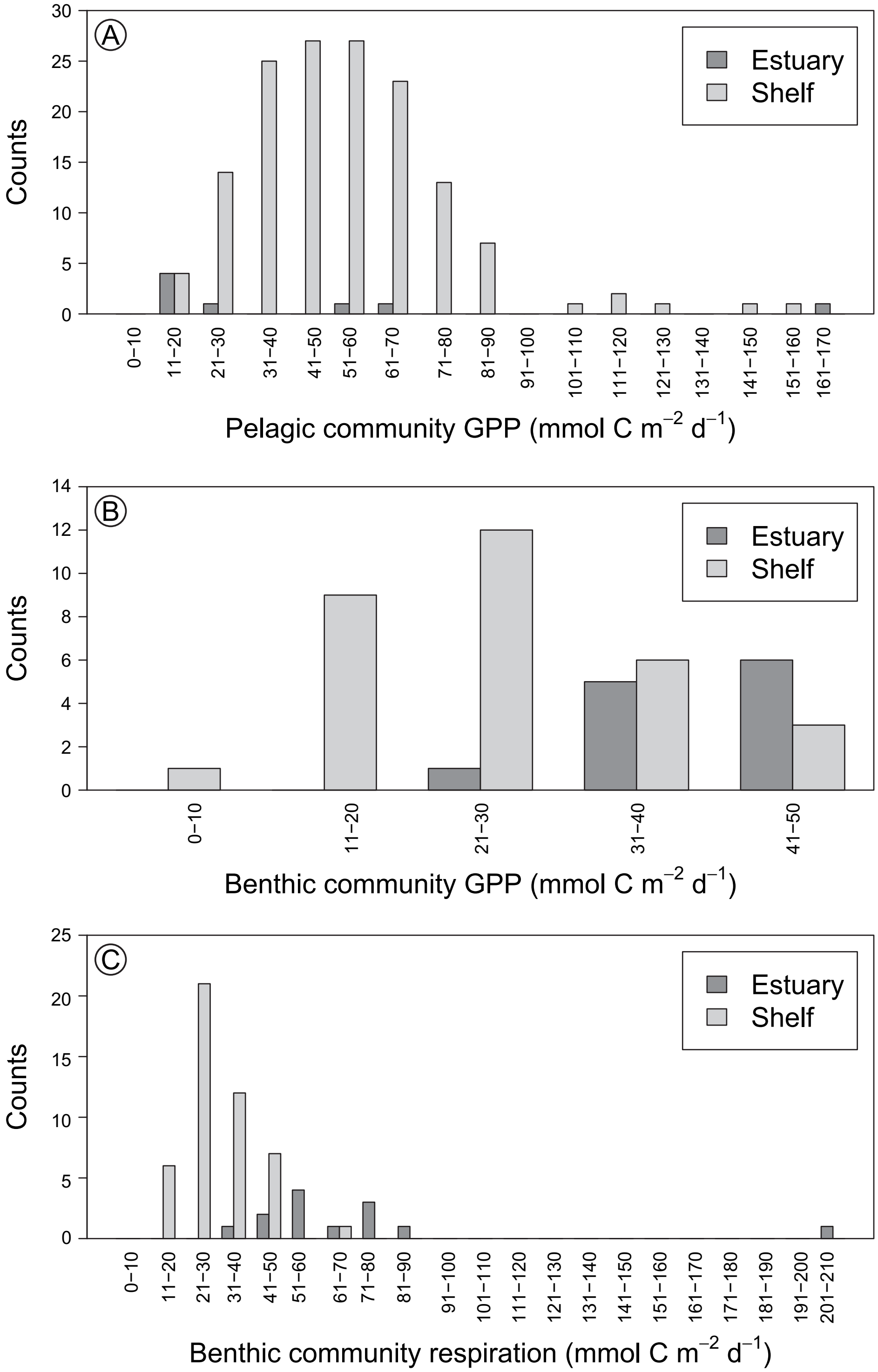

Fig. 8. Frequency distribution of (A) pelagic gross primary production, (B) benthic gross primary production, and (C) community respiration in estuaries (black bars) and open shelf systems (open bars).

of course will negatively affect upscaling. In contrast with data on pelagic GPP, most of the studies are based on the oxygen method (70%).

Calculation of depth-integrated GPP requires either data across the depth range or information on the decrease of GPP as a function of depth, the deepest benthic production (6 mmol C m^{-2} d^{-1}) being measured in the Gulf of Trieste at a depth of 22 m (Herndl et al., 1989). However, very few studies have investigated the decrease of GPP with depth although benthic GPP is assumed to occur at depths greater than 20 m (Cahoon, 1999). Data for the three major regions show different

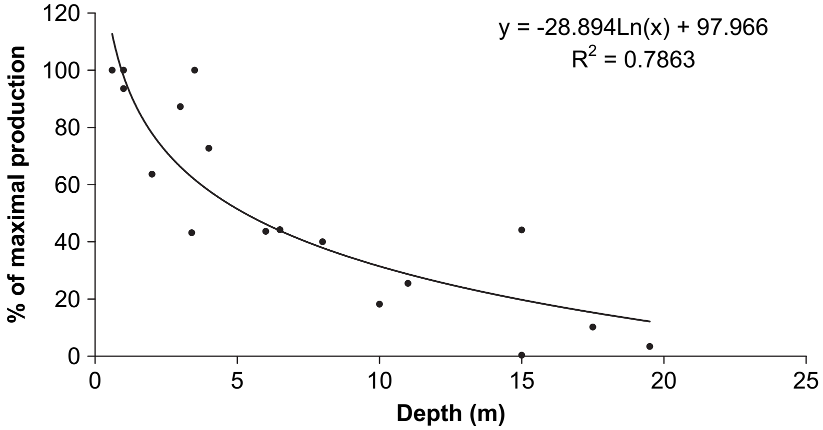

Fig. 9. Decrease with depth of microphytobenthic gross primary production (GPP) in the Baltic Sea, based on data from Gargas (1970), Sundbäck and Jönsson (1988), and Meyercordt and Meyer-Reil (1999).

depth ranges; 22 m in the Mediterranean Sea and 20 m in the Baltic Sea regions, but only 5 m in the Atlantic/North Sea region. In the latter and the Baltic Sea regions, the same function for decrease of benthic GPP with depth was used. Depth-integrated (0–200 m) GPP was calculated by the relationship between GPP (% of maximal value) and depth (see Fig. 9) derived in the Baltic Sea using data from Gargas (1970), Sundbäck and Jönsson (1988), and Meyercordt and Meyer-Reil (1999): $\%P_{max} = -28.894 \times \mathrm{LN}\ (\mathrm{Depth}) + 97.966$ ($r^2 = 0.7863$, $P < 0.01$, $n = 17$; LN is the natural logarithm).

In the Mediterranean Sea, where water column turbidity is lower, GPP was estimated at three depth ranges (0–5 m, 5–10 m and 10–30 m) from published data, and the depth-integrated GPP (0–200 m) was calculated assuming that GPP is 0 below 30 m.

Benthic GPP exhibits high geographical variations in the Baltic Sea, with no production found at 3.4 m in Kirr-Bucht, Darss-Zingst Bodden, southern Baltic Sea (Meyercordt and Meyer-Reil, 1999) and the highest value reported in Faellesstrand lagoon, Denmark (34 mmol C m^{-2} d^{-1}; Kristensen, 1993). Thus, the shallow (0–5 m) benthic production for this region (14±12 mmol C m^{-2} d^{-1}, Table 8) must be taken with caution. Averaged over the 0–20 m zone and weighted by the surface of the coastal areas with depths <20 m, the average microphytobenthic GPP of the Baltic Sea is about 2 mmol C m^{-2} d^{-1} (Table 8), only 4% of the pelagic GPP. Our estimate is lower than that of Cahoon (1999) (4 mmol C m^{-2} d^{-1}) but similar to that of Elmgren (1984) (1.2 mmol C m^{-2} d^{-1}) for the whole Baltic Sea benthic compartment (including the macrophytobenthos).

The Atlantic/North Sea and Mediterranean regions are less documented than the Baltic Sea. Both regions exhibit low variation, with mean values of 22 (±5) mmol C m^{-2} d^{-1} and 16 (±6) mmol C m^{-2} d^{-1} in shallow areas of the Atlantic/North Sea and Mediterranean Sea regions (Table 8 and Fig. 8B for frequency distribution). Using the relationship described above, a microphytobenthic GPP in the Atlantic/North Sea of about 1 mmol C m^{-2} d^{-1} (2% of the pelagic GPP) was estimated.

It must be stressed that few data are available for the Mediterranean Sea region and may not be representative of the whole area. The average benthic GPP in the Mediterranean Sea declines from 16 (±6) mmol C m^{-2} d^{-1} in the depth range 0–5 m to 5 (±1) mmol C m^{-2} d^{-1} at 10–30 m (Table 8). The depth-integrated benthic GPP is around 2.5 mmol C m^{-2} d^{-1} in the Mediterranean Sea (13% of pelagic GPP), lower than the value estimated by Cahoon (1999) (4 mmol C m^{-2} d^{-1}). Cahoon (1999) and Charpy-Roubaud and

Table 8
Annual microphytobenthic gross primary production (GPP) in European coastal regions

	Annual microphytobenthic GPP (mmol C m^{-2} d^{-1})			Area (km^2)	Ref. no.
	Mean	SD	N		
Baltic Sea					
0–5 m	14	12	17	61706	2, 13, 62–68
0–200 m	2	–	–	398693	
Atlantic/North Sea					
0–5 m	22	5	8	55750	27, 69–74
0–200 m	1	–	–	1227700	
Mediterranean Sea					
0–5 m	16	6	5	35632	60, 75, 76
5–10 m	11	9	2	16565	60, 77
10–30 m	5	1	3	71625	60, 77
0–200 m	2.5			443570	
Weighted average and total European coastal zone	1.5	–	–	2069963	

The list of references is available at http://www.obs-vlfr.fr/~gattuso/ECSS_ref.htm.

Sournia (1990) reported mean values of benthic primary production for worldwide temperate shallow areas (all ecosystem types included) of around 20 mmol C $m^{-2} d^{-1}$ and 23 mmol C $m^{-2} d^{-1}$, respectively. Our estimate (mean value for the 0–5 m depth range in European coastal waters: 17 mmol C $m^{-2} d^{-1}$) is slightly lower, and certainly due to our separate consideration of shelves and estuaries which present higher production values (see next section).

Finally, the average microphytobenthic GPP along European coastlines (0–200 m) is about 1.5 mmol C $m^{-2} d^{-1}$ (Table 8; 3.6% of pelagic GPP), lower than values estimated for worldwide continental shelves by Cahoon (1999) for temperate regions and Charpy-Roubaud and Sournia (1990).

3.2.3. *Macrophytobenthic net primary production*

Macrophyte (seagrass and macroalgae) beds are expected to be very productive areas. Indeed, Charpy-Roubaud and Sournia (1990) reported NPP values in temperate regions from 100 to >450 mmol C $m^{-2} d^{-1}$, mainly from intertidal or shallow areas. They estimated a production value in the 0–50 m depth fringe of about 170 mmol C $m^{-2} d^{-1}$ (vs. 11 mmol C $m^{-2} d^{-1}$ for microphytobenthos), but their procedure for estimating the decrease in production with depth is not clear.

GPP by macrophytes was not uspscaled to the whole European coastal zone for three reasons: (i) very few annual studies were found in the literature for these areas (five to date), (ii) the distribution and production of macrophytes along the depth gradient is not resolved and (iii) the surface area covered by macrophytes in Europe is not yet estimated (Duarte, personal communication, 2003).

Also primary production by macrophytes seems to be relatively small in several European coastal systems. Wasmund (1986) estimated that micro- and macrophytobenthos contribute 7% of total NPP in shallow coastal lagoons of the Baltic Sea and Elmgren (1984) attributed 3% of total NPP to phytobenthos in the whole Baltic Sea. In the Wadden Sea (North Sea), where tidal flats represent approximately 50% of the surface area (Cadée and Hegeman, 1974), macroalgal production is negligible (Cadée, 1980).

The surface area potentially covered by the seagrass *Posidonia oceanica* in the Mediterranean Sea is about 0.035×10^6 km^2 (Pasqualini et al., 1998), or only 8% of the surface area of the Mediterranean coastal zone. This value is similar to that of Whittaker and Likens (1975) for the global distribution of macrophytes. The depth-integrated (0–200 m) NPP (leaves plus rhizomes) for *P. oceanica* is about 1 mmol C $m^{-2} d^{-1}$ in the coastal Mediterranean Sea, based on data for 22 sites at three different depths (Pergent-Martini et al., 1994) and for the Bay of Calvi (Corsica) at 30 m (Bay, 1984) (see Table 9 for calculation details). It is difficult to compare this value to the total (pelagic+benthic) net primary production in the Mediterranean Sea region but, assuming that phytoplankton and microphytobenthos respiration (R) ranges between 5 and 50% of GPP, the contribution of *P. oceanica* to the total NPP was estimated to lie between 5 and 10%. This value contrasts strongly with the 40% of total NPP estimated for worldwide continental shelves (Charpy-Roubaud and Sournia, 1990).

Table 9
Annual net primary production by *Posidonia oceanica* (leaves plus rhizomes) in the Mediterranean coastal area based on values from Pergent-Martini et al. (1994) at 5, 10 and 20 m and Bay (1984) at 30 m

Depth range (m)	Measured depth (m)	Annual NPP (mmol C $m^{-2} d^{-1}$)[a]	Area[b] (km^2)
0–7.5	5	73 (53–93)	3173
7.5–15	10	45 (35–55)	2340
15–25	20	20 (18–22)	2725
25–35	30	13.2[c]	2318
Weighted average and total Mediterranean Sea region	0–200	1	445883

[a] Assuming a dry weight carbon content of 40% (Mateo and Romero, 1997).

[b] Assuming that 8% of the Mediterranean coastline is covered by *P. oceanica* (Pasqualini et al., 1998).

[c] Leaf blades NPP was reported (12.4 mmol C $m^{-2} d^{-1}$). According to Pergent-Martini et al. (1994), rhizomes NPP represents 6.4% of leaf NPP.

3.2.4. *Pelagic community respiration*

Very few measurements of depth-integrated community respiration (CR) based on the oxygen incubation method, even in the euphotic zone, were found during our compilation of data. Moreover, in contrast to primary production, planktonic CR occurs throughout the water column (Williams, 1984), and it is therefore not possible to compare rates integrated over different depth ranges. Consequently, CR is shown in volumetric units in Table 10 (μmol C $l^{-1} d^{-1}$) when directly measured by the oxygen bottle method in the euphotic or aphotic zone (two references only for the latter). When only integrated values were reported, these were divided by the depth of the water column, assuming a constant rate over that depth range.

In the Baltic Sea, measurements of pelagic CR were made in the euphotic zone of the Gulf of Finland (Kuparinen, 1984; Kuparinen, 1987). These data, together with the GPP data discussed above, enable estimation of how much of GPP is remineralized in the upper water column. The euphotic CR represents 34% of the pelagic GPP integrated over the euphotic layer (10 m; GPP = 25 mmol C $m^{-2} d^{-1}$). Therefore, net community production (NCP = GPP−CR) in the euphotic zone is 66% of pelagic GPP. Furthermore, Kuparinen et al. (1984) speculated that pelagic CR in the aphotic zone

Table 10
Annual pelagic community respiration (CR) in European coastal regions

Region	Depth layer (m)	Annual pelagic CR (μmol C l^{-1} d^{-1})	Ref. no.
Baltic Sea			
Gulf of Finland	Euphotic (0–10 m)	0.9	16
Gulf of Finland	Euphotic (0–10 m)	0.8	17
Gulf of Gdánsk	Euphotic (0–7 m)	14.8	78
Gulf of Gdánsk	Euphotic (2.5 m)	11.2	79
Kattegat	Aphotic (15–30 m)	1.3	80
Kattegat	Aphotic (15–25 m)	2.2	4
Pomeranian Bay	Epipelagique (0–20 m)	4.3	15
Gulf of Gdánsk	Water column	2.7	19
Atlantic/North Sea			
North Sea	Euphotic (15 m)	2.6	81
North Sea	Water column (0–50 m)	2.4	82
Bay of Biscay	Euphotic (0–20 m)	1.8	41
Ría de Vigo	Euphotic (0–12 m)	4	42
Mediterranean Sea			
Bay of Blanes	Euphotic (15 m)	5.2	83
Bay of Calvi	Euphotic (0–15 m)	6.2	84
Gulf of Lions	Euphotic (0–60 m)	3.5	58

The list of references is available at http://www.obs-vlfr.fr/~gattuso/ECSS_ref.htm.

(>10 m) is 50% of the euphotic NCP (30% of pelagic GPP). Thus, the amount of organic matter remineralized in the whole water column is about 70% of pelagic GPP. This result is consistent with the one found by Elmgren (1984) who used data from sediment traps in the whole Baltic Sea to estimate organic matter utilization in the whole water column of about 60% of pelagic GPP. Rydberg et al. (1990) estimated CR rates in aphotic deep waters of the south-eastern Kattegat. Based on their results and pelagic GPP estimated for this region (36 mmol C m^{-2} d^{-1}), the amount of organic matter remineralized in the aphotic deep-water column is estimated to 30%. In the same area, using data from Granéli (1992), a somewhat higher value of 45% of pelagic GPP was found. Based on indirect methods in the Baltic proper, Shaffer (1987), Rahm (1987), and Pers and Rahm (2000) estimated organic matter mineralization in aphotic deep-waters below the $S=8$ isohaline of 12, 11.5 and 10.5 mmol C m^{-2} d^{-1} ($RQ=1$). This corresponds to about 25% of the pelagic GPP for this region and is consistent with the value found by Olesen and Lundsgaard (1995) in the Kattegat.

CR is much higher in the Gulf of Gdánsk (Witek et al., 1997; Witek et al., 1999; York et al., 2001) and the Pomeranian Bay (Witek et al., 2001), especially in surface waters. These systems receive high loads of organic matter from the Vistula and Oder rivers and CR integrated over the entire water column is higher than autochthonous production of organic matter over most of the year.

In the Atlantic/North Sea region, only four annual values were found, all measured in the euphotic zone. The lowest value was found in the Bay of Biscay (1.8 μmol C l^{-1} d^{-1}; Serret et al., 1999) and the highest value in the upwelling area of the Ría de Vigo (4 μmol C l^{-1} d^{-1}; Moncoiffé et al., 2000). CR data for the Mediterranean Sea region are high with the highest value reported for the Bay of Calvi (6.2 μmol C l^{-1} d^{-1}; Velimirov and Walenta-Simon, 1992). As these data were obtained in areas supporting relatively high rates of pelagic and benthic GPP, they may not be representative of the Mediterranean Sea region as a whole.

Measurements of pelagic CR in the European coastal zone are clearly too sparse to yield an accurate picture of the fate of organic matter produced in the water column. However, previous considerations of the Baltic Sea (excluding river plumes and mainly based on indirect methods) suggest that roughly 60% of pelagic GPP is consumed in the water column (30% in the euphotic and 30% in the aphotic zones). This is higher than previous estimates of coastal mineralization rates (Gattuso et al., 1998; Wollast, 1998) that indicate only 30% of the autochthonous production is consumed in the water column.

3.2.5. *Benthic community respiration*

The average benthic CR in the Atlantic/North Sea and Baltic Sea regions are 16 (±8, $n=17$) and 17 mmol C m^{-2} d^{-1} (±8, $n=20$; Table 11). Benthic CR rates from literature are not well distributed within regions, especially in the Baltic Sea where no data were found for the entire eastern Baltic Sea (Baltic proper, Gulf of Finland, Bothnian Sea and Bothnian Bay). Respiration rates are temperature-dependent but also controlled by the quality and quantity of organic matter available. Thus, lower rates should be found in these low productive regions, and our value of 17 mmol C m^{-2} d^{-1} may be slightly overestimated.

As with other metabolic parameters, few benthic CR measurements have been conducted in the Mediterranean Sea region (10 data points or sets were found), the most documented area being the northern Adriatic Sea (6 values) but no data were found for the most oligotrophic part (eastern basin). Thus, our estimates should be considered tentative and subject to uncertainty. The highest benthic CR rates were reported in coastal lagoons, Thau lagoon (31 mmol C m^{-2} d^{-1};

Table 11
Annual benthic community respiration (CR) in European coastal regions

	Annual benthic CR (mmol C $m^{-2} d^{-1}$)			Area (km^2)	Ref. no.
	Mean	SD	*N*		
Baltic Sea	17	8	20	398693	4, 13, 19, 66–68, 80, 85–90
North Sea/Atlantic	16	8	17	1227700	28, 38, 87, 91–97
Mediterranean Sea	22	6	10	443570	60, 76, 77, 98–101
Weighted average and total European coastal zone	17			2069963	

The list of references is available at http://www.obs-vlfr.fr/~gattuso/ECSS_ref.htm.

Barranguet et al., 1994) in France and Saca di Goro (55 mmol C $m^{-2} d^{-1}$; Bartoli et al., 1996) in the northern Adriatic Sea. The benthic CR for the entire Mediterranean Sea region weighted according to surface area is 22 mmol C $m^{-2} d^{-1}$. The weighted average of the three regions provides a benthic CR value of 17 mmol C $m^{-2} d^{-1}$ for shelf areas in Europe (see also Fig. 8C for frequency distribution).

Based on a global benthic CR dataset, Middelburg et al. (2004) proposed a similar value for global coastal benthic CR (17 mmol C $m^{-2} d^{-1}$). Gattuso et al. (1998) and Wollast (1998) reported benthic mineralization of about 30% of pelagic GPP. The benthic CR rate estimated in our study represents 40% of the estimated pelagic GPP (41 mmol C $m^{-2} d^{-1}$). It should be noted that almost all the compiled data were collected in shallow areas where available organic matter and the rate of mineralization are probably higher. Since the ratio benthic:pelagic mineralization decreases with increasing depth (Jørgensen, 1983; Heip et al., 1995), a significant overestimation might be expected. On the other hand, several studies showed that the oxygen method can strongly underestimate total carbon mineralization rates in low oxygen environments because reduced metabolites cannot be completely reoxidized. For instance, Jørgensen (1982) estimated that sulfide burial resulting from net sulfate reduction can represent 10% of carbon mineralization. Overall, our estimate that benthic CR is 40% of pelagic GPP is the best present estimate of benthic mineralization in European coastal areas.

3.3. *Estuaries*

Estuaries are the main transition zone between the freshwater of the land and the salt water of the oceans (Heip et al., 1995). Receiving high amounts of nutrient, organic matter and suspended particles, estuaries are extremely dynamic systems usually characterized by strong physico-chemical gradients, enhanced biological activity, and intense sedimentation and resuspension (Ketchum, 1983). Our database contains metabolic values from 29 papers in which benthic measurements (GPP and CR) represent almost 70% of available annual values. One of the striking outcomes (Table 12 and Fig. 8) is the strong variability in pelagic GPP compared to intertidal or shallow benthic GPP. Pelagic values range from 1.7 (Ems-Dollard estuary; Van Es, 1977) to 153.3 mmol C $m^{-2} d^{-1}$ in the highly productive Urdaibaï estuary (Revilla et al., 2002). The smaller range of benthic GPP extends from 22.3 mmol C $m^{-2} d^{-1}$ in the Colne River estuary (Thornton et al., 2002) to 37.8 mmol C $m^{-2} d^{-1}$ in the western Scheldt estuary (Barranguet et al., 1998). The average benthic GPP of 31 (±5) mmol C $m^{-2} d^{-1}$ is almost twice the benthic GPP estimated in intertidal or shallow open shelf areas (see previous section). This supports our approach of investigating and synthesizing separately the open shelves and

Table 12
Annual community metabolism rates in European estuaries (mmol C $m^{-2} d^{-1}$)

Site	Pelagic GPP	Benthic GPP	Pelagic CR	Benthic CR	Ref. no.
Western Scheldt	40.4	–	–	–	102
Western Scheldt	–	31	–	–	103
Western Scheldt	52.7	–	–	–	104
Western Scheldt	–	37.8	–	–	105
Western Scheldt	–	–	–	194.2	106
Eastern Scheldt	75.7	–	–	–	107
Eastern Scheldt	–	35.6	–	–	108
Ems-Dollard	1.7	26.7	20.8	44.7	109
Ems-Dollard	–	36	–	40.5	110
Ems-Dollard	–	22.6	–	–	111
Ems-Dollard	3	–	–	–	69
Ems-Dollard	–	36.4	–	47.5	112
Norsminde Fjord	–	–	–	40.1	113
Norsminde Fjord	–	–	–	52	114
Limforden	–	–	–	34	115
Bristol Channel	17	–	–	–	116
Ythan	–	26.5	–	–	117
Lynher	18.5	32.6	–	–	118
Thames	–	–	–	64	119
Colne	–	22.3	–	65.1	120
Colne	2	–	–	–	121
Southampton water	40.4	–	–	–	34
Great Ouse	–	–	–	79.5	122
Great Ouse (Upper)	–	–	–	64	123
Urdaibai	153.3	–	84.4	–	124
Douro	–	30	–	26.4	125
Tagus	–	35.6	–	–	126
Tagus	–	–	–	37.5	127
Elbe	–	26.4	–	–	128
Mean (SD)	40 (47)	31 (5)	53 (45)	61 (43)	
n	10	13	2	13	

The list of references is available at http://www.obs-vlfr.fr/~gattuso/ECSS_ref.htm.

estuaries values. Moreover, the high values and the small variation in benthic GPP between estuaries suggest that most of the systems studied were eutrophic and not nutrient limited. It is noteworthy that all measurements were made on intertidal or very shallow sediments where there was little or no light limitation. Extrapolating these rates over the whole surface area of each estuary will lead to a much greater variation in values, reflecting differences in geomorphology (e.g. relative surface area of shallow and deep water) and light availability at the seafloor. This also suggests that GPP in the pelagic compartment of estuaries is mainly driven by physical parameters such as residence time, turbidity and vertical stratification rather than by nutrient concentrations (Boynton et al., 1982; Heip et al., 1995). Moreover, the production of organic matter by chemoautotrophic bacteria such as nitrifiers, which are reported to be very active in eutrophic estuaries (Heip et al., 1995), was not taken into account. van Spaendonk et al. (1993) estimated primary production by these organisms as 32% of the total primary production in the inner Scheldt estuary. The importance of this process generally decreased seaward, becoming negligible relative to phytoplankton production (Heip et al., 1995).

With only two references of depth-integrated pelagic CR (Van Es, 1977; Revilla et al., 2002), it is difficult to provide any conclusion about its magnitude in European estuaries. In contrast to benthic GPP, benthic CR exhibits large variability between sites with minimal values in estuaries of the Portuguese coast (Cabrita and Brotas, 2000; Magalhães et al., 2002) and a very high mean annual rate in the Scheldt estuary (Middelburg et al., 1996). Intermediate values (60–80 mmol C $m^{-2} d^{-1}$) were found in estuaries along the English coast (Colne, Great Ouse and Thames rivers). The average benthic CR in estuaries (61 ± 43 mmol C $m^{-2} d^{-1}$) is much higher than that on open shelves (17 mmol C $m^{-2} d^{-1}$, see previous section). Almost all the benthic CR data were measured in intertidal or very shallow areas. Benthic CR should decrease with increasing depth because of the absence of microphytobenthos and a decrease in available organic matter due to decomposition in the water column.

3.4. Metabolic balance

In this section, the metabolic balance (NCP) in both the pelagic and benthic compartments of open shelf areas and estuaries is examined, and 19 papers reporting such data in the European coastal zone were found. GPP is plotted as a function of CR in Figure 10. The data points above the 1:1 line are autotrophic with respect to carbon, whereas, those below that line are heterotrophic. Pelagic metabolic values for both open shelves and estuaries were integrated over the entire euphotic zone or the water column, if the depth was less than the euphotic zone. The database contains nine values of annual pelagic NCP for open shelf areas. Three sites had a heterotrophic euphotic zone, with minimal NCP in the Gulf of Gdánsk (−37 mmol C $m^{-2} d^{-1}$; Witek et al., 1999). The most productive area is the upwelling in the Ría de Vigo with a NCP of 65 mmol C $m^{-2} d^{-1}$. Large variations in the GPP/CR ratio in European shelves (1.5 ± 0.9) prevent any meaningful upscaling. Moreover, the pelagic GPP/CR ratio is certainly lower as this estimate only addresses the euphotic zone.

Only two studies of the metabolic balance in pelagic compartment of estuaries were found in the literature. The water column of the Urdaibaï estuary is autotrophic on an annual basis with a NCP of nearly 70 mmol C $m^{-2} d^{-1}$ (Revilla et al., 2002) while Van Es (1977) reported a value of −20 mmol C $m^{-2} d^{-1}$ in the Ems-Dollard estuary. This is clearly insufficient data from which to draw conclusions about the metabolic balance in European estuaries.

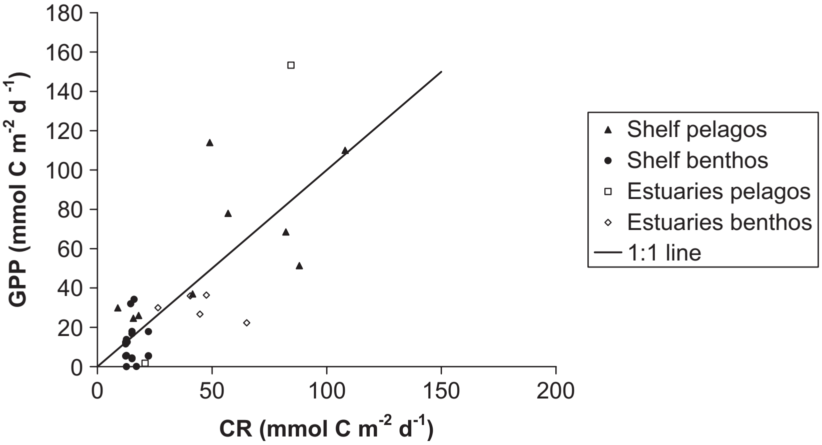

Fig. 10. Community gross primary production (GPP) as a function of community respiration (CR) in the benthos and pelagos of European estuaries and shelf environments.

A strong variation is also observed in the benthic compartment of shallow (0–5 m) European coastal areas (GPP/CR = 0.8 ± 0.7) with a minimal NCP reported in Kirr-Bucht (Darss-Zingst Bodden), a coastal lagoon of the south-western Baltic Sea (−17 mmol C $m^{-2}\,d^{-1}$; Meyercordt et al., 1999), and a maximal value in the west coast of Sweden (18 mmol C $m^{-2}\,d^{-1}$; Sundbäck and Miles, 2000).

Based on our global estimations of benthic GPP and CR over the 0–200 m depth range, benthic NCP is −15 mmol C $m^{-2}\,d^{-1}$ in the Baltic Sea and Atlantic/North Sea regions and −19.5 mmol C $m^{-2}\,d^{-1}$ in the Mediterranean Sea. These values must be considered as preliminary, considering the uncertainty in the estimation of both benthic GPP and CR due to the relatively poor spatial distribution especially in the Mediterranean Sea. Only one estuarine benthic area was found to be net autotrophic (Douro river estuary; Magalhães et al., 2002) while all the other sites were heterotrophic, with a minimal NCP value (−43 mmol C $m^{-2}\,d^{-1}$) measured in the Colne River estuary (Thornton et al., 2002). The benthic compartment in estuaries seems therefore to be heterotrophic even at shallow depths. Using the average benthic GPP and CR in estuarine shallow areas, a benthic NCP of −17 mmol C $m^{-2}\,d^{-1}$ is calculated. It must be stressed that this estimate, similar to that found in Baltic Sea and Atlantic/North Sea open shelves, only concerns shallow depths (< 5 m) and, then, cannot be extrapolated to the whole surface area of estuaries, due to the site-specific variation of both GPP and CR with depth. Another approach to assessing the metabolism of coastal ecosystems was developed through budgeting methods (Gordon et al., 1996). These budgets estimate net ecosystem production (NEP, expressed as *p-r* in the LOICZ terminology) and the balance between nitrogen fixation and nitrogen loss through denitrification (nfix-ndenit) from the non-conservative flux of nitrogen and phosphorus in a system. This procedure implies that the changes in dissolved inorganic phosphorus in a system depends on exchange processes with adjacent systems and on the difference between consumption by primary production and release by mineralization processes (NEP) assuming an elemental particulate organic matter C:P ratio. This procedure might be biased when applied in very turbid areas, where physico-chemical adsorption/desorption of phosphorus on or from particles is supposed to occur (Froelich, 1988).

Table 13
Net ecosystem production of the 'preferred' LOICZ budget sites in Europe

Location	NEP (mmol C $m^{-2}\,d^{-1}$)
Baltic Sea	
Baltic Proper	0.2
Belt Sea	0.0
Bothnian Bay	0.0
Bothnian Sea	0.0
Curonian lagoon	−1.4
Luleälven estuary	−10
Gulf of Gdánsk	17.4
Gulf of Riga	0.6
Szczecin lagoon	6.3
Baltic global	0.5
Kattegat	3.5
Atlantic/North Sea	
Southern North Sea	0.9
Irish Sea	1.9
Ría of Vigo	12.8
Lough Hyne	3.4
Solent estuary	10.7
Mediterranean Sea	
Sacca di Goro lagoon	−16
Valli di Comacchio	0
Gulf of Lions	16
Inner Thermaikos Gulf	5
Black Sea	
Malii Adzalik	19
Dnieper-Bug	−21
Dniester	11
Donuzlav	0.4

Downloaded from the LOICZ environmental database on 29 April, 2003: (http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm).

The NEP data derived by the LOICZ method for European sites are summarized in Table 13 and show that most of sites are balanced, with net metabolism around zero. Three of the sites that depart from a balanced status are included in our database and offer the opportunity to determine consistency: the Ría of Vigo, the Gulf of Lions and the Gulf of Gdánsk. No direct measurement of ecosystem metabolism in these areas is available for comparison, although pelagic GPP and CR values reported by Lefèvre et al. (1997) and Moncoiffé et al. (2000) in the euphotic zone of the Gulf of Lions and the Ría of Vigo suggest an autotrophic status for these areas, in agreement with the LOICZ estimate. However, Witek et al. (1997) showed that pelagic CR exceeded depth-averaged pelagic GPP in the Gulf of Gdánsk in 1993, which is counter to the NEP estimated by the LOICZ method for the same period. It was estimated above (Section 3.2.4) that the pelagic CR in the Baltic Sea represents approximately 60% of pelagic GPP. Assuming that benthic CR is 40% of pelagic GPP, NEP should be about 0 in this area, an estimate that is consistent with that obtained with the LOICZ method.

3.5. Coastal ecosystems and the eutrophication problem

Eutrophication refers to an increase in the rate of supply of organic matter to an ecosystem, which most commonly is related to nutrient enrichment enhancing primary production (Nixon, 1995). Several papers recently reported such phenomena in European coastal areas. For example, inputs of nutrients to the Baltic Sea have drastically increased since the 1940s due to changes in land use, excessive use of fertilizers in agriculture, loss of wetlands, sewage outlets and emissions of nitrogen from fossil fuel burning (Larsson et al., 1985; Kautsky and Kautsky, 2000). This was also demonstrated in the North Sea (Cadée and Hegeman, 2002) although a recent decrease of nutrient loads in these areas was observed in the 1990s (Ducrotoy et al., 2000; HELCOM, 2002). The effect of these increases is a general enhancement of pelagic GPP in the Baltic (Renk et al., 1988; Richardson and Heilmann, 1995; Kaczmarek et al., 1997; Wasmund et al., 2001) and North Seas (Ducrotoy et al., 2000; Cadée and Hegeman, 2002), and intertidal microphytobenthos production increased in the Wadden Sea (Cadée, 1984). This enhanced phytoplankton production has several consequences: (1) increased water turbidity in several areas (Sandén and Hakansson, 1996; Cadée and Hegeman, 2002) decreasing light availability for benthic producers, and (2) higher sedimentation and respiration rates in deep waters leading to anoxic conditions in several places (Ducrotoy et al., 2000; Kautsky and Kautsky, 2000). Eutrophication in coastal areas has also resulted in changes in the macroalgal community, reduced biodiversity and appearance of toxic blooms (Kautsky et al., 1992; Ducrotoy, 1999; Ærtebjerg, 2001). In the Mediterranean Sea, Ærtebjerg (2001) reported a general increase of nitrogen and phosphorus loading from rivers, although only one long-term pelagic GPP study was found in the literature which concluded that no systematic eutrophication in the Gulf of Lions due to the Rhône River outflow was evident over the last 30 years (Lefèvre et al., 1997).

4. Conclusion

Upscaling is the process of functional generalization of data at small spatial scale (well-studied sites) to a much larger area. It has two prerequisites: (1) a classification of the area under consideration (the EU coastal zone); and (2) a relatively unbiased database of parameters (in our case, primary production and respiration) collected at study sites which are well characterized with respect to the available typology. Once this information is available, the data obtained in each category of the typology may be upscaled using a bottom-up approach: the property measured at a small scale is multiplied by the surface area of the relevant category of the typology.

This approach has both inherent limitations and limitations which are specific to its application to coastal areas. The most critical limitation is the lack of a typology for the coastal zone of the EU or for the global CZ. This goal is being actively pursued at a global scale by LOICZ using its global environmental database and a classification tool (LOICZView; Maxwell and Buddemeier, 2002). Perhaps the major obstacle which, so far, has constrained development of a global functional typology is the lack of global datasets geo-referenced at a scale of 0.5° or less that describe biotic variables, such as the percent cover of submerged macrophytes or marine sediments. For example, the surface area of the EU coastal zone covered by, say, lagoons or macrophytes is unknown. Similarly, the proportion of vegetated vs. non-vegetated marine sediments is unknown.

Also, the community composition of the study sites cannot be considered as homogeneous both in space and time. Rather, they are mosaics of various communities, sometimes changing with time, each with distinct metabolic properties. For example, should a coastal lagoon harbouring extensive seagrass beds be classified into the lagoon or macrophytes-dominated category?

The diversity of habitats and communities in the coastal zone is very high. The classification used here, and in other recent reviews (Gattuso et al., 1998; Middelburg et al., 2004), does have a functional basis but it is sometimes too simplistic. For example, all estuaries are grouped in a single category despite having attributes, such as turbidity and residence time, that can exhibit very large differences and result in distinct metabolic properties.

This first assessment of ecosystem metabolism in the European coastal zone enables identification of geographical areas and processes which are well- or poorly-documented. Indeed, much more data were found for the Baltic Sea and Atlantic/North Sea regions than for the Mediterranean Sea region. Moreover, available data are not evenly distributed within each region. For instance, relatively few information was found for the eastern parts of the Baltic and Mediterranean Seas and the northern North Sea.

Pelagic GPP on open shelves is, by far, the better documented parameter in our database. Problems related to the use of the ^{14}C-tracer method (net vs. gross, particulate vs. dissolved), which is the most used method to measure pelagic GPP were already discussed. Then, due to these methodological problems and to a non-perfect spatial coverage, our global estimate (41 mmol C $m^{-2} d^{-1}$) for the European coastal zone contains some uncertainties. Anyway, this value is believed to be the most robust estimate of our study. While microphytobenthic GPP is often believed to be an important metabolic process in coastal areas, a production averaged over the entire 0–200 m depth range of <4% of pelagic GPP (1.5 mmol C $m^{-2} d^{-1}$) is calculated. However, our procedure for estimating the decrease of production with depth is not ideal, especially in the Atlantic Ocean and the North Sea sub-regions, and adds more to the uncertainty in these first regional estimates than the limited geographical coverage of data. More relevant data are urgently needed to allow a better evaluation of benthic GPP on a global scale.

Macrophytes were not included in our study, mainly because of their unknown distribution along European coastlines. While Charpy-Roubaud and Sournia (1990) attributed 40% of total shelf production to macrophytobenthos, an estimate cannot be provided at this stage. However, many studies in European coastal areas suggest that this value is too high and cannot be applied to European shelves. As for benthic GPP, our estimation of open shelves benthic CR (17 mmol C $m^{-2} d^{-1}$) suffers from some uncertainties due to the insufficient geographical coverage, especially in the eastern Mediterranean and Baltic Seas regions and to the lack of data at depths greater than 100 m. Although this estimate is consistent with a previous one (Middelburg et al., 2004), our value is believed to be slightly overestimated. Pelagic CR is clearly the least-documented metabolic process in our database, especially in the aphotic zone. Such data are required to have a better understanding of pelagic remineralization.

While benthic GPP in estuaries was found to be relatively constant between sites (mean value, 31 mmol C $m^{-2} d^{-1}$), pelagic GPP and benthic CR exhibited strong spatial variability. Moreover, as for open shelves, very few pelagic CR measurements were found in the literature.

Considering these various uncertainties, it is clearly not possible at this stage to upscale the available data and to obtain a meaningful metabolic balance estimate for the EU coastal zone.

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Chapitre 3

L'échelle locale

3.1 La baie de Palma

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Whole-system metabolism and CO_2 fluxes in a Mediterranean Bay dominated by seagrass beds (Palma Bay, NW Mediterranean)

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Abstract

The relationship between whole-system metabolism estimates based on planktonic and benthic incubations (bare sediments and seagrass, *Posidonia oceanica* meadows), and CO_2 fluxes across the air-sea interface were examined in the Bay of Palma (Mallorca, Spain) during two cruises in March and June 2002. Moreover, planktonic and benthic incubations were performed at monthly intervals from March 2001 to October 2002 in a seagrass vegetated area of the bay. From the annual study, results showed a contrast between the planktonic compartment, which was heterotrophic during most of the year, except for occasional bloom episodes, and the benthic compartment, which was slightly autotrophic. Whereas the seagrass community was autotrophic, the excess organic carbon production therein could only balance the excess respiration of the planktonic compartment in shallow waters (< 10 m) relative to the maximum depth of the bay (55 m). This generated a horizontal gradient from autotrophic or balanced communities in the shallow, seagrass-covered areas of the bay, to strongly heterotrophic communities in deeper areas, consistent with the patterns of CO_2 fields and fluxes across the bay observed during the two extensive cruises in 2002. Finally, dissolved inorganic carbon and oxygen budgets provided NEP estimates in fair agreement with those derived from direct metabolic estimates based on incubated samples over the *Posidonia oceanica* meadow.

1. Introduction

The role of coastal ecosystems in carbon and nutrient fluxes can be conveniently summarised by their trophic status, referring to the balance between the production of organic matter, as represented by the gross primary production (GPP) of the ecosystem and its degradation through community respiration (CR; Odum 1956). Autotrophic systems, where GPP > |CR| (if CR is expressed in negative units), produce organic matter in excess and thereby act as sinks of inorganic nutrients and CO_2 from surrounding water. In contrast, heterotrophic ecosystems, where GPP < |CR|, rely on allochtonous inputs of organic matter and act as sources of inorganic nutrients and CO_2 to the surrounding water (Duarte and Prairie submitted).

The net flux of CO_2 across the air-water interface is modulated by this metabolic balance but also by external inputs of dissolved inorganic carbon (DIC; upwelling, river inputs…), calcium carbonate ($CaCO_3$) precipitation/dissolution, and purely thermodynamic effects related to temperature changes or mixing of water masses with different chemical characteristics.

Coastal ecosystems contain highly productive communities, such as macrophyte beds which tend to be autotrophic (Duarte and Cebrián 1996; Gattuso et al. 1998; Hemminga and Duarte 2000). As they also receive important inputs of organic matter from land, both GPP and |CR| tend to be elevated relative to open ocean waters (Duarte and Agustí 1998; Gattuso et al. 1998; Hopkinson and Smith in press).

Smith and Hollibaugh (1993) argued that coastal ecosystems are a heterotrophic compartment of the biosphere. In contrast, other authors suggested that they produce organic matter in excess relative to local demands (Duarte and Cebrián 1996; Gattuso et al. 1998; Wollast 1998) and then act as sources of organic matter for the open ocean (Wollast 1998; Liu et al. 2000; Chen et al. 2003). Duarte and Agustí (1998) and

Hopkinson and Smith (in press) concluded, on the basis of comparative analyses of coastal communities, that the metabolic balance of coastal ecosystems would be dependent on their production: e.g. autotrophic productive areas vs. heterotrophic unproductive areas.

Oligotrophic coastal systems, with unproductive planktonic communities, often support highly productive benthic components. This implies that an assessment of their metabolism requires the integration of both benthic and planktonic compartments over relevant temporal and spatial scales. Nevertheless, an examination of coastal metabolism datasets (Duarte and Agustí 1998; Gattuso et al. 1998; Hopkinson and Smith in press) reveals that most coastal communities were examined at small spatial scales (bottle incubations or benthic chambers) rather than based on research conducted at the ecosystem scale. This may be attributable to the difficulties to encompass the variability within ecosystems using discrete measurements and to extrapolate these estimates to large areas.

To overcome this problem, more integrative approaches, based on material mass balances at the ecosystem scale have been proposed (e.g. Land-Ocean Interaction in the Coastal Zone, LOICZ approach, Gordon et al. 1996). However, these methods require salinity gradients to compute water exchanges and are, therefore, best used in estuarine systems and cannot be readily used in other coastal areas.

Assessments of (oxygen) O_2 concentration and the partial pressure of CO_2 (pCO_2) may be also used to derive integrative estimates of net ecosystem production (NEP = GPP + CR). However, these estimates are not straightforward, as temperature changes, the history and residence time of water masses and other physical and biogeochemical factors may also affect O_2 concentration and pCO_2 (Frankignoulle et al. 1996; Frankignoulle et al. 2001). For instance, the computation of the CO_2 air-water flux can be critical in the estimation of NEP based on DIC budgets (Gazeau et al. submitted), especially in coastal environments such as estuaries where simple parameterisations of the gas transfer velocity as a function of wind speed have been shown to be site specific (Borges et al. 2004).

To our knowledge, no comparison of the coherence of NEP estimates derived from the assessment of GPP and CR based on incubations and inferred from CO_2 and O_2 fluxes at the ecosystem scale were carried out in the past.

In this paper, the whole system metabolism of the Bay of Palma (Mallorca, NW Mediterranean) is presented and the coherence between the two approaches described above is tested. This study is carried out on the basis of (1) an annual time series of benthic and planktonic metabolism at a fixed station over a seagrass meadow and (2) extensive surveys in the bay at two contrasting periods of the annual cycle.

2. Methods

2.1 - Study site

The Bay of Palma (Mallorca, NW Mediterranean) is an oligotrophic system with a surface area of 217 km^2, a width of 30 km and a mean depth of 28.5 m (Fig. 1). It receives negligible freshwater inputs and, in the absence of appreciable astronomical tides, exchanges with the offshore waters are dominated by wind stress (Ramis et al. 1990). The Bay of Palma contains extensive seagrass (*Posidonia oceanica*) meadows that extend down to 34 m depth and cover more than 30% of the bay. As the water is rather clear (average ± SE extinction coefficient = 0.06 ± 0.02 m-1, Navarro et al. submitted), the sediment floor remains within the euphotic layer throughout the bay. The city of Palma de Mallorca (385,000 permanent inhabitants) supports intense tourism activities and a large harbour.

Benthic and planktonic metabolisms were estimated, using *in situ* incubations, at a fixed station from March 2001 to November 2002, and at a grid of stations during two cruises in March (EUBAL-I) and June 2002 (EUBAL-II). During these two cruises, gas fluxes and hydrography (current velocity) were also examined.

2.2 - Hydrography, current velocity and residence time

Five CTD (Conductivity Temperature Depth) surveys were conducted in the Bay of Palma during each of the EUBAL-I (1, 3, 7, 11 and 12/03/2002) and EUBAL-II (19, 21, 25, 26 and 27/06/2003) cruises. During the first survey of EUBAL-I, a total of 32 CTD casts were performed with an average horizontal sampling resolution of 2.8 x 2.8 km. The other surveys consisted of 11 CTD casts each, reducing the sampling resolution to 5.2 x 5.2 km. Profiles were vertically averaged every 0.5 m. Direct current measurements were obtained on four surveys during EUBAL-I (1, 3, 9 and 11/03/2002) and one survey during EUBAL-II (25/06/2002) with a ship-hull mounted 150 kHz RD instrument ADCP (Acoustic Doppler Current Profiler). This latter was set up to record currents from surface (10 m) to the bottom with a vertical resolution of 4 m and a 2 min ensemble period using a firmware version 3.03 (EUBAL-I) and 3.04 (EUBAL-II) of the Transect Acquisition Software. In order to reduce the instrumental errors, raw ADCP data were averaged to 10 min ensembles. Absolute ADCP velocities were computed using bottom-tracking mode, which delivers accurate estimation of the ship velocity. Post-processing of ADCP data was carried out following the methodology described by Allen et al. (1997). Unfortunately, the ship was not equipped with a 3D GPS (Global Positioning System) that provides accurate heading to account for the gyrocompass error. Hence, a typical error for a conventional gyrocompass of 2° (Griffiths 1994) is assumed in the post-processing of ADCP data. The maximum error velocity has been estimated at about 4 cm s^{-1}.

The CTD observations were interpolated over a regular 0.5 x 0.5 km grid, using an objective analysis based on Optimal Statistical Interpolation. The two main parameters of this scheme are the characteristic scale and the cut-off length scale. The first determines the influence between observations and the second gives the filtering of scales which were not resolved by the sampling strategy. For the first CTD survey of EUBAL-I (dense sampling), the characteristic scale was set-up to 5 km and the cut-off scale to 10 km. For the other CTD surveys (coarse sampling), the scale derived from statistics was 7.5 km and the cut-off length scale was set to 15 km. For further details about this technique refer to Pedder (1993).

In order to have a qualitative view of the general circulation in the Mallorca channel, a database of daily sea surface temperature (SST) was compiled, for the EUBAL-I period, from remote sensing products (Instituto Espanyol de Oceanografia; http://www.teledeteccion-oceanografica.net/).

2.3 - Community metabolism

The community metabolism in a *Posidonia oceanica* meadow and unvegetated sediments were studied monthly from March 2001 to October 2002 using *in situ* benthic incubation chambers at the shallow (7 m depth) Posidonia station in the Western side of the bay (Fig. 1). Benthic incubations were set up in the vegetated (4 chambers) and unvegetated (3 chambers) sediment to estimate the net community production (NCP). The benthic chambers consisted of a PVC cylinder inserted in the sediment and a gas-tight polyethylene plastic bag fitted to the cylinder with a sampling port (Hansen et al. 2000). Water samples were withdrawn with syringes at the start of the incubation and after 24 h. Samples for dissolved O_2 were transferred into Winkler bottles, fixed and measured by the Winkler technique following Carrit and Carpenter (1966) using an automated precise titration system (Mettler DL21 Auto-titrator) with potentiometric (redox electrode) end-point detection (Oudot et al. 1988). The average precision achieved in replicates was %CV = 0.29. In order to express dissolved O_2 changes per unit area, the volume of water enclosed in the benthic chambers was estimated from the dilution of a phosphate solution (0.25 mol l^{-1}) in the benthic chambers and measurements of phosphate concentrations by spectrophotometry (Hansen and Koroleff 1999) from samples collected after an equilibration period of 5 min. Dissolved O_2 changes, adjusted to 24 h, within the benthic chambers were used to calculate NCP. Further details and procedures are provided in Barrón et al. (submitted).

During both EUBAL cruises, the community metabolism of *Posidonia oceanica* meadow and unvegetated sediment communities were studied at Posidonia (7 m) and Cap Enderrocat stations (15 m) using *in situ* benthic incubations as described above. Moreover, during EUBAL-II, incubations of both communities were performed along a depth gradient at Posidonia station (4, 7, 15 and 22 m). The variation of benthic NCP with depth at this station was upscaled to the entire bay using estimates of the surface area of vegetated and unvegetated sediments based on the detailed study of Rey and Diaz del Rio (1984), using a General Information System (ArcView software package).

The planktonic metabolism was measured, at monthly intervals, from June 2001 to October 2002 at the Posidonia station. The water column was vertically mixed throughout the study, as evidenced by CTD profiles. Integrated (0 to 7 m) water samples were carefully siphoned into twelve 125 ml biological O_2 demand (BOD) bottles. Five replicates were used to determinate the initial O_2 concentration and seven replicate clear bottles were suspended *in situ* at a depth of 4 m and incubated for 24 h. NCP was calculated from the difference between final and initial O_2 concentrations measured as described above and integrated to a depth of 7 m.

Planktonic GPP and CR were measured at 4 stations in the bay during each of the EUBAL cruises (Fig. 1). Samples (5 replicates) were incubated *in situ* at 4 depths for 24 h in both transparent and dark 60 ml BOD bottles. O_2 concentrations were measured before and after incubation using an automated Winkler titration technique with potentiometric end-point detection. Analyses were performed with an Orion redox electrode (9778-SC) and a custom built titrator. Reagents and standardizations were similar to those described by Knap et al. (1996). Daily planktonic CR and NCP were estimated by regressing O_2 in the dark and transparent bottles against time, respectively. Daily GPP was estimated as the difference between NCP and CR.

At each station and incubation depth, samples were taken for chlorophyll *a*. Water was filtered through GF/F filters that were stored frozen until extraction and analysis by high-performance liquid chromatography (Barranguet et al. 1997). Light penetration in the water column was measured using a LI-COR quantum LI-1935A and a LI-1400 data-logger twice during each incubation period. During two surveys on each cruise, vertical CTD (SeaBird SBE19) profiles of fluorescence (Chelsea and Sea tech sensors during EUBAL-I and -II, respectively) were performed at 11 stations in the bay (Fig. 1), and were calibrated using concomitant measurements of surface chlorophyll *a* concentration (same method as above). Surface irradiance was measured every 15 min during each cruise using a LI-COR cosine corrected quantum sensor (LI-1925A) and a LI-1400 data-logger. Strong variations were observed during the first cruise, while during the second cruise light conditions were relatively constant (data not shown). As phytoplanktonic GPP is strongly dependent on the available light intensity, a correction was applied to compare results obtained under different light conditions during EUBAL-I. Relationships between daily GPP rates normalized per unit of chlorophyll *a* and the averaged daily irradiance were established for each station using the model of Platt et al. (1980). The resulting PI (production vs. irradiance) curves were then used to recalculate GPP for the mean daily surface irradiance over the whole campaign (421.5 μmol m^{-2} s^{-1}).

2.4 - CO_2 / O_2 fluxes and NEP estimates

Underway parameters (seawater pCO_2, O_2, salinity and *in situ* temperature) were sampled with a frequency of 1 min from the seawater supply of the ship (pump inlet at a depth of about 2 m) during six surveys of the EUBAL-I cruise (1, 3, 7, 9, 11 and 12/03/2002) and during five surveys of the EUBAL-II cruise (19, 21, 25, 26 and 27/06/2003). Total alkalinity (TA) and O_2 were sampled from the seawater supply to cover the spatial variability during the surveys (on average 10 samples per survey). Vertical profiles of pH, TA and O_2 were obtained at four reference stations (Fig. 1). During the EUBAL-II cruise, vertical profiles of pCO_2 were established during 24 h cycles at three reference stations (Posidonia, Bahia and Cap Enderrocat, Fig. 1). A non-dispersive infrared gas analyser (IRGA, LI-COR, LI-6262) was used to measure pCO_2 in wet air equilibrated with seawater. The IRGA was calibrated daily using three dry gas standards: pure nitrogen (0.0 ppm; Air Liquide Belgium) and two gas mixtures with a CO_2 molar fraction of 360.5 and 773.8 ppm (National Oceanic and Atmospheric Administration). The temperature at the outlet of the equilibrator was monitored with a platinum resistance thermometer (PT100, Metrohm) with an estimated accuracy of ± 0.05°C and pCO_2 values were corrected for the temperature difference between *in-situ* seawater and water in the equilibrator using the algorithm proposed by Copin-Montégut (1988). The offset in temperature was typically 0.5°C. The accuracy of the pCO_2 measurement by equilibration is estimated to ± 2 ppm (cumulated errors on temperature correction and instrument calibration). For further details on the equilibrator design and performance tests refer to Frankignoulle et al. (2001). A second IRGA was used to measure atmospheric pCO_2 sampled at the bow of the ship. Vertical pCO_2 profiles were established every 3.5 h with a resolution of 1 m, by pumping water from a given depth with a peristaltic field pump (ISCO 150) through a Liqui-Cel equilibrator (mini-module, 9”) at a rate of about 1.5 l min^{-1}. The pCO_2 was measured using a portable IRGA (EGM-3, PPSystems) with an estimated precision of ± 2 ppm. TA was determined using the classical Gran electro-titration method, on 100 ml GF/F filtered samples with a reproducibility of ± 2 $\mu mol\ kg^{-1}$ and an estimated accuracy of ± 3 µmol kg^{-1}. The measurement of pH was obtained using a combined electrode (Metrohm), calibrated on the Total Hydrogen Ion Concentration Scale (mol kg SW^{-1}), using the buffers proposed by Dickson (1993). The reproducibility of pH measurement is estimated to ± 0.004 pH units. DIC was calculated from pCO_2 and TA (underway data) and from pH and TA (vertical profile data) with the dissociation constants of carbonic acid and borate from Roy et al. (1993), the dissociation constant of boric acid from Dickson (1990) and the CO_2 solubility coefficient of Weiss (1974). The accuracy of DIC computed from the pCO_2-TA and the pH-TA couples is estimated to ± 5 and ± 10 µmol kg^{-1}, respectively. DIC was normalized to a constant salinity according to:

$$DIC_{37} = 37\,\frac{DIC_{observed}}{Salinity_{observed}} \tag{1}$$

pCO_2 was normalized to a constant temperature using the algorithm proposed by Copin-Montégut (1988).

Discrete dissolved O_2 concentration was measured according to the Winkler method using a potentiometric end-point determination with an estimated accuracy of ± 2 µmol kg^{-1}. Underway O_2 concentration was measured with a polarographic electrode (Oxyguard) calibrated against the discrete O_2 samples with an estimated accuracy of ± 3 µmol kg^{-1}. Apparent oxygen utilisation (AOU) was computed using the concentration of O_2 at saturation calculated with the algorithm proposed by Benson and Krause (1984). Salinity and *in-situ* temperature were measured using a SeaBird SBE21 thermosalinograph. Vertical profile data were obtained from a 12 bottle rosette coupled to a CTD (SeaBird SBE19). The estimated errors on salinity and *in situ* temperature measurements are ± 0.05 and ± 0.01°C, respectively. Wind speed was measured at approximately 10 m height with a Batos (5 s sampling interval during EUBAL-I) and Aanderaa (1 min sampling interval during EUBAL-II) cup anemometer.

The air-sea CO_2 flux (F; mmol C m^{-2} d^{-1}) was computed from the air-sea gradient of pCO_2 ($\Delta pCO_2 = pCO_{2\,water} - pCO_{2\,atmosphere}$; ppm), the gas transfer velocity (k; m d^{-1}) and the solubility coefficient of CO_2 (α; mmol m^{-3} ppm^{-1}), using equation:

$$F = \alpha\, k\, \Delta pCO_2 \qquad (2)$$

As a convention, a positive flux corresponds to a source for the atmosphere. Computations were made using various algorithms of k as a function of wind speed (Liss and Merlivat 1986; Wanninkhof 1992; Wanninkhof and McGillis 1999; Nightingale et al. 2000; McGillis et al. 2001), although, we mainly discuss the values computed with the parametrization by Wanninkhof and McGillis (1999) for a consistent comparison with values from the Dyfamed station (Bégovic and Copin-Montégut 2002). For each survey, the $\alpha\ \Delta pCO_2$ data were interpolated on a grid of 0.0034°E x 0.0025°N. To account for the strong non-linearity of the k parametrizations, the flux computations were carried out using hourly bins of wind speed (assuming that the whole area is uniformly submitted to wind speed measured anywhere during the survey) and then averaged for a given survey.

NEP over the *Posidonia oceanica* meadow was computed based on a DIC budget, according to the equation:

$$NEP_{DIC} = \rho\, h_{pos} \frac{\left(DIC_{bay'} + t_{bay'} \dfrac{F_{bay'}}{\rho\, h_{bay'}} \right) - \left(DIC_{pos} + t_{pos} \dfrac{F_{pos}}{\rho\, h_{pos}} \right)}{t_{pos}} \qquad (3)$$

where NEP_{DIC} is expressed in mmol C m^{-2} d^{-1}, ρ is the water density (kg m^{-3}), DIC_* is DIC_{37} (mmol kg^{-1}), t_* is the water residence time (d), h_{pos} is the average water column height over the *Posidonia oceanica* meadow (m), $h_{bay'}$ is the average mixed layer depth in the Bay of Palma (excluding the *Posidonia oceanica* meadow, m), F_* is the air-sea CO_2 exchange computed using the Wanninkhof and McGillis (1999) k parametrization, subscript *pos* denotes data over the *Posidonia oceanica* meadow and subscript *bay'* denotes data over the rest of the Bay of Palma (excluding the *Posidonia oceanica* meadow).

An identical equation was used to computed NEP from O_2 concentrations (NEP_{O2} in mmol O_2 m^{-2} d^{-1}); the flux air-sea of O_2 was computed using the Wanninkhof and McGillis (1999) k parametrization and the Schmidt number (Sc) formulation for seawater given by Wanninkhof (1992), assuming a k dependency proportional to $Sc^{-0.5}$.

The relative water residence time over the *Posidonia oceanica* meadow and in the Bay of Palma (excluding the *Posidonia* meadow) were computed according to:

$$t_{pos} = t_{total} \frac{V_{pos}}{V_{total}} \tag{4}$$

$$t_{bay'} = t_{total} \frac{V_{bay'}}{V_{total}} \tag{5}$$

where V_* is the volume (km^3), t_* is the water residence time (d), subscript *total* denotes data in the whole Bay of Palma, subscript *pos* denotes data over the *Posidonia oceanica* meadow and subscript *bay'* denotes data over the rest of the Bay of Palma (excluding the *Posidonia oceanica* meadow).

3. Results and Discussion

3.1 - Monthly metabolism at Posidonia station

The *Posidonia oceanica* community tended to be autotrophic and the bare sediment community tended to be heterotrophic during the study (Fig. 2A). The seagrass community ranged from heterotrophy with a lowest NCP in August 2002

(-24.7 mmol O_2 m^{-2} d^{-1}) to autotrophy with a highest NCP in April 2002 (88.8 mmol O_2 m^{-2} d^{-1}). The unvegetated sediment community ranged from heterotrophy (-4.8 mmol O_2 m^{-2} d^{-1} in April 2001) to autotrophy (NCP = 5.0 mmol O_2 m^{-2} d^{-1} in July 2001). The benthic community metabolism at Posidonia station showed considerable variability along the study period, with the highest NCP found in spring and early summer (Fig. 2B). In contrast, the planktonic NCP showed no clear seasonality. Indeed, most monthly NCP estimates in 2001 indicated a heterotrophy while those in 2002 suggested an autotrophy. Overall, the NCP of the planktonic compartment averaged -4.6 ± 5.9 mmol O_2 m^{-2} d^{-1}, indicating a metabolic balance (i.e. H_o: mean NCP = 0, $P > 0.05$), with a tendency towards heterotrophy whereas the benthic compartment was overall net autotrophic (16.2 ± 5.2 mmol O_2 m^{-2} d^{-1}). NEP (sum of benthic and planktonic NCP) was dominated by the benthic compartment in spring and summer, and by the planktonic community in the fall and winter. At an annual scale, NEP was nearly balanced, with a tendency towards autotrophy (7.7 ± 7.7 mmol O_2 m^{-2} d^{-1}).

3.2 - Hydrography, water currents and residence time during EUBAL-I and -II cruises

The horizontal velocity fields based on the ADCP surveys during the EUBAL-I and -II cruises differed considerably. In March, the flow pattern was initially characterised by a clear clockwise circulation with maximum velocities of 19 and 22 cm s^{-1}, on 01/03 and 09/03/2002 respectively (Fig. 3A&B). The water entered the bay on its Western side, while the water outflow is dominant on the Eastern side. The circulation changed to the opposite direction towards the end of the cruise (12/03/2002; Fig. 3C) when the flow pattern became anticlockwise and the flow intensified to reach a value of 40 cm s^{-1}. This flow reversion was consistent with a shift between the beginning and the end of the cruise, from a relatively cool, high-salinity (37.5 to 37.6) to a warmer and less saline water mass (+ 0.5 ºC; 37.2; Fig. 4). This pattern was evident both from CTD surveys and examination of satellite SST data (not shown).

The flow pattern during EUBAL-II was similar to the one observed at the end of EUBAL-I, with a general anticlockwise circulation (Fig. 3D). It should be noted that the current velocities were, on average, lower than those during EUBAL-I (6 - 7 cm s^{-1} vs. 20 - 24 cm s^{-1}).

The water residence time in the Bay of Palma was estimated from the current velocities recorded during each survey. The average water residence time was much shorter during EUBAL-I (2.5 ± 0.2 d) than during EUBAL-II (10 d). Due to the low velocities and the consequent noise during EUBAL-II, the computed residence time is subject to a strong uncertainty.

3.3 - Ecosystem metabolism during EUBAL-I and -II cruises

Integrated chlorophyll *a* concentrations at the incubated stations were on average significantly higher in March than in June, except at Posidonia station which presented similar values during both cruises (Table 1). Minimal and maximal concentrations were found, respectively, at Cap Enderrocat station in June (1.5 mg m^{-2}) and at Bahia station in March (17.3 mg m^{-2}). Light attenuation coefficients (*K*) were rather low (< 0.16 m^{-1} during both cruises) with slightly higher values in March, except for Posidonia station.

During EUBAL-I, surface planktonic GPP rates ranged from 2.8 mmol O_2 m^{-3} d^{-1} (Posidonia) to 5.2 mmol O_2 m^{-3} d^{-1} (Cap Enderrocat) with an average value of 3.7 ± 1.2 mmol O_2 m^{-3} d^{-1} (Fig. 5). During EUBAL-II, surface planktonic GPP rates were slightly higher (mean: 4.7 ± 1.2 mmol O_2 m^{-3} d^{-1}) with a minimal value at Cap Enderrocat (3.3 mmol O_2 m^{-3} d^{-1}) and a maximal one at station 4 (6.3 mmol O_2 m^{-3}

d^{-1}). Average water-column planktonic CR strongly increased between March and June, from 1.5 ± 0.8 mmol O_2 m^{-3} d^{-1} to 3.4 ± 1.9 mmol O_2 m^{-3} d^{-1}, respectively. Higher vertical and horizontal gradients were found during the EUBAL-II cruise.

During EUBAL-I, maximal integrated planktonic GPP values were observed at stations Bahia and 4 (98 and 92 mmol O_2 m^{-2} d^{-1}) and the minimal one at Posidonia station (36 mmol O_2 m^{-2} d^{-1}, Table 2). During EUBAL-II, integrated planktonic GPP ranged from 29 mmol O_2 m^{-2} d^{-1} at Cap Enderrocat to 86 mmol O_2 m^{-2} d^{-1} at Bahia. Integrated planktonic CR showed a low spatial variability during the first cruise with a mean value of -35 ± 7.4 mmol O_2 m^{-2} d^{-1}. In contrast, during the second cruise, strong geographical variations were highlighted with a minimal value measured at Posidonia (-45 mmol O_2 m^{-2} d^{-1}) and a maximal one at station 4 (-107 mmol O_2 m^{-2} d^{-1}). The planktonic compartment was autotrophic at all incubated stations during EUBAL-I while during EUBAL-II, two stations (Station 4 and Cap Enderrocat) presented a heterotrophic status.

Significant relationships were found between integrated planktonic GPP and integrated chlorophyll *a* concentration during both cruises (Fig. 6A). As chlorophyll *a* concentrations were estimated at 11 stations on two surveys during each cruise, these relationships were used to extrapolate GPP, integrated across the euphotic layer (34 m during EUBAL-I and 46 m during EUBAL-II) to the whole bay (Table 3). During both surveys in March, the lowest chlorophyll *a* values and consequently the lowest planktonic GPP were found at Posidonia and Cap Enderrocat stations while maximal rates were found in deep waters in the middle of the bay. During the second cruise, due to lower chlorophyll *a* concentrations, planktonic GPP were much lower and higher spatial variations were observed in comparison to March, reaching a mean value of 33 ± 44 mmol O_2 m^{-2} d^{-1} (vs. 93 ± 43 mmol O_2 m^{-2} d^{-1} during EUBAL-I). The highest values were generally estimated over the *Posidonia oceanica* meadow.

During the first cruise, for all stations investigated during the surveys, planktonic integrated CR rates were calculated by multiplying the mean volumetric rate observed during the incubations (-1.5 ± 0.8 mmol O_2 m^{-2} d^{-1}) by the depth of each station. Planktonic integrated CR was, therefore, maximal at deep stations reaching a maximal value at station 8 (60m depth; -89 mmol O_2 m^{-2} d^{-1}), but was always lower than planktonic GPP except for one station during the first survey (Cap Enderrocat). Consequently, the planktonic compartment was autotrophic during EUBAL-I with an average value of 46 ± 41 mmol O_2 m^{-2} d^{-1}.

Due to the strong heterogeneity in CR observed during EUBAL-II at the four incubated stations, the same procedure was not applied. During this cruise, a significant relationship was observed between GPP and CR integrated across the water column, excluding the last incubated depth (Fig. 6B). It should be mentioned that CR rates measured near the bottom and therefore near the *Posidonia oceanica* meadow do not fit with this relationship. This suggests that near the bottom, planktonic CR may be fuelled by organic matter from the *Posidonia oceanica* meadow rather than by the planktonic production. Therefore, CR rates collected at the four incubated stations were upscaled only to the area covered by the *Posidonia oceanica* meadow, while integrated CR was calculated based on the estimated GPP in the rest of the bay where chlorophyll *a* and consequent GPP rates are much lower.

On average, integrated and extrapolated planktonic CR was similar during both cruises (-47 ± 24 and -43 ± 27 mmol O_2 m^{-2} d^{-1} in March and June, respectively). Therefore, due to a higher GPP during the first cruise, the planktonic compartment was autotrophic in March and heterotrophic in June (46 ± 41 and -10 ± 45 mmol O_2 m^{-2} d^{-1}, respectively).

Seagrass communities were autotrophic at all depths during both cruises, with the highest NCP found at the shallowest station (Table 4). In contrast, bare sediment communities remained net heterotrophic during both cruises, except for the shallowest community investigated during EUBAL II (4 m). The upscaled results suggest that the NCP of the *Posidonia oceanica* meadow was marginally autotrophic during EUBAL-I (1 mmol O_2 m^{-2} d^{-1}) and significantly autotrophic, with an average NCP of 26 mmol O_2 m^{-2} d^{-1}, during EUBAL-II.

Combining these estimates with concurrent estimates of planktonic NCP over the *Posidonia oceanica* meadow, a NEP over the *Posidonia oceanica* meadow of 60 and 34 mmol O_2 m^{-2} d^{-1} was estimated for EUBAL-I and -II, respectively.

Considering the entire bay, where the bare sediments and the seagrass meadow cover respectively 70 and 30% of its surface, benthic NCP was estimated at -1 and 7 mmol O_2 m^{-2} d^{-1} for EUBAL-I and -II, respectively. Therefore, a whole-system NEP of 45 and -3 mmol O_2 m^{-2} d^{-1} was estimated in March and June, respectively, indicating that the Bay of Palma acted as an autrotrophic ecosystem in March and as a heterotrophic one in June.

As mentioned previously, monthly time series were obtained at one station in the bay (Posidonia). The NEP measured at this station was 40 and 4 mmol O_2 m^{-2} d^{-1} during EUBAL-I and -II, respectively while similar values (45 and -3 mmol O_2 m^{-2} d^{-1}) were reported for the entire bay during the same cruises (see above). Therefore, this suggests that the annual NEP estimated at Posidonia station (7.7 mmol O_2 m^{-2} d^{-1}; see above) might be a relatively confident indicator of the metabolism of the entire Bay of Palma over an annual cycle, although this extrapolation procedure could lead to a slight overestimate especially during low planktonic GPP periods as during EUBAL-II.

3.4 - Spatial and temporal variations of DIC, AOU and air-sea CO_2 fluxes during EUBAL-I and -II cruises

The comparison of pCO_2 among cruises required the normalization to a constant temperature of 19°C ($pCO_{2(19°C)}$), as temperature strongly affects the equilibrium constants of DIC and, in particular, the solubility coefficient of CO_2, so that pCO_2 rises of about 4% when temperature increases of 1°C. Normalization of pCO_2 values to a constant temperature allows to remove temperature effects and to focus on potential biological controls of pCO_2. The correlation between AOU and $pCO_{2(19°C)}$ (Fig. 7A) strongly suggests that both variables were controlled by biological effects during the two EUBAL cruises. The $pCO_{2(19°C)}$ and AOU values were on average lower during EUBAL-II than during EUBAL-I. This is related to the longer residence time of the water mass in the bay during summer (see above) that leads to an enhanced impoverishment in CO_2 and enrichment in O_2 in June despite the fact that the NEP was lower in June than in March (see above). The $pCO_{2(19°C)}$ and AOU values observed were much lower than those at the Dyfamed station (located in the open waters of the Ligurian Sea, about 620 km North from the Bay of Palma) for the corresponding periods. This suggests that in the Western Mediterranean Sea, the continental shelf is more productive than the open oceanic waters.

During both EUBAL cruises, TA was well correlated to salinity (Fig. 7B) suggesting that $CaCO_3$ precipitation/dissolution rates were too low and/or water residence time too short to significantly affect surface water TA values. The linear regression function based on data from both EUBAL cruises was very similar to that reported by Copin-Montégut (1993) for the Alboran Sea. Based on the linear regression function of TA as a function of salinity, DIC was computed from continuous pCO_2 measurements. DIC was normalized to a constant salinity value of 37 to remove the variations of DIC due to changes in salinity owing to mixing, evaporation or dilution.

Strong spatial gradients of $pCO_{2(19°C)}$ and AOU were observed during both EUBAL cruises (Fig. 8). During the six EUBAL-I surveys, $pCO_{2(19°C)}$ and AOU surface distributions exhibited variable patterns with no recurrent spatial features. This suggests either highly variable NEP in space and time and/or the advection of water masses with different $pCO_{2(19°C)}$ and AOU signatures. The latter explanation is consistent with shifts in the water mass and residual current patterns observed between the start and the end of the cruise (see above). During the EUBAL-II surveys, AOU and $pCO_{2(19°C)}$ minima were systematically observed near-shore, above the *Posidonia oceanica* meadow (Fig. 8 and Table 5). Also, during the EUBAL-II surveys, lower near-shore values of AOU and $pCO_{2(19°C)}$ were systematically observed on the Western side of the bay in comparison to the Eastern side (Fig. 8). This is consistent with the anti-clockwise pattern of residual currents (Fig. 3), leading to an impoverishment in CO_2 and an enrichment in O_2 as the water mass is advected above the *Posidonia oceanica* meadow. Also, a higher planktonic NCP was observed on the Western side of the bay during two EUBAL-II surveys, suggesting overall higher NEP on this side of the bay (Table 2).

The variability of the flux computations related to the choice of the *k* parametrization is huge as shown in other studies (e.g. Borges and Frankignoulle 2002). The fluxes computed using the Wanninkhof and McGillis (1999) *k* parametrization were on average identical to those using the Liss and Merlivat (1986) *k* parametrization, and, corresponded to 57, 66 and 63% of those computed using, respectively, the *k* parametrization given by Wanninkhof (1992), Nightingale et al. (2000) and McGillis et al. (2001).

The Bay of Palma was a sink for atmospheric CO_2 during EUBAL-I (on average -1.7 mmol C m^{-2} d^{-1}) and a source during EUBAL-II (on average 2.7 mmol C m^{-2} d^{-1}, Table 5). At the Dyfamed station, the CO_2 fluxes ranged between -2.9 and -8.7 mmol C m^{-2} d^{-1} in March 1998-99 and between 2.8 and 3.3 mmol C m^{-2} d^{-1} in June 1998-1999 (Bégovic and Copin-Montégut 2002). The stronger fluxes at Dyfamed are related to higher wind speeds since the ΔpCO_2 are more marked in the Bay of Palma: -56 ppm during EUBAL-I (-39 ppm at Dyfamed in March 1998-99) and 68 ppm during EUBAL-II (20 ppm at Dyfamed in June 1998-99).

The temperature effect on the solubility coefficient of CO_2 strongly contributes to the seasonal variability of air-sea CO_2 flux in the Bay of Palma, as also shown in open oceanic waters (Dyfamed; Bégovic and Copin-Montégut 2002) and other coastal waters (Bay of Calvi – Corsica; Frankignoulle 1988) of the Western Mediterranean Sea. Indeed, pCO_2 and ΔpCO_2 values were higher during EUBAL-II than EUBAL-I, although, $pCO_{2(19°C)}$ and DIC_{37} were actually lower during EUBAL-II (Table 5). Thus, the fact that the Bay of Palma is a source of CO_2 in June seems to be largely related to a temperature effect, since $pCO_{2(19°C)}$ and AOU data were lower than in March (Fig. 7A, Fig. 8 and Table 5). At any rate, the contrasting role of the bay as a sink in March and a source in June is coherent with the positive NEP found in March and the net heterotrophy observed in June.

Our results also show that the potential impact of *Posidonia oceanica* meadows on the CO_2 air-sea flux budget in the Western Mediterranean continental shelf during summer could be small. The average CO_2 flux observed over the *Posidonia* meadow during EUBAL-II (2.54 mmol C m^{-2} d^{-1}; Table 5) was only 10%

lower than that for unvegetated areas during the same cruise (2.76 mmol C m^{-2} d^{-1}). As *Posidonia oceanica* meadows are believed to cover about 25% of the shelf area (Bethoux and Copin-Montégut 1986), they can only decrease the summertime CO_2 emission from the Mediterranean continental shelf by less than 2.5%, which is a modest contribution.

3.5 - DIC- and O_2-derived NEP estimates over the *Posidonia oceanica* meadow during EUBAL-II

NEP estimates over the *Posidonia oceanica* meadow during EUBAL-II based on surface water DIC_{37} and O_2 were highly variable and the ecosystem metabolism ranges from distinctly autotrophic status to a nearly balanced status (Table 6). The day-to-day variability of NEP seems to be mainly related to light availability, as there was a strong relationship between the NEP and surface irradiance (Fig. 9), which explained about 91 and 70% of the variance of, respectively, NEP_{DIC} and NEP_{O2}. Based on these linear regressions and continuous surface irradiance measurements, NEP over the *Posidonia oceanica* meadow was integrated for the full duration of the EUBAL-II cruise (19-27 June): at 22 ± 12 mmol C m^{-2} d^{-1} and 10 ± 7 mmol O_2 m^{-2} d^{-1} for, respectively, NEP_{DIC} and NEP_{O2}. The difference between NEP_{DIC} and NEP_{O2} could be related to net $CaCO_3$ production that was not included in the DIC budget. Net $CaCO_3$ production was measured using *in situ* benthic chambers on 20/06/2002, yielding a value of 15 mmol C m^{-2} d^{-1} for the *Posidonia oceanica* vegetated community and 1 mmol C m^{-2} d^{-1} for bare sediments of the Bay of Palma (Barrón et al. submitted). Based on the relative sea-floor coverage by these benthic communities, the integrated net $CaCO_3$ production between the shore and 30 m depth is 10 mmol C m^{-2} d^{-1} and corresponds to the difference between NEP_{DIC} and NEP_{O2}.

NEP_{O2} and NEP_{DIC} are well correlated and the slope of the linear regression (Table 6) gives an indication on the ΔO_2:ΔDIC ratios of both GPP and CR processes. The photosynthetic quotient (PQ) corresponds to the molar ratio of the release of O_2 to the consumption of DIC during photosynthesis while the respiratory quotient (RQ) corresponds to the molar ratio of the release of DIC to the consumption of O_2 during organic matter mineralization. As mentioned by Thamdrup and Canfield (2000), an important uncertainty in using O_2 uptake as a measure of mineralization in sediments lies in the assumption that anaerobic respiration and reoxidation of inorganic species are at steady state. Holmer et al. (2003) reported low concentrations of sulfides in seagrass sediments around Mallorca Island suggesting that the previous assumption is realistic in these sediments. Therefore, in the present study, a RQ of 1 was assumed and the NEP_{O2} *vs.* NEP_{DIC} ratio was used to compute a PQ value. This latter is slightly lower but not significantly different than 1. This would suggest that NEP over the *Posidonia oceanica* meadow is mainly related to the photosynthetic activity of the seagrass community. Indeed, one can compute a PQ of 1.06, based on the C:N:P elemental molar ratio of 956:39:1 reported by Atkinson and Smith (1983) for *Posidonia oceanica* leaves. The C:N:P elemental molar ratio of roots is 3550:61:1 (Atkinson and Smith 1983) but the below-ground production of *Posidonia oceanica* is much lower than the above-ground production (about 10%; Duarte and Chiscano 1999) and does not significantly affect the PQ estimate. Based on the C:N:P molar elemental composition of phytoplankton reported by Redfield (1963) and Hedges et al. (2002), the predicted PQ values are higher than 1, respectively, 1.30 and 1.45.

Error estimates on these NEP values (Table 6) are largely derived from the uncertainty on the water residence time. The analytical error on DIC_{37} and O_2 should not significantly affect the NEP estimates, since the variables used in the computations are averages of a large number of observations (assuming that analytical errors are random and not systematic). The air-sea flux correction introduces a significant uncertainty in the computations. NEP_{DIC} computed using the air-sea CO_2 fluxes calculated with Wanninkhof and McGillis (1999) *k* parametrization corresponds on average to 99.4, 102.7, 94.7 and 95.0% of NEP_{DIC} computed using the *k* parametrizations given by, respectively, Liss and Merlivat (1986), Wanninkhof (1992), Nightingale et al. (2000) and McGillis et al.(2001). NEP_{O2} computed using the air-sea O_2 fluxes calculated with Wanninkhof and McGillis (1999) *k* parametrization corresponds on average to 98.5, 96.7, 96.5 and 97.2% of NEP_{O2} computed using the *k* parametrization given by, respectively, Liss and Merlivat (1986), Wanninkhof (1992), Nightingale et al. (2000) and McGillis et al. (2001). The choice of the *k* parametrization for air-sea flux correction also affects the PQ estimate, the lowest one corresponding to the NEP computations using the Wanninkhof and McGillis (1999) *k* parametrization (Table 6) and the highest one (1.1 ± 0.2) corresponding to the NEP computations using the Wanninkhof (1992) *k* parametrization. The less constrained uncertainty in the computations of NEP above the *Posidonia oceanica* meadow during EUBAL-II probably comes from the representativeness of the underway surface water data for the whole water column DIC_{37} and O_2. This approach is attractive because it is based on large data sets that adequately resolve the spatial variability, but it is based on the assumption that the variables are homogeneous in the water column (no vertical gradients).

Examination vertical profiles of DIC_{37} and O_2 at the four reference stations sampled during EUBAL-II (Fig. 10) shows that these vertical gradients are more marked for O_2 than DIC_{37} but they remain smaller than the spatial gradients, for both variables. We attempted to adjust the surface values of O_2 and DIC_{37} to represent the whole column values of these variables. Station 4 (located at the edge but outside the *Posidonia oceanica* meadow) was considered to represent the incoming water from the bay and the other three stations were considered to be representative of the *Posidonia oceanica* meadow. NEP computed from adjusted DIC_{37} and O_2 values, assuming that surface DIC_{37} is 1 and 4 μmol kg^{-1} (for the entire bay and *Posidonia oceanica* meadow, respectively) lower than whole column DIC_{37} and that surface O_2 is 9 and 4 μmol kg^{-1} (for bay and *Posidonia oceanica* meadow, respectively) lower than whole column O_2, were much larger than NEP estimates based on surface water values, but, the PQ value remains unchanged (Table 6). NEP estimates based on the adjusted DIC_{37} and O_2 values are also well correlated to surface irradiance (not shown), allowing the integration for the full duration of the EUBAL-II cruise (19-27 June) to yield estimates of 35 ± 8 mmol C m^{-2} d^{-1} and 48 ± 7 mmol O_2 m^{-2} d^{-1} for, respectively, NEP_{DIC} and NEP_{O2}. In this case, net $CaCO_3$ production cannot explain the difference between NEP_{DIC} and NEP_{O2}, and the difference between NEP_{DIC} and NEP_{O2} is probably mostly related to the error on the slope and y-intercept of the linear regressions as a function of surface irradiance that are higher for NEP_{O2}. However, considering potential sources of error associated to each method, these estimates are in fair agreement with the NEP estimate based on the upscaled incubation measurements of 34 mmol O_2 m^{-2} d^{-1} over the *Posidonia oceanica* meadow during this cruise (see above).

3.6 - Daily variations of DIC during EUBAL II

The daily variations of DIC_{37} at stations Posidonia and Cap Enderrocat follow the daily oscillation expected from the diel alternation between photosynthesis and respiration; DIC_{37} decreases from dawn to dust and increases during the night (Fig. 11). However, at station Bahia, the DIC_{37} time-course during the 24 h cycle was erratic. This can be attributed to the fact that station Bahia is much deeper (33 m) than stations Posidonia (13 m) and Cap Enderrocat (16 m). It is then probable that due to the water column depth, the impact on water column DIC from metabolic activity is much smaller at station Bahia and is not discernable from the background noise.

The difference of average DIC values from the top half of the water column and from the bottom half of the water column (ΔDIC) provides qualitative information on the relative importance of metabolic rates from the planktonic and benthic compartments. During the 24 h cycle at Posidonia station, in the lower half of the water column higher average DIC values were observed during night-time while lower average DIC values were observed at the end of the day (Fig. 11). This suggests higher metabolic rates in the benthic compartment than in the planktonic one, at the Posidonia station. Indeed, the metabolic rates measured by O_2 incubations show that, at this station, benthic CR is about 1.8 times higher than planktonic CR and that benthic GPP is about 1.5 times higher than planktonic GPP. At station Bahia, the reverse trend in ΔDIC is observed, suggesting higher metabolic rates in the planktonic compartment compared to the benthic one. This conclusion is not surprising considering that reference station Bahia is deeper than reference station Posidonia and that benthic metabolic rates are expected to be lower due to stronger light-limitation.

Day-time net community production (NCP_d) was estimated from the time course of DIC values from dawn to dust. Considering the scatter in the data, a simple linear regression was used. We did not attempt to estimate CR because only 3 profiles were obtained at night. NCP_d estimates were in fair agreement with those based on O_2 incubations and reproduce the same spatial trend, with higher NCP_d at Posidonia station than at Cap Enderrocat station (Table 7). We can conclude that the daily DIC time-course approach can be used with confidence to estimate metabolic rates but its application is limited to relatively shallow waters (≤ 15 m).

4. Conclusion

The results presented in this study provided estimates of the metabolism of the Bay of Palma on the basis of multiple approaches, encompassing monthly time series at one station in the bay, extensive surveys of direct metabolic estimates and estimates indirectly derived from DIC and O_2 fields, as well as diel cycles of DIC. Our results reveal a contrasting behaviour between the benthic and planktonic compartments. The areas of the benthic compartment dominated by the seagrass *Posidonia oceanica* remained autotrophic throughout the study, whereas the unvegetated sediments are, except for the shallowest areas, a net heterotrophic component of the metabolism of the Bay of Palma ecosystem. The autotrophic nature of seagrass meadows is consistent with previous reports for these ecosystems (Duarte and Cebrián 1996; Gattuso et al. 1998; Hemminga and Duarte 2000).

The planktonic community was largely heterotrophic, although showing episodes of autotrophy, associated to phytoplankton blooms, when planktonic GPP increased greatly, as in March 2002 (EUBAL-I), the time of the spring bloom in the NW Mediterranean (Duarte et al. 1999). Despite the clarity of these waters, planktonic and benthic GPP were strongly related to the incoming irradiance, leading to an overall relationship between NEP and surface irradiance over the *Posidonia oceanica* meadow. Indeed, the autotrophic, seagrass-dominated benthic compartment is confined to waters reaching slightly over half of the maximum depth of the Bay of Palma, so that macrophyte-derived autotrophy only contributes to elevate NEP at the shallower waters, as reflected in the distribution of pCO_2 and O_2 in the surface waters. Despite the contribution of the seagrass community, even shallow (Posidonia station: 7 m) sites within the bay were near metabolic balance at the annual time scale, where seagrass autotrophy barely compensates the planktonic heterotrophy. Overall, the depth of the Bay of Palma (mean: 28.5 m) leads to a dominance of planktonic over benthic communities in the metabolism of the entire ecosystem. Whereas excess production by seagrass can compensate (or even create) planktonic carbon deficits in shallow areas (< 10 m), planktonic metabolism dominates in deeper waters. Moreover, the short water residence time in the bay suggests that the extended planktonic heterotrophic periods, that dominate most of the year, cannot be supported by carbon in excess accumulated during autotrophic periods. As such, the whole ecosystem might be, in general, heterotrophic, especially during summer, when the strong increase in CR, driven by the increased temperature, greatly exceeded ecosystem GPP. Instead, the heterotrophic nature of the ecosystem and the planktonic community must be supported by allochtonous organic carbon inputs, probably derived from the human populations surrounding the Bay of Palma.

During the summer cruise, the spatial variability of pCO_2 and O_2 fields and the direction of CO_2 fluxes were consistent with NEP derived from incubations. The short water residence time in the bay (2 to 10 d) renders use of pCO_2 and O_2 fields to estimate ecosystem metabolism cumbersome. However, more elaborated mass balance formulations which account for the water residence time in the bay, allowed the derivation of NEP estimates that were in fair agreement with those derived from direct metabolic estimates from incubated samples over the *Posidonia oceanica* meadow. Our results also provide evidence that simple day-night whole water column DIC variations may also be useful to derive NEP estimates in shallow waters of seagrass ecosystems.

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Tables

Table 1 Characteristics of the incubation stations during the EUBAL cruises in 2002. Salinity and temperature values were averaged and chlorophyll *a* concentrations were integrated over the water column. *K* is the light attenuation coefficient.

Station	Date	Bottom depth m	Salinity	Temperature °C	Integrated chlorophyll *a* mg m^{-2}	*K* m^{-1}
EUBAL-I						
Posidonia	04/03/2002	18	37.61	14.4	4.2	0.15
Bahia	06/03/2002	35	37.65	14.3	17.3	0.14
Station 4	08/03/2002	37	37.53	14.3	16.7	0.11
Cap Enderrocat	10/03/2002	20	37.62	14	11.4	0.14
EUBAL-II						
Posidonia	20/06/2002	13	37.80	22.6	3.3	0.16
Bahia	22/06/2002	33	37.78	22.4	4.9	0.09
Station 4	18/06/2002	33	37.76	20.8	2.6	0.08
Cap Enderrocat	24/06/2002	16	37.76	23	1.5	0.09

Table 2 Integrated planktonic planktonic gross primary production (GPP), community respiration (CR) and net community production (NCP) at four stations during the EUBAL-I and -II cruises.

Station	Bottom depth m	GPP	CR	NCP
		mmol O_2 m^{-2} d^{-1}		
EUBAL-I				
Posidonia	18	36	-33	3
Bahia	35	98	-45	53
Station 4	37	92	-35	57
Cap Enderrocat	20	73	-27	46
EUBAL-II				
Posidonia	13	72	-45	27
Bahia	33	86	-75	11
Station 4	33	56	-107	-51
Cap Enderrocat	16	29	-59	-30

Table 3 Integrated chlorophyll *a* concentrations, planktonic gross primary production (GPP), community respiration (CR) and net community production (NCP) estimated on two surveys during each of the EUBAL cruises.

Station	Date	Integrated chlorophyll *a* mg	GPP	CR	NCP
			mmol O_2 m^{-2} d^{-1}		
Posidonia	07/03/2002	16	44	-33	11
Bahia	“	8	93	-45	48
Cap Enderrocat	“	3	20	-27	-7
4	“	15	84	-35	49
8	“	15	90	-89	1
18	“	14	78	-18	60
19	“	8	45	-16	29
20	“	15	86	-67	19
22	“	15	89	-49	40
23	“	15	89	-61	28
26	“	16	94	-74	20
Mean (± SD)	07/03/2002	13 ± 4	74 ± 25	-47 ± 24	27 ± 29
Posidonia	11/03/2002	7	42	-33	9
Bahia	“	30	175	-45	130
Cap Enderrocat	“	9	53	-27	26
4	“	35	204	-35	169
8	“	19	109	-89	20
18	“	12	72	-18	54
19	“	15	88	-16	72
20	“	24	140	-67	73
22	“	22	128	-49	79
23	“	16	92	-61	31
26	“	23	131	-74	57
Mean (± SD)	11/03/2002	19 ± 9	112 ± 50	-47 ± 24	65 ± 48
Posidonia	21/06/2002	2.1	41	-45	-4
Bahia	“	4.2	81	-75	6
Cap Enderrocat	“	0.5	9	-59	-50
4	“	0.8	16	-107	-91
8	“	0.5	12	-23	-11
18	“	4.1	80	-41	39
19	“	0.9	18	-37	-19
20	“	1	20	-28	-8
22	“	0.1	1	-16	-15
23	“	0.1	3	-17	-14
26	“	0.4	8	-20	-13
Mean (± SD)	21/06/2002	1.3 ± 1.5	26 ± 29	-43 ± 28	-17 ± 33
Posidonia	26/06/2002	2.1	40	-45	-5
Bahia	“	7.1	138	-75	63
Cap Enderrocat	“	0.5	10	-59	-49
4	“	0.8	15	-107	-92
8	“	0.3	6	-19	-13
18	“	8.5	165	-41	125
19	“	1.2	24	-37	-14
20	“	0.6	15	-25	-10
22	“	0.7	13	-24	-11
23	“	0.4	8	-21	-13
26	“	0.2	6	-19	-13
Mean (± SD)	26/06/2002	2 ± 2.9	40 ± 56	-43 ± 28	-3 ± 56
EUBAL-I Mean (± SD)	March 2002	16 ± 7	93 ± 43	-47 ± 24	46 ± 41
EUBAL-II Mean (± SD)	June 2002	1.7 ± 2.3	33 ± 44	-43 ± 27	-10 ± 45

Table 4 Mean (± SE) benthic net community production (NCP) in March (EUBAL-I) and June 2002 (EUBAL-II).

Cruise	Community	Depth (m)	NCP ± SE mmol O_2 m^{-2} d^{-1}
EUBAL-I	*P. oceanica*	7	29.7 ± 10.8
		15	17.1 ± 3.3
	Sediment	7	-0.3 ± 0.2
		15	-0.4 ± 0.1
EUBAL-II	*P. oceanica*	4	44.2 ± 13.6
		7	12.0 ± 11.0
		15	24.6 ± 3.9
		22	19.1 ± 11.1
	Sediment	4	5.7 ± 0.5
		7	-4.0 ± 0.4
		15	-3.7 ± 0.3
		22	-6.4 ± 0.4

Table 5 Average ± SD of AOU, pCO_2, pCO_2 normalized to a constant temperature ($pCO_{2(19°C)}$), DIC_{37}, wind speed (*u*), the air-sea gradient of pCO_2 (ΔpCO_2), in the surface waters, and atmospheric CO_2 flux computed using the gas transfer velocity given by Wanninkhof and McGillis (1999) (*F*), over the *Posidonia* meadow and in the rest of the bay, on the surveys carried out during the EUBAL-I and -II cruises. Data were interpolated using the Kriging procedure on a grid of 0.0034°E x 0.0025°N and averaged.

	AOU µmol kg^{-1}	pCO_2 ppm	$pCO_{2(19°C)}$ ppm	DIC_{37} mmol kg^{-1}	ΔpCO_2 ppm	*u* m s^{-1}	*F* mmol C m^{-2} d^{-1}
Bay (excluding *Posidonia* meadow)							
01/03/2002	-4.6 ± 2.3	324 ± 3	386 ± 4	2.142 ± 0.002	-46 ± 16	3.9 ± 1.6	-1.0 ± 0.9
04/03/2002	-10.5 ± 1.8	320 ± 2	384 ± 3	2.140 ± 0.002	-64 ± 1	6.9 ± 1.8	-5.8 ± 4.5
07/03/2002	-2.4 ± 0.6	320 ± 1	388 ± 2	2.144 ± 0.001	-54 ± 2	4.5 ± 2.2	-1.9 ± 2.3
09/03/2002	-0.8 ± 0.9	320 ± 1	386 ± 3	2.143 ± 0.001	-57 ± 3	2.9 ± 0.9	-0.4 ± 0.3
11/03/2002	-3.2 ± 0.5	320 ± 1	381 ± 2	2.140 ± 0.001	-55 ± 4	3.3 ± 0.9	-0.5 ± 0.4
12/03/2002	-4.2 ± 0.9	321 ± 2	380 ± 2	2.140 ± 0.001	-53 ± 7	3.3 ± 1.0	-0.5 ± 0.5
19/06/2002	-15.8 ± 3.5	420 ± 7	363 ± 7	2.121 ± 0.004	50 ± 12	4.7 ± 2.1	1.7 ± 1.4
21/06/2002	-13.3 ± 3.3	426 ± 10	361 ± 7	2.120 ± 0.004	52 ± 18	4.1 ± 2.2	1.6 ± 2.0
25/06/2002	-10.0 ± 2.4	442 ± 10	361 ± 5	2.118 ± 0.003	82 ± 10	6.3 ± 1.4	5.9 ± 3.4
26/06/2002	-10.5 ± 4.0	444 ± 11	358 ± 8	2.116 ± 0.005	77 ± 20	3.6 ± 1.2	1.1 ± 1.1
27/06/2002	-10.8 ± 1.1	443 ± 3	360 ± 1	2.119 ± 0.001	83 ± 3	5.4 ± 1.4	3.6 ± 2.5
Posidonia meadow							
01/03/2002	-6.1 ± 2.4	323 ± 2	384 ± 3	2.141 ± 0.002	-56 ± 17	3.9 ± 1.6	-1.0 ± 0.9
04/03/2002	-14.8 ± 2.7	316 ± 3	379 ± 4	2.138 ± 0.002	-63 ± 1	6.9 ± 1.8	-5.7 ± 4.5
07/03/2002	-2.0 ± 1.6	323 ± 5	395 ± 6	2.147 ± 0.003	-54 ± 4	4.5 ± 2.2	-1.9 ± 2.4
09/03/2002	0.0 ± 0.6	323 ± 8	394 ± 10	2.147 ± 0.005	-58 ± 9	2.9 ± 0.9	-0.4 ± 0.4
11/03/2002	-2.6 ± 0.6	320 ± 1	383 ± 2	2.141 ± 0.001	-64 ± 8	3.3 ± 0.9	-0.6 ± 0.5
12/03/2002	-4.2 ± 1.1	321 ± 3	379 ± 2	2.140 ± 0.001	-59 ± 12	3.3 ± 1.0	-0.6 ± 0.5

Table 5 continued

	AOU µmol kg^{-1}	pCO$_2$ ppm	pCO$_{2(19°C)}$ ppm	DIC$_{37}$ mmol kg^{-1}	ΔpCO$_2$ ppm	*u* m s^{-1}	*F* mmol C m^{-2} d^{-1}
19/06/2002	-24.0 ± 5.8	405 ± 17	346 ± 15	2.110 ± 0.010	40 ± 21	4.7 ± 2.1	1.4 ± 1.1
21/06/2002	-18.0 ± 4.7	420 ± 18	351 ± 13	2.114 ± 0.009	45 ± 31	4.1 ± 2.2	1.3 ± 1.7
25/06/2002	-14.1 ± 3.9	433 ± 14	351 ± 10	2.111 ± 0.007	74 ± 15	6.3 ± 1.4	5.3 ± 3.1
26/06/2002	-12.6 ± 5.8	445 ± 18	354 ± 12	2.114 ± 0.008	79 ± 31	3.6 ± 1.2	1.1 ± 1.1
27/06/2002	-12.7 ± 2.2	449 ± 7	358 ± 5	2.117 ± 0.003	87 ± 11	5.4 ± 1.4	3.7 ± 2.6

Table 6 Net ecosystem production (NEP) and the photosynthetic quotient (PQ), over the *Posidonia oceanica* meadow during the EUBAL-II cruise. DIC_{37} and O_2 data were interpolated as explained in legend of Table 5. Top half of the table corresponds to NEP computed from the observed surface distributions of DIC_{37} and O_2. Lower half of the table corresponds to NEP computed from the surface distributions of DIC_{37} and O_2 that were adjusted to account for their vertical gradients (see text for details). The uncertainty on NEP was computed assuming an error on t_{total} of ± 1 d. The uncertainty on PQ corresponds to SE on the slope of the linear regression of NEP_{O2} *vs.* NEP_{DIC}.

	NEP_{DIC} mmol C m^{-2} d^{-1}	NEP_{O2} mmol O_2 m^{-2} d^{-1}	PQ
Based on observed surface distribution			
19/06/2002	41 ± 3	31 ± 3	0.93 ± 0.18 (r^2 = 0.926)
21/06/2002	25 ± 2	10 ± 1	
25/06/2002	27 ± 2	9 ± 1	
26/06/2002	9 ± 1	2 ± 1	
27/06/2002	7 ± 1	-5 ± 1	
Based on adjusted surface distribution to account for vertical gradients			
19/06/2002	59±4	77 ± 7	0.92 ± 0.18 (r^2 = 0.902)
21/06/2002	42 ± 4	56 ± 3	
25/06/2002	45 ± 2	54 ± 3	
26/06/2002	27 ± 2	48 ± 2	
27/06/2002	25 ± 3	40 ± 1	

Table 7 Day-time net community production (NCP_d) from the EUBAL-II cruise based on O_2 incubations in both planktonic and benthic compartments and based on the day-time DIC evolution. NCP_d is computed from the slope of the linear regression of water column averaged DIC values (the error estimate on NCP_d is based on SE on the slope).

	O_2 incubations			DIC evolution
	Planktonic NCP_d	Benthic NCP_d	NEP_d	NEP_d
	mmol O_2 m^{-2} d^{-1}			mmol C m^{-2} d^{-1}
Posidonia	2.9	3.7	6.6	15.0 ± 2.1
Cap Enderrocat	-0.5	4.1	3.6	9.2 ± 5.0

Figure captions

Figure 1. Map of the Bay of Palma showing the bathymetry (dotted lines), the distribution of the *Posidonia oceanica* meadow (green area, adapted from Rey and Diaz Del Rio 1984), the four reference stations where incubations for metabolic processes were carried out (red stars) and stations where vertical profiles were carried out (blue circles).

Figure 2. Monthly net community production (NCP) in the benthic and planktonic compartment, and the combined net ecosystem production at the Posidonia station (cf. Fig. 1).

Figure 3. Velocity distribution during EUBAL-I at 14 m for A) 01 March 2002, B) 03 March 2002 and C) 12 March 2002; and EUBAL-II at 10 m D) for 25 June 2002.

Figure 4. Salinity distribution during EUBAL-I at 2 m for A) 01 March 2002, B) 03 March 2002; C) 12 March 2002.

Figure 5. Depth profiles of planktonic daily CR and GPP (mmol O_2 m^{-3} d^{-1}) measured at four stations in the Bay of Palma during A) EUBAL-I and B) EUBAL-II cruises (cf. Fig. 1).

Figure 6. A) Linear relationships between integrated gross primary production (GPP) and integrated chlorophyll *a* concentrations (Chl *a*) at four stations (cf. Fig. 1) during EUBAL-I and II cruises. B) Linear relationship between GPP and respiration (CR) integrated in the water column above the *Posidonia oceanica* meadow at four stations during the EUBAL-II cruise.

Figure 7. A) AOU (µmol kg^{-1}) versus pCO_2 normalized to a constant temperature ($pCO_{2(19°C)}$, ppm) in surface waters from all the surveys during the EUBAL-I and II cruises. The range of variation of AOU and $pCO_{2(19°C)}$ at the Dyfamed station for the March 1998-99 and June 1998-99 periods (Copin-Montégut and Bégovic 2002; Bégovic and Copin-Montégut 2002) are indicated by the horizontal and vertical lines . B) TA (mmol kg^{-1}) versus salinity in surface waters during the EUBAL-I and II cruises. Dotted line corresponds to the regression function reported by Copin-Montégut (1993) for the Alboran Sea (TA = -1.072 (± 0.016) + 0.09485 (± 0.0004) x salinity) and the solid line corresponds to the regression function based on the EUBAL-I and II cruises (TA = -0.346 (± 0.007) + 0.0756 (± 0.003) x salinity; $r^2 = 0.869$; n = 119; $p < 0.0001$). The error bar on the lower left corner of the plot corresponds to the estimated accuracy on TA measurements (B).

Figure 8. Surface distributions of pCO_2 normalized to a constant temperature ($pCO_{2(19°C)}$, ppm) and AOU (μmol kg^{-1}) obtained on 3 March 2002 (EUBAL-I cruise) and 19 June 2002 (EUBAL-II cruise).

Figure 9. NEP_{DIC} (A; mmol C m^{-2} h^{-1}) and NEP_{O2} (B; mmol O_2 m^{-2} h^{-1}) over the *Posidonia oceanica* meadow *versus* surface irradiance (I_0; μmol m^{-2} s^{-1}) during the EUBAL-II cruise. NEP_{DIC} and NEP_{O2} data were adjusted linearly to 12:00 Universal Time (UT; all surveys ended in mid-afternoon, ranging from 14:30 to 16:45 UT). Surface irradiance was averaged from dawn to 12:00 UT.

Figure 10. Vertical profiles of DIC normalized to a constant salinity (DIC_{37} in mmol kg^{-1}) and O_2 (μmol kg^{-1}) at four reference stations (cf. Fig. 1).

Figure 11. A) Variations of water column averaged DIC normalized to a constant salinity (DIC_{37} in mmol kg^{-1}) during 24 h at Posidonia (20-21 June), Bahia (22-23 June) and Cap Enderrocat (24-25 June; cf. Fig. 1). B) Variations during the 24 h cycles of the difference of DIC (ΔDIC in μmol kg^{-1}) between the average value from the top half of the water column and the average value from the bottom half of the water column. DIC was computed from the pCO_2 measurements (vertical resolution of 1 m), TA values computed from the linear regression against salinity (legend of Fig. 7) and salinity and temperature profiles from CTD casts contemporary to the pCO_2 profiles.

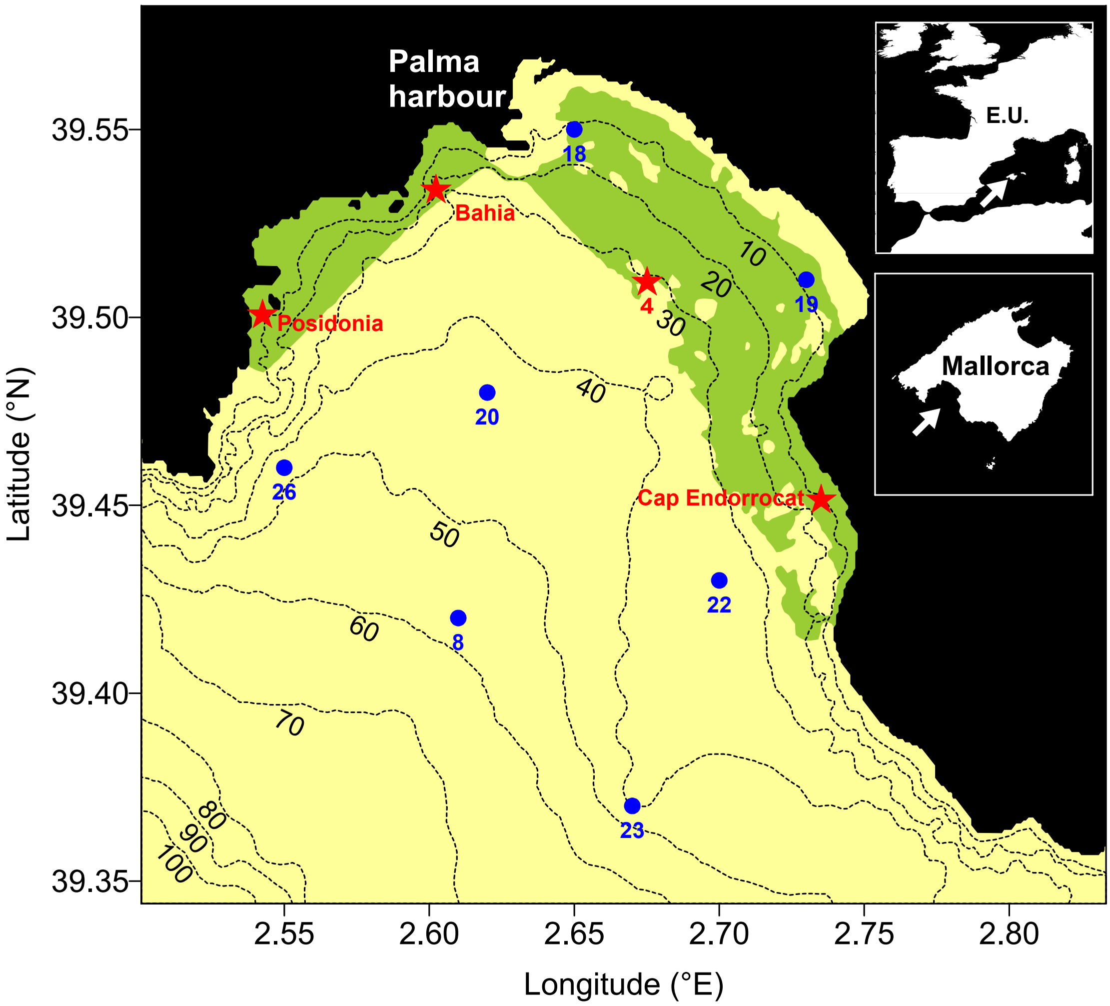

Palma harbour
E.U.
Mallorca
Bahia
Posidonia
4
Cap Endorrocat
18
19
20
26
22
8
23
10
20
30
40
50
60
70
80
90
100
39.55
39.50
39.45
39.40
39.35
Latitude (°N)
2.55
2.60
2.65
2.70
2.75
2.80
Longitude (°E)

Fig. 1

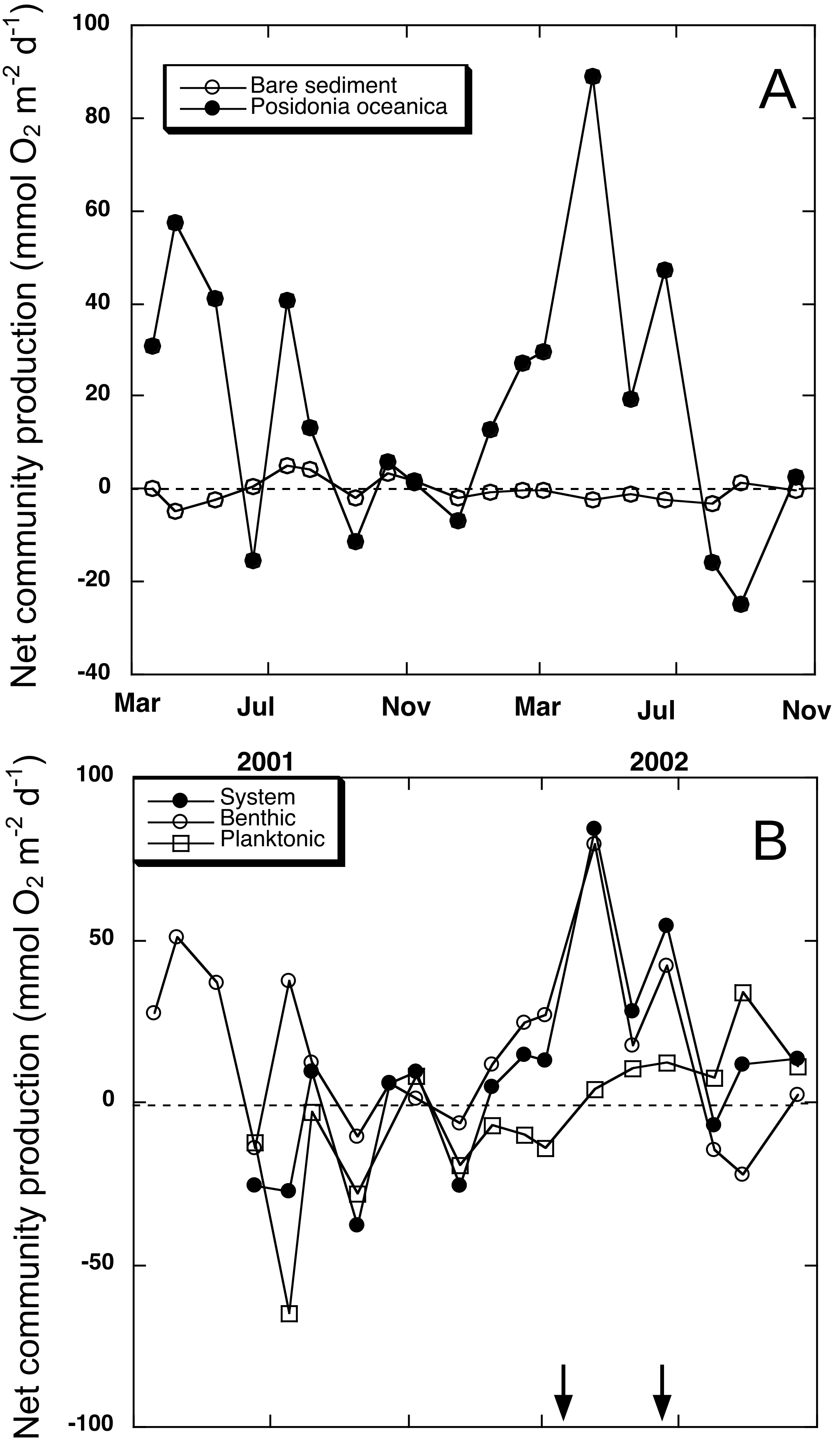
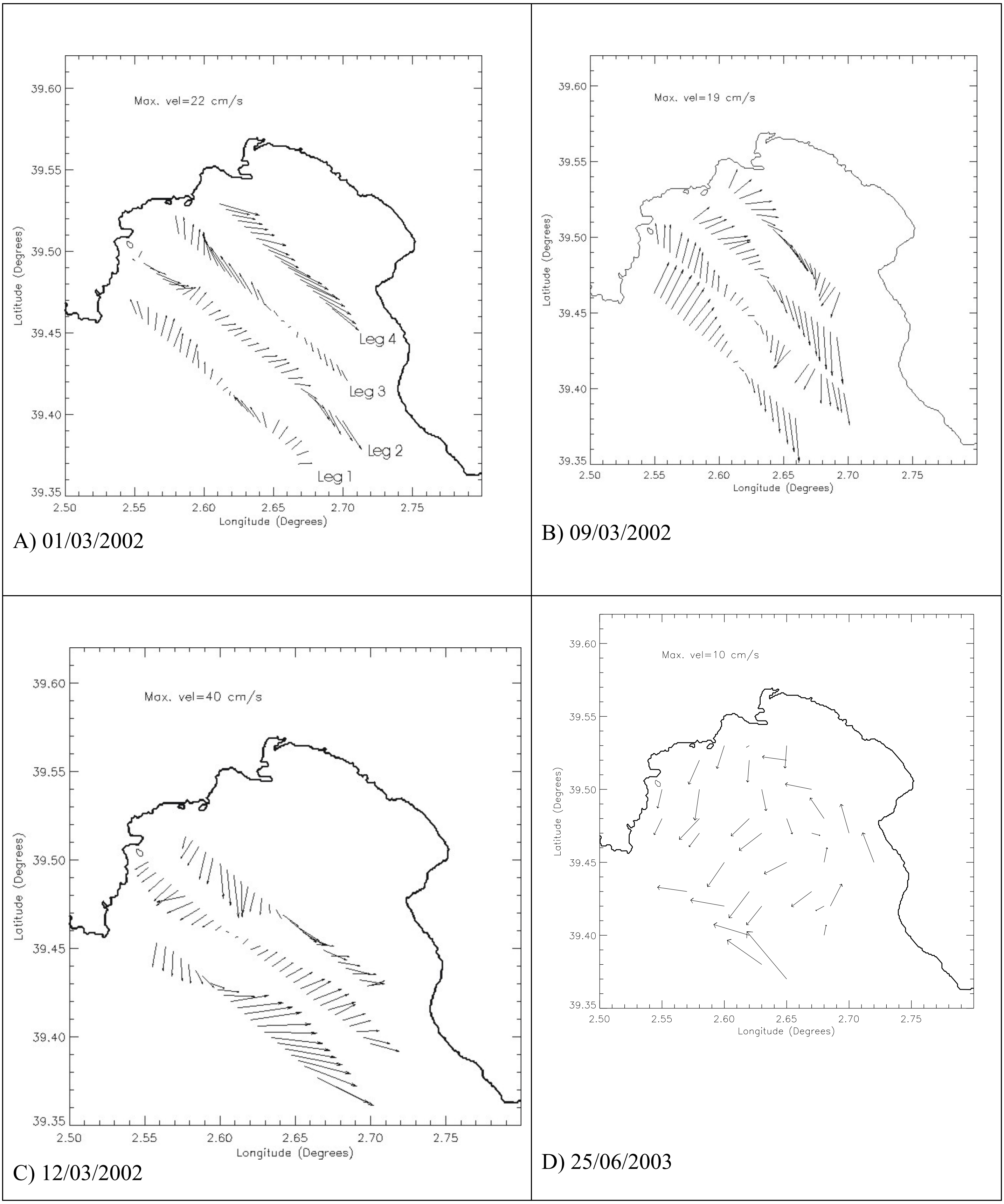

A
Bare sediment
Posidonia oceanica
Net community production (mmol O_2 m^{-2} d^{-1})
100
80
60
40
20
0
-20
-40
Mar
Jul
Nov
Mar
Jul
Nov
2001
2002
B
System
Benthic
Planktonic
Net community production (mmol O_2 m^{-2} d^{-1})
100
50
0
-50
-100
Mar
Jul
Nov
Mar
Jul
Nov
2001
2002

Fig. 2



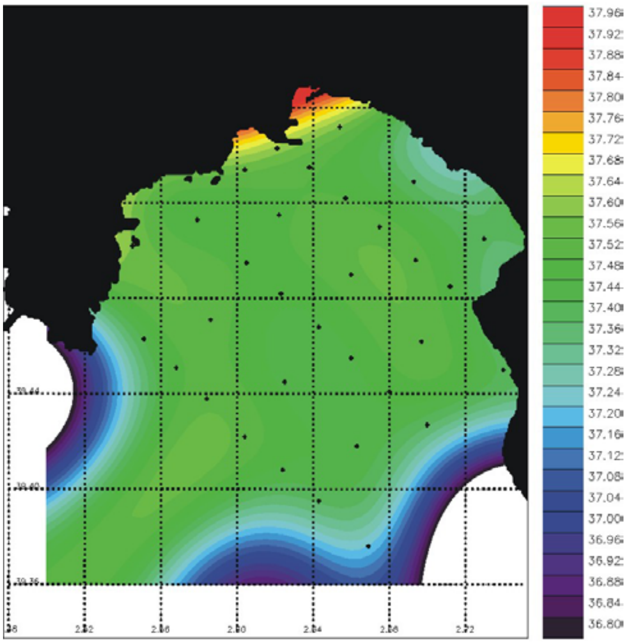
A) 01/03/2002

B) 09/03/2002

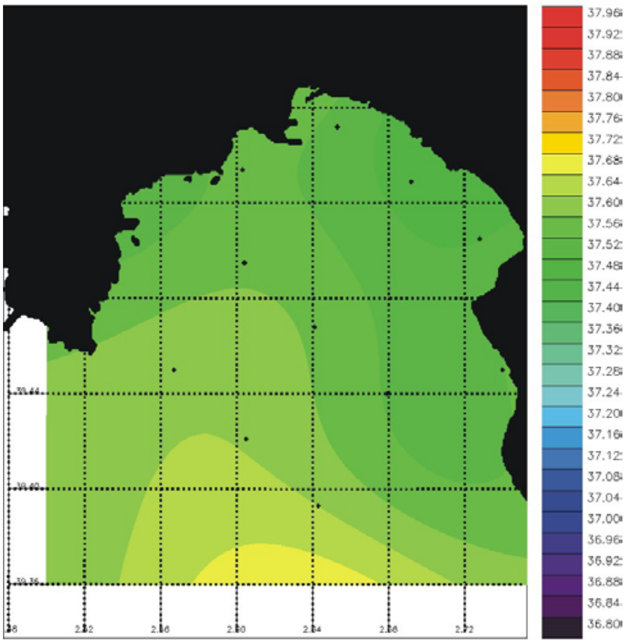
C) 12/03/2002

D) 25/06/2003

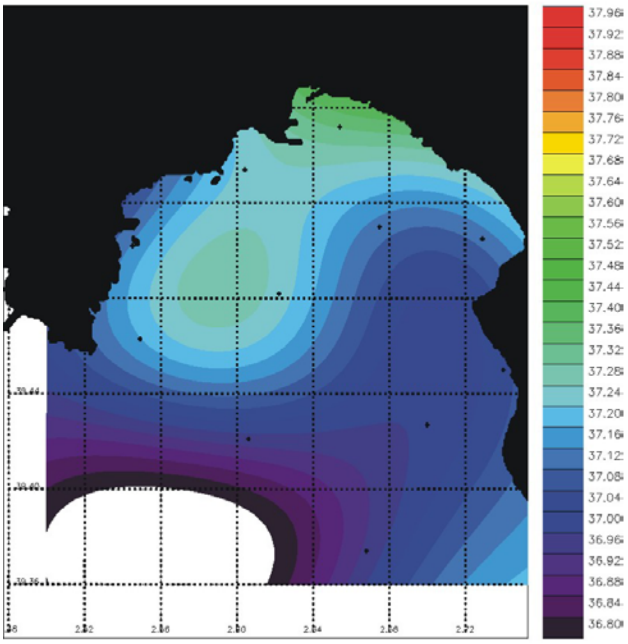
Fig. 3



A) 01/03/2002



B) 03/03/2002



C) 12/03/2002

Fig. 4

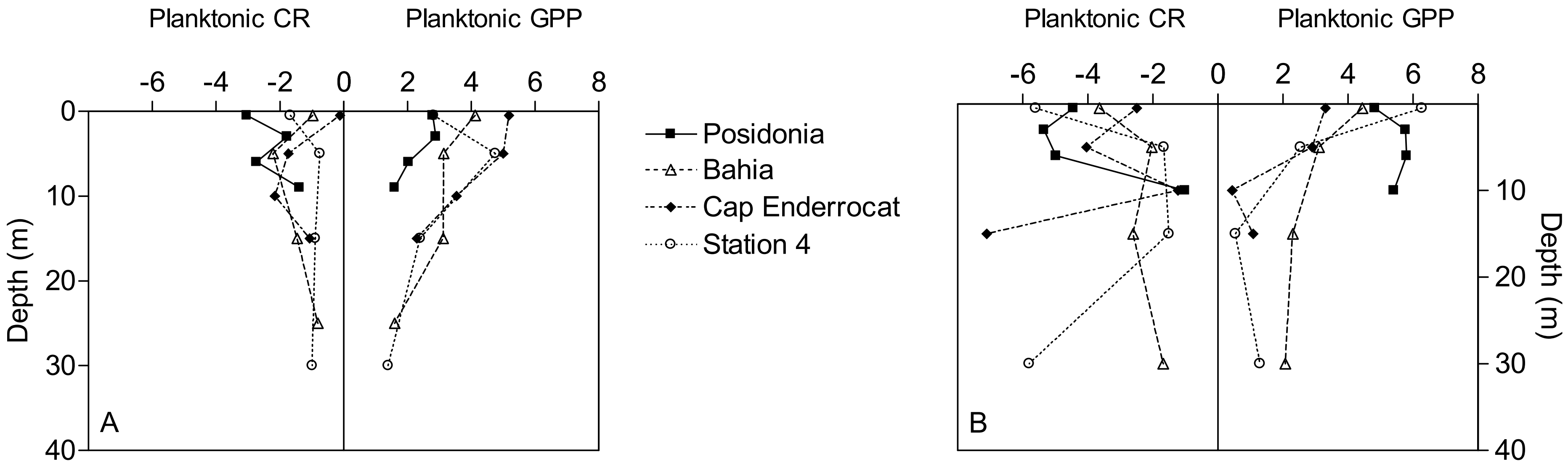

Planktonic CR
Planktonic GPP
-6
-4
-2
0
2
4
6
8
Depth (m)
0
10
20
30
40
A
Posidonia
Bahia
Cap Enderrocat
Station 4
Planktonic CR
Planktonic GPP
-6
-4
-2
0
2
4
6
8
Depth (m)
10
20
30
40
B

Fig. 5

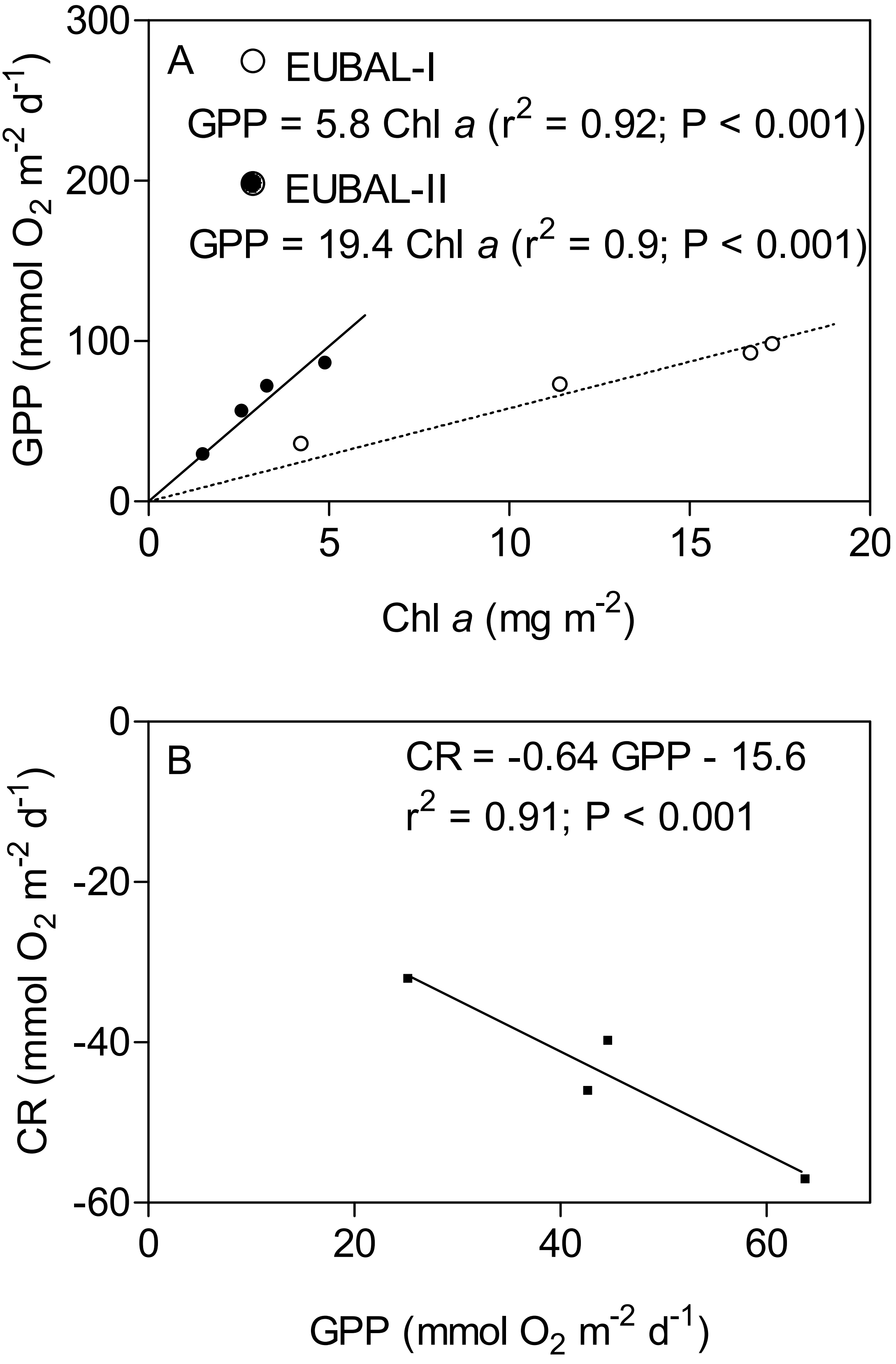

A
○ EUBAL-I
GPP = 5.8 Chl a (r2 = 0.92; P < 0.001)
● EUBAL-II
GPP = 19.4 Chl a (r2 = 0.9; P < 0.001)
GPP (mmol O2 m-2 d-1)
300
200
100
0
0
5
10
15
20
Chl a (mg m-2)
B
CR = -0.64 GPP - 15.6
r2 = 0.91; P < 0.001
CR (mmol O2 m-2 d-1)
0
-20
-40
-60
0
20
40
60
GPP (mmol O2 m-2 d-1)

Fig. 6

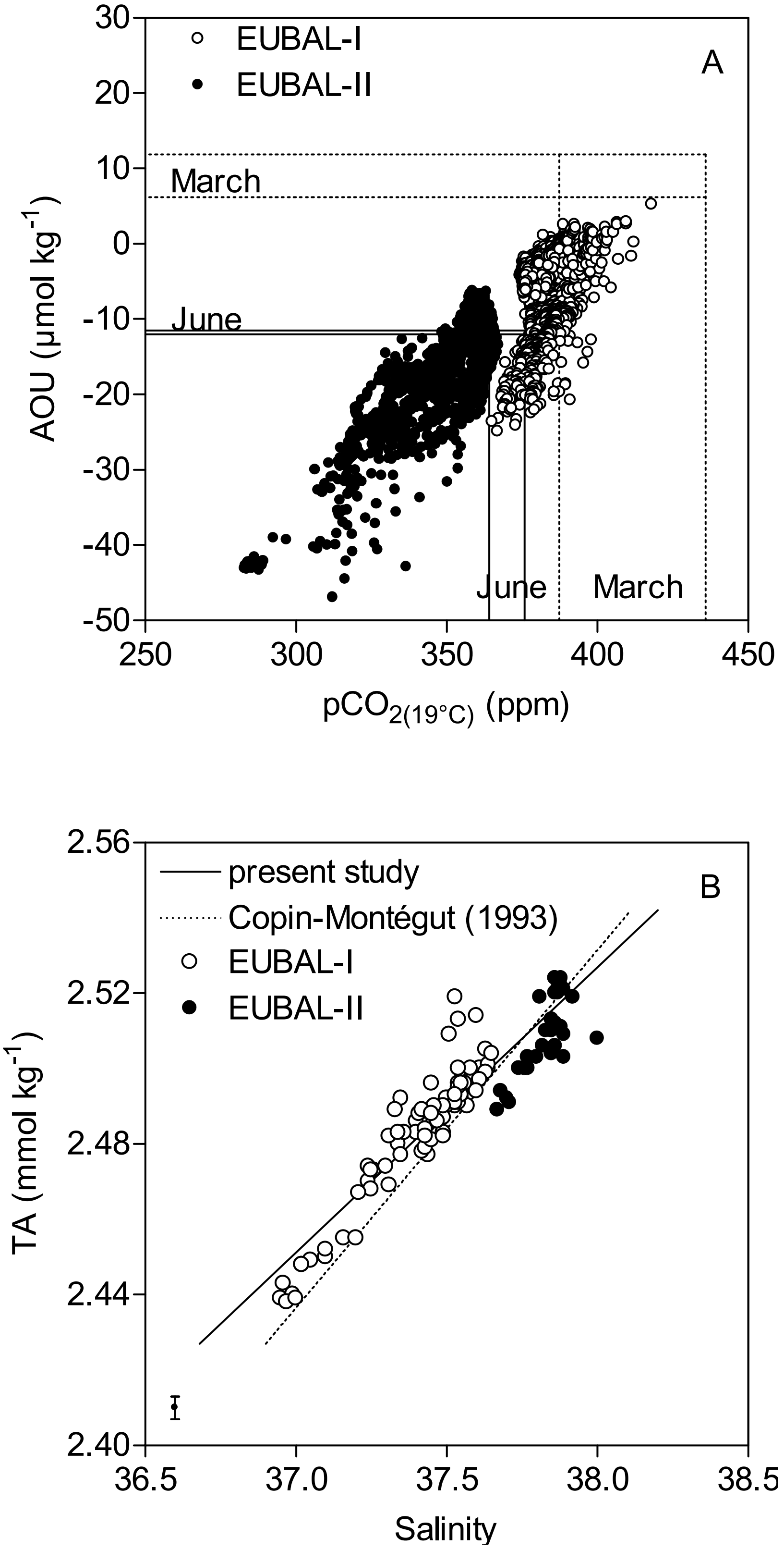

EUBAL-I
EUBAL-II
A
March
June
June
March
AOU (μmol kg^{-1})
30
20
10
0
-10
-20
-30
-40
-50
250
300
350
400
450
pCO$_{2(19°C)}$ (ppm)
present study
Copin-Montégut (1993)
EUBAL-I
EUBAL-II
B
TA (mmol kg^{-1})
2.56
2.52
2.48
2.44
2.40
36.5
37.0
37.5
38.0
38.5
Salinity

Fig. 7

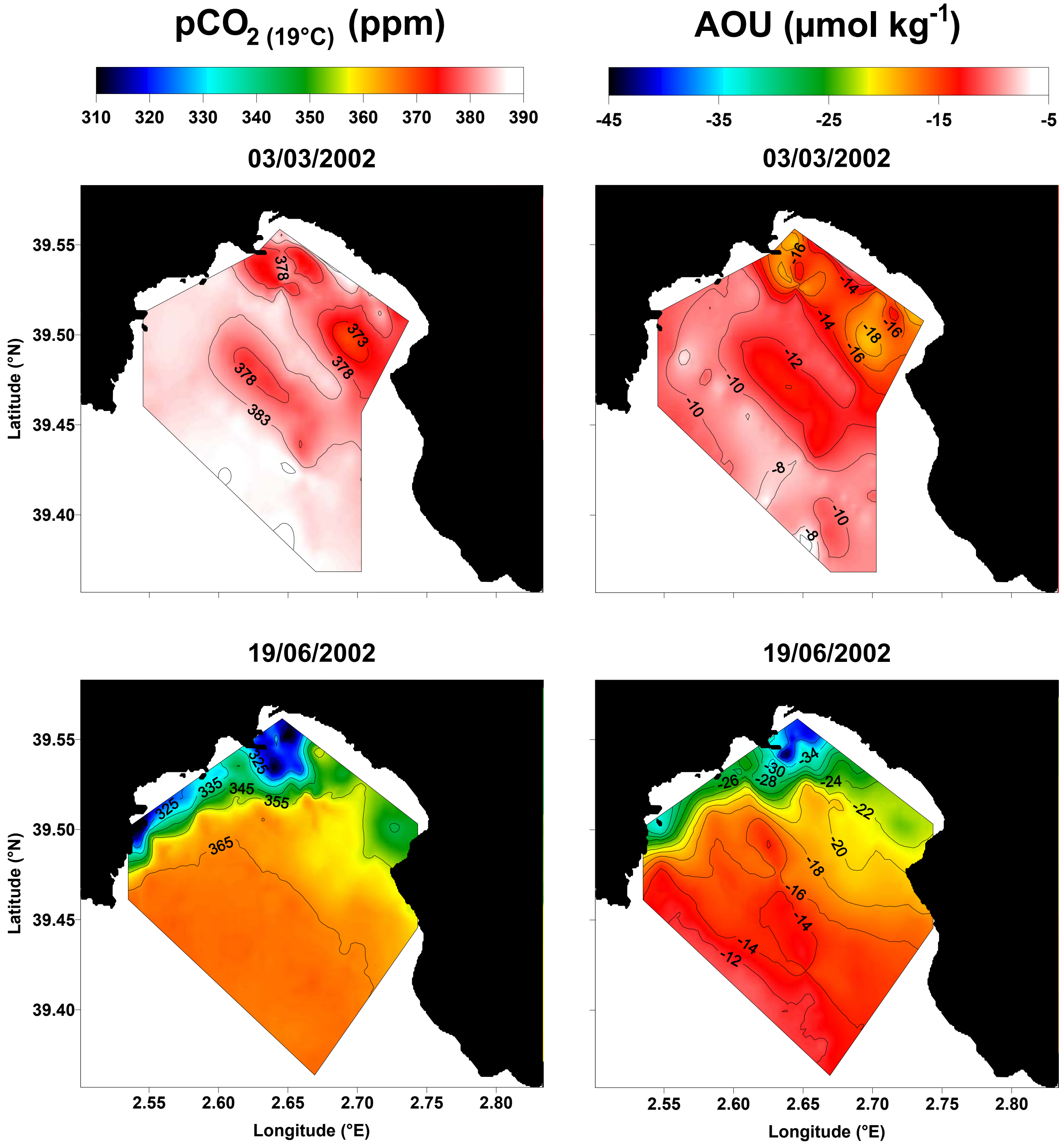
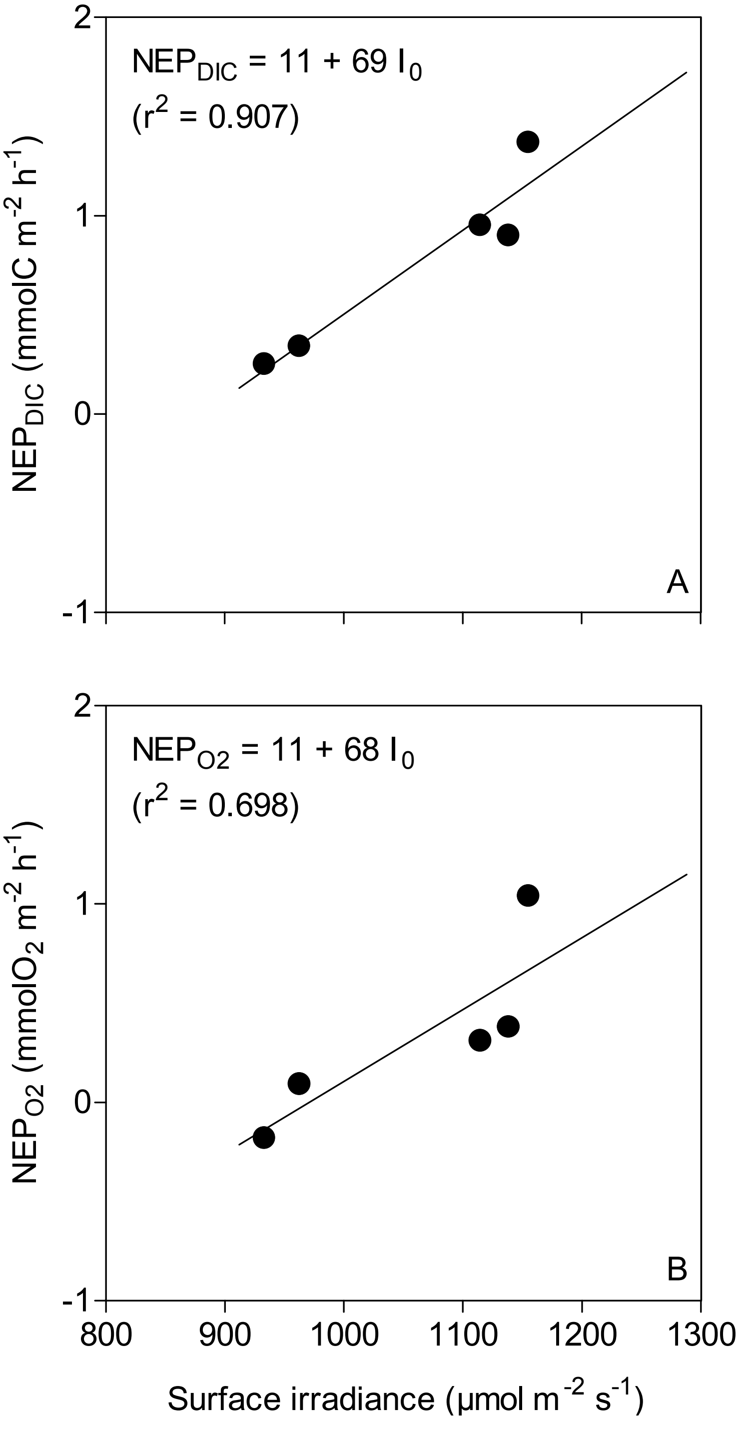

pCO₂ (19°C) (ppm)
310 320 330 340 350 360 370 380 390
AOU (µmol kg⁻¹)
-45 -35 -25 -15 -5
03/03/2002
03/03/2002
19/06/2002
19/06/2002
Latitude (°N)
39.55
39.50
39.45
39.40
378
373
378
383
-16
-14
-14
-18
-16
-16
-12
-10
-10
-8
-10
-8
325
325
335
345
355
365
-34
-30
-28
-26
-24
-22
-20
-18
-16
-14
-14
-12
2.55 2.60 2.65 2.70 2.75 2.80
Longitude (°E)

Fig. 8



NEP_{DIC} = 11 + 69 I_0
(r^2 = 0.907)
A
NEP_{DIC} (mmolC m^{-2} h^{-1})
2
1
0
-1
NEP_{O2} = 11 + 68 I_0
(r^2 = 0.698)
B
NEP_{O2} (mmolO_2 m^{-2} h^{-1})
2
1
0
-1
800
900
1000
1100
1200
1300
Surface irradiance (µmol m^{-2} s^{-1})

Fig. 9

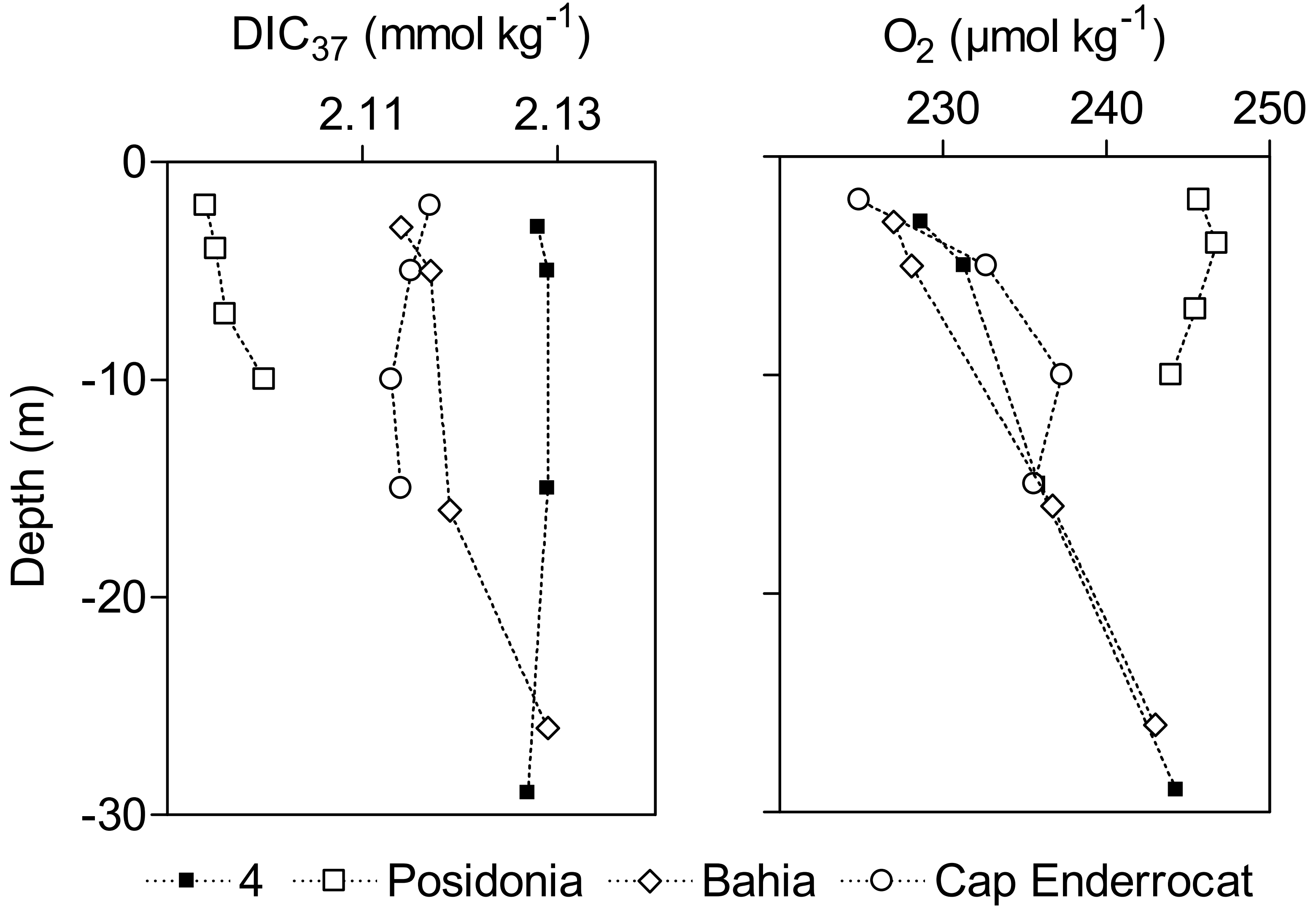

DIC_{37} (mmol kg^{-1})
2.11
2.13
O_2 (µmol kg^{-1})
230
240
250
0
-10
-20
-30
Depth (m)
4
Posidonia
Bahia
Cap Enderrocat

Fig. 10

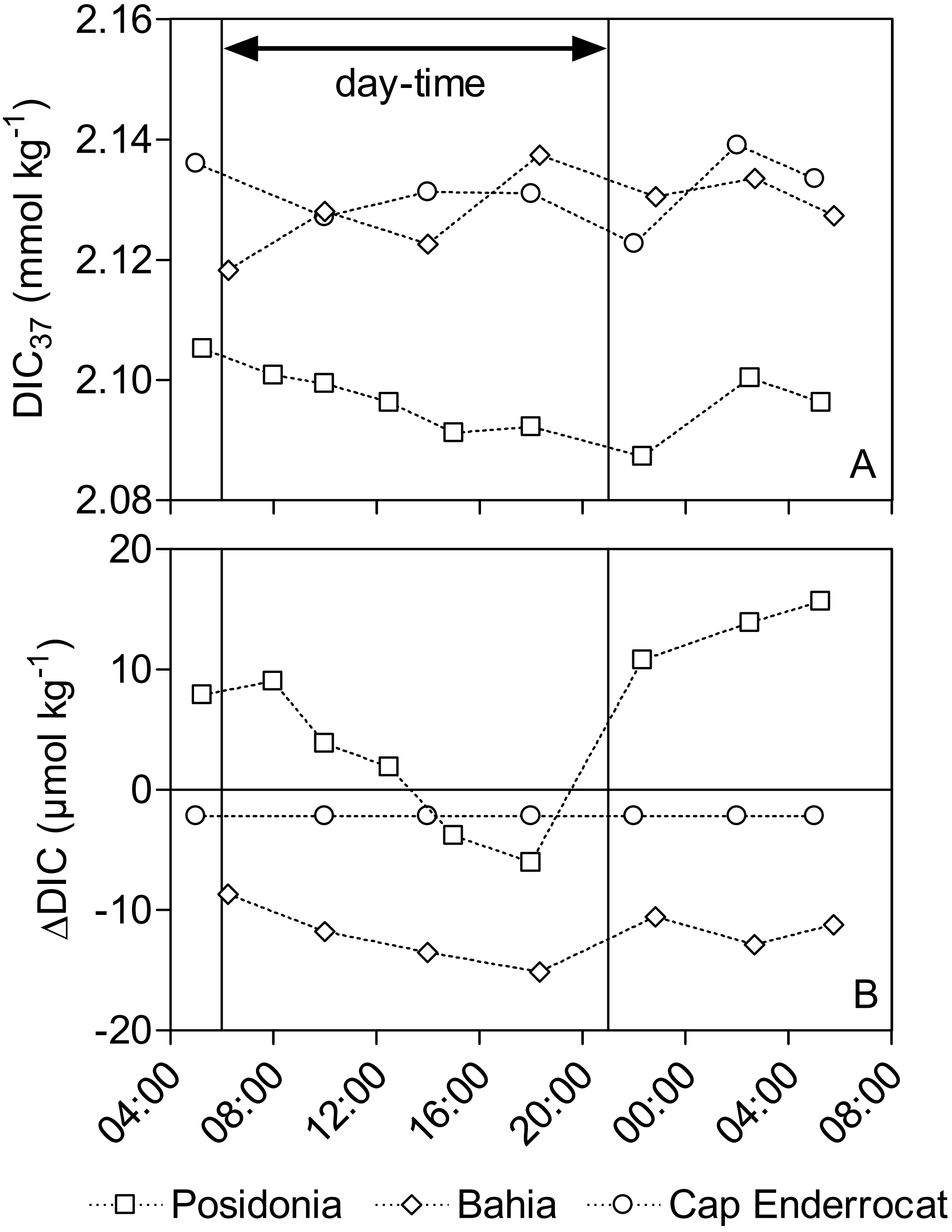

2.16
2.14
2.12
2.10
2.08
DIC_{37} (mmol kg^{-1})
day-time
A
20
10
0
-10
-20
ΔDIC (µmol kg^{-1})
B
04:00
08:00
12:00
16:00
20:00
00:00
04:00
08:00
Posidonia
Bahia
Cap Enderrocat

Fig. 11

3.2 Coefficient d'échange dans les estuaires

Borges A. V., Delille B., Schiettecatte L. -S., Gazeau F., Abril G. & Frankignoulle M.
Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt and Thames) (2004)
Limnology and Oceanography 49(5).

Limnol. Oceanogr., 00(0), 2004, 000–000

Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt, and Thames)

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Abstract

We measured the flux of CO_2 across the air–water interface using the floating chamber method in three European estuaries with contrasting physical characteristics (Randers Fjord, Scheldt, and Thames). We computed the gas transfer velocity of CO_2 (k) from the CO_2 flux and concomitant measurements of the air–water gradient of the partial pressure of CO_2 (pCO_2). There was a significant linear relationship between k and wind speed for each of the three estuaries. The differences of the y-intercept and the slope between the three sites are related to differences in the contribution of tidal currents to water turbulence at the interface and fetch limitation. The contribution to k from turbulence generated by tidal currents is negligible in microtidal estuaries such as Randers Fjord but is substantial, at low to moderate wind speeds, in macrotidal estuaries such as the Scheldt and the Thames. Our results clearly show that in estuaries a simple parameterization of k as a function of wind speed is site specific and strongly suggest that the y-intercept of the linear relationship is mostly influenced by the contribution of tidal currents, whereas the slope is influenced by fetch limitation. This implies that substantial errors in flux computations are incurred if generic relationships of the gas transfer velocity as a function of wind speed are employed in estuarine environments for the purpose of biogas air–water flux budgets and ecosystem metabolic studies.

Based on organic carbon flux budgets, the overall picture of the net ecosystem metabolism in the coastal ocean is that temperate open continental shelves (bordered by a continental margin) are net autotrophic (net exporters of carbon and thus potential sinks for atmospheric CO_2) while near-shore systems influenced by anthropogenic and/or terrestrial organic carbon inputs, in particular temperate estuaries, are net heterotrophic (e.g., Smith and Mackenzie 1987; Gattuso et al. 1998). This picture has recently been confirmed by direct measurements of the air–water gradient of pCO_2 with a sufficient temporal and spatial resolution to allow the annual integration of the computed air–water CO_2 fluxes. Temperate open continental shelves are net sinks for atmospheric CO_2 (e.g., Tsunogai et al. 1999; Frankignoulle and Borges 2001*a*; Borges and Frankignoulle 2002*a*; DeGranpre et al. 2002), while temperate estuaries are net sources of CO_2 to the atmosphere (e.g. Frankignoulle et al. 1998; Cai et al. 2000; Raymond et al. 2000; Borges and Frankignoulle 2002*b*). Although the surface area of estuaries is globally about 20 times smaller than that of open continental shelves, the air–water fluxes of CO_2 in the temperate estuaries so far studied are about two orders of magnitude higher (about $+100$ mmol m^{-2} d^{-1}) than over temperate open continental shelves (about -5 mmol m^{-2} d^{-1}). A global integration of the CO_2 fluxes in these two systems is not possible at present time because of the lack of adequate data coverage. Indeed, few data are available at subtropical and tropical latitudes in both estuaries and continental shelves. The recent work by Cai et al. (2003) in the U.S. South Atlantic Bight shows that, unlike temperate continental shelves, subtropical continental shelves could in general be sources of CO_2. However, regional comparisons strongly suggest that CO_2 fluxes in es-

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Table 1. Basic data of the three studied sites. The surface area, length, and width are for the region of salinity mixing (the tidal freshwater region is excluded). The average estuary depth is at low tide and for the region of salinity mixing; however, note that measurements were made in the navigation channel.

	Randers Fjord	Thames	Scheldt
Type	microtidal	macrotidal	macrotidal
Catchment area (10^3 km^2)	3.3	14	21
Surface area (km^2)	22	215	268
Length (km)	27	85	75
Width (km)	1.0	2.1	3.3
Average depth (m)	2	8	10
Navigation channel depth (m)	7	12	13
Tidal amplitude (m)	0.1–0.2	3–6	2–5
Fresh water discharge (km^3 yr^{-1})	1.2	9.5	3.8
Residence time (days)	5–10	20–40	30–90

tuaries could be very significant. For instance, the integrated emission of atmospheric CO_2 from Europe's estuaries (30 to 60 × 10^9 kg C yr^{-1}; Frankignoulle et al. 1998) is of the same order of magnitude as the integrated sink over the European open continental shelf (90 to 170 × 10^9 kg C yr^{-1}, Frankignoulle and Borges 2001*a*). Thus, more data of pCO_2 in estuaries and continental shelves are needed worldwide to allow the computation and global integration of the related air–water CO_2 fluxes. This also requires a better constraint on the formulation of the gas transfer velocity, which is the subject of a long-lived debate that at present time seems unresolved in both open oceanic waters (e.g., Liss and Merlivat 1986; Wanninkhof 1992; Jacobs et al. 1999; Wanninkhof and McGillis 1999; Nightingale et al. 2000; McGillis et al. 2001) and estuarine environments (e.g., Raymond and Cole 2001; Kremer et al. 2003*a*). Finally, the computation of gas exchange is also critical in the study of ecosystem metabolism based on the open-water method using O_2 and dissolved inorganic carbon measurements (e.g., Smith and Key 1975; Kremer et al. 2003*a*).

The flux of CO_2 across the air–water interface can be computed according to

$$F = \varepsilon k \alpha \Delta pCO_2 \tag{1}$$

where α is the solubility coefficient of CO_2, ΔpCO_2 is the air–water gradient of pCO_2, k is the gas transfer velocity of CO_2 (also referred to as piston velocity), and ε is the chemical enhancement factor of gas exchange.

In both open oceanic and coastal environments, highly precise and accurate methods to measure ΔpCO_2 are available; thus, the largest uncertainty in the computation of F comes from the k term (α is straightforwardly computed from salinity and water temperature, and the contribution from ε is usually negligible, except under very low turbulent conditions, see, e.g., Wanninkhof 1992 for open oceanic waters and Raymond and Cole 2001 for estuarine environments). Based on numerous theoretical, laboratory, and field studies, it is well established that k depends on a variety of variables such as capillary and breaking waves, boundary layer stability, air bubbles, surfactant surface films, evaporation/condensation, and precipitation, but the most important one is turbulence at the air–water interface (in the case of sparingly soluble gases such as CO_2 the critical variable is turbulence in the liquid phase). In open oceanic waters, the gas transfer velocity of CO_2 is usually parameterized as a function of wind speed because wind stress is the main generator of turbulence in these systems.

In a recent review that compiles available measurements of k based on different methodologies in various estuaries, Raymond and Cole (2001) suggested that the parameterization of k as a function of wind speed could be significantly different in estuarine environments from those developed in open oceanic waters (higher values of k in estuaries for the same wind speed). To contribute to the debate, we analyze in the present paper a reasonably large data set of k values, based on the floating chamber method, in three European estuaries with contrasting physical characteristics (Randers Fjord, Denmark; Scheldt, Belgium/the Netherlands; and Thames, United Kingdom).

Materials and methods

Pertinent characteristics of the three studied estuaries are summarized in Table 1. During the Thames and the Scheldt cruises, sampling was carried out to cover the full salinity range, typically by steps of 2.5 of salinity. During the Scheldt cruise of November 2002, four stations (51.13°N 4.31°E, 51.23°N 4.40°E, 51.41°N 4.04°E, 51.39°N 4.21°E) were occupied for 24 h and flux measurements were carried out approximately every 10 min during daytime (10 h). During the Randers Fjord cruises, three stations (56.46°N 10.04°E, 56.62°N 10.23°E, 56.61°N 10.30°E) were occupied for 24 h and flux measurements were carried out hourly.

During the Thames cruises and most of the Scheldt cruises (Table 2), pCO_2 was computed from the measurements of pH and total alkalinity (TAlk) sampled from a Niskin bottle in subsurface water. During the three most recent Scheldt cruises (Table 2), pCO_2 was measured directly (1-min recording interval) with an infrared gas analyzer (IRGA, Licor Li-6262) in air equilibrated with subsurface water (pumped from a depth of 2.5 m), using the equilibrator described by Frankignoulle et al. (2001). During the Randers Fjord cruises, pCO_2 was measured directly by equilibration with the floating equilibrator system (FES) described by Frankignoulle et al. (2003). In brief, the FES is a buoy containing an equilibrator, an IRGA, water and air temperature probes, an anemometer, and a data logger (1-min recording interval),

Table 2. Sampling dates and range of variables (salinity, water pCO_2 [ppm]; atmospheric pCO_2 [ppm]; air–water CO_2 fluxes [mmol m^{-2} day^{-1}]) during the cruises carried out in the three studied estuaries. *n*, total number of air–water CO_2 flux measurements.*

	Salinity	pCO_{2water}	pCO_{2air}	Air–water CO_2 flux	*n*	*n**
Randers Fjord						
25 Apr–29 Apr 2001	2–19	206–1011 (FES)	370–400	−36–65	27	10
20 Aug–28 Aug 2001	0–21	370–3910 (FES)	355–435	0–290	66	46
Scheldt						
27 Nov–29 Nov 1995	1–29	605–6800 (pH/TAlk)	362–455	63–850	36	36
08 Jul–12 Jul 1996	1–30	472–7170 (pH/TAlk)	365–401	43–1465	48	45
09 Dec–13 Dec 1996	0–30	608–5632 (pH/TAlk)	349–390	23–740	42	42
25 May–28 May 1998	1–30	299–7718 (pH/TAlk)	392–460	−21–767	34	22
05 Oct–08 Oct 1998	0–27	956–7741 (pH/TAlk)	414–458	104–2270	34	34
04 Jul–06 Jul 2000	1–31	523–8351 (Eq)	387–445	15–1178	24	21
06 Nov–08 Nov 2000	0–20	614–5512 (Eq)	401–455	92–1328	12	10
06 Nov–12 Nov 2002	0–17	993–7553 (Eq)	368–422	66–2028	112	112
Thames						
11 Sep–18 Sep 1996	2–35	458–4617 (pH/TAlk)	404–457	41–1728	58	55
16 Feb-18 Feb 1999	0–33	281–3025 (pH/TAlk)	400–460	0–1587	34	26

* *n*, number of flux measurements for an absolute air–water pCO_2 gradient > 200 ppm; FES = pCO_2 measurements carried out with the floating equilibrator system; Eq = pCO_2 measurements carried out with an equilibrator from the subsurface water supply of the *R/V Belgica*; pH/TAlk = pCO_2 computed from the measurements of pH and TAlk sampled from a Niskin bottle in subsurface waters (*see Materials and methods for details*).

powered by four 12-volt batteries and a solar panel, providing an autonomy up to 30 h. For a detailed description of the pH and TAlk measurement methods, the computations of pCO_2 from pH and TAlk and the calibration procedure of the IRGA refer to Frankignoulle and Borges (2001*b*). Note that the measurements of pCO_2 by equilibration and the computed values of pCO_2 from pH and TAlk are consistent within ±1.5% (Frankignoulle and Borges 2001*b*).

The air–water CO_2 fluxes were measured with the floating chamber method described by Frankignoulle (1988) from a drifting rubber boat to avoid the interference of water turbulence within the chamber created by passing water current observed in earlier measurements carried out from a fixed point (Frankignoulle unpubl. data). The chamber is a plastic right circular cone (top radius = 49 cm; bottom radius = 57 cm; height = 28 cm) mounted on a float and connected to a closed air circuit with an air pump (30 L min^{-1}) and an IRGA, both powered with a 1-volt battery. The IRGA was calibrated daily using pure nitrogen (Air Liquide Belgium) and a gas mixture with a CO_2 molar fraction of 351 ppm (Air Liquide Belgium). The readings of pCO_2 in the chamber were written down every 30 s during 5 min in the Scheldt and Thames estuaries and during 10 min in the Randers Fjord because in the latter the flux signal was weaker than in the former two estuaries (*see Table 2*). The flux was computed from the slope of the linear regression of pCO_2 against time (r^2 usually ≥ 0.99) according to Frankignoulle (1988). The uncertainty of the flux computation due to SE on the regression slope is on average ±3%.

The floating chamber technique has been dismissed by several workers (Liss and Merlivat 1986; Raymond and Cole 2001), and one of the critiques of this technique is that the chamber covers the water surface and eliminates wind stress. However, for sparingly soluble gases such as CO_2, gas transfer is controlled by turbulence in the liquid phase. Thus, if the floating chamber does not disrupt the underlying water turbulence, then the corresponding gas transfer measurements should be reasonable estimates of those from the undisturbed surface. The disturbance of the floating chamber on the surface wind boundary layer was tested experimentally by Kremer et al. (2003*b*). They measured O_2 fluxes using a floating chamber with an adjustable speed fan to generate air turbulence and using a control floating chamber in parallel. Under moderate wind conditions, the additional air turbulence from the fan only increased the fluxes by 2% to 12% compared to the control chamber. Kremer et al. (2003*b*) also report a series of experiments comparing the floating chamber technique with mass balance approaches of O_2, ^{222}Rn, and ^{3}He in various experimental settings (laboratory tanks, outdoor tanks, mesocosms, and lakes). Fluxes based on the floating chamber technique agreed with the other direct methods within 10% to 30%. However, two publications report large discrepancies between the floating chamber technique and other approaches (Belanger and Korzum 1991; Matthews et al. 2003) that, in our opinion, highlight the limits of the method rather than dismiss it altogether. Belanger and Korzum (1991) compared O_2 evasion rates from pools by a mass balance approach and floating chamber measurements. They concluded that the floating chamber measurements were biased by changes of temperature and pressure during the experiments. However, the duration of these measurements was several hours and temperature and pressure changes are not expected to interfere during very short deployments of the floating chamber (such as in our case). Matthews et al. (2003) compared *k* estimates in a small sheltered boreal reservoir, based on floating chamber and SF_6 evasion techniques. However, during their experiment, wind speeds were extremely low, on average 0.2 m s^{-1} and never exceeding 0.5 m s^{-1}. As noted by Kremer et al. (2003*b*), the fluxes measured in nearly motionless waters with a floating chamber should be taken with caution. Also, estuarine environments (such as in our case) are much more turbulent because of tidal currents than the reservoir studied by Matthews et al. (2003). Finally, an indirect validation of this technique is given by Frankignoulle et al. (1996), who showed that floating chamber measurements over several coral reef systems give k estimates that fall between those based on the empirical formulations of Liss and Merlivat (1986) and Wanninkhof (1992).

The gas transfer velocity of CO_2 was computed from the CO_2 flux and ΔpCO_2 measurements (atmospheric pCO_2 was measured and recorded at the start of each flux measurement), using the CO_2 solubility coefficient formulated by Weiss (1974) and normalized to a Schmidt number (Sc) of 600 (k_{600}), assuming a dependency of the gas transfer velocity proportional to $Sc^{-0.5}$. Estuaries are highly turbulent systems (*see Discussion*), and the dependency of k proportional to $Sc^{-2/3}$ usually applied in open oceanic waters for the smooth surface regime, i.e., at wind speeds below 3 m s^{-1} (e.g., Liss and Merlivat 1986), probably does not hold true. The Schmidt number was computed for a given salinity from the formulations for salinity 0 and 35 given by Wanninkhof (1992) and assuming that Sc varies linearly with salinity.

During the Thames and Scheldt cruises, wind speed was measured at 18 m height with a Friedrichs 4034.000 BG cup anemometer and recorded every 10 s. During the Randers Fjord cruises, wind speed measurements at 2 m height from a Young 03002VP cup anemometer were recorded every 60 s. The winds speeds were referenced to a height of 10 m (u_{10}) according to Smith (1988) using concomitant air and water temperature measurements and were averaged for the period of each flux measurement. Water current speeds in subsurface waters were measured with an Aanderaa RCM7 and were recorded every minute during the Randers Fjord cruises and the November 2002 Scheldt cruise and were averaged for the period of each flux measurement.

Results

During all cruises and in the three estuaries, the full gradient of salinity was sampled (Table 2), except during the November 2000 Scheldt cruise because of bad weather conditions and during the November 2002 Scheldt cruise because of a different sampling strategy (*see Materials and methods*). The range of water pCO_2 values spans one order of magnitude and is highest in the Scheldt estuary, although variable from one cruise to another. Oversaturation of CO_2 with respect to atmospheric equilibrium is observed in all three estuaries, although significant undersaturations are observed on some occasions, systematically in the high-salinity region of the estuary (Randers Fjord in April, Scheldt in May, and Thames in February) (Table 2). The range of CO_2 air–water fluxes spans two orders of magnitude and is smaller in the Randers Fjord, while the Scheldt and the Thames show similar ranges. The atmospheric pCO_2 values are above typical global average values, as observed in other nearshore coastal systems (e.g., Bakker et al. 1996; Borges and Frankignoulle 2001). Indeed, atmospheric pCO_2 values in the Randers Fjord, Scheldt, and Thames are on average 3 (±14 SD), 27 (±22 SD), and 42 (±11 SD) parts per million (ppm) above the "uncontaminated" values from Weather Station Mike (66.00°N 2.00°E), representative of the open North Sea waters (from the National Oceanic and Atmospheric Administration Climate Monitoring and Diagnostics Laboratory air samples network, available on the internet at http://www.cmdl.noaa.gov/). The individual atmospheric pCO_2 values for each cruise were compared with the corresponding monthly value at Weather Station Mike, where from 1995 to 2002 the annual mean increased from 361 to 373 ppm.

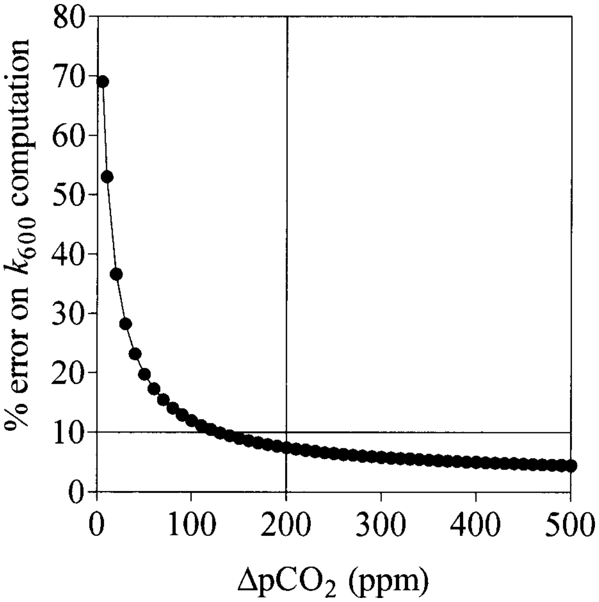

Fig. 1. Theoretical error (±%) on the computation of the gas transfer velocity of CO_2 (k_{600}) as a function of the air–water gradient of CO_2 (ΔpCO_2 in ppm), assuming a constant uncertainty on ΔpCO_2 of ±3%.

The k_{600} data sets were filtered before further analysis because as ΔpCO_2 values approach zero, the computation of k_{600} becomes more sensitive to error. This was investigated by assuming a reasonable error on ΔpCO_2 of ±3% and then assessing the corresponding error on the computation of k_{600} (Fig. 1). An absolute value of ΔpCO_2 equal to 200 ppm was chosen as the threshold value below which the k_{600} data were rejected because it corresponds to a good compromise between an acceptable error on the k_{600} computation (below ±10%, Fig. 1) and maintains a fairly large number of filtered variables. After this filtering, the remaining k_{600} data sets correspond to 60%, 88%, and 94% of the original data sets for the Randers Fjord, Thames, and Scheldt, respectively (Table 2). The k_{600} data were averaged over wind speed bins of 2 m s^{-1}, a common practice in gas transfer velocity studies (e.g., Cole and Caraco 1998; Fairall et al. 2000; McGillis et al. 2001), but one that changes the statistical power of regression and hypothesis testing. A rather large interval of wind speed bins was chosen because the data sets for the Randers Fjord and Thames are small compared to the one for the Scheldt (Table 2).

Figure 2 shows unbinned k_{600} versus wind speed in the Randers Fjord, the Scheldt, and the Thames. In the three estuaries, a distinct increasing trend of k_{600} values with wind

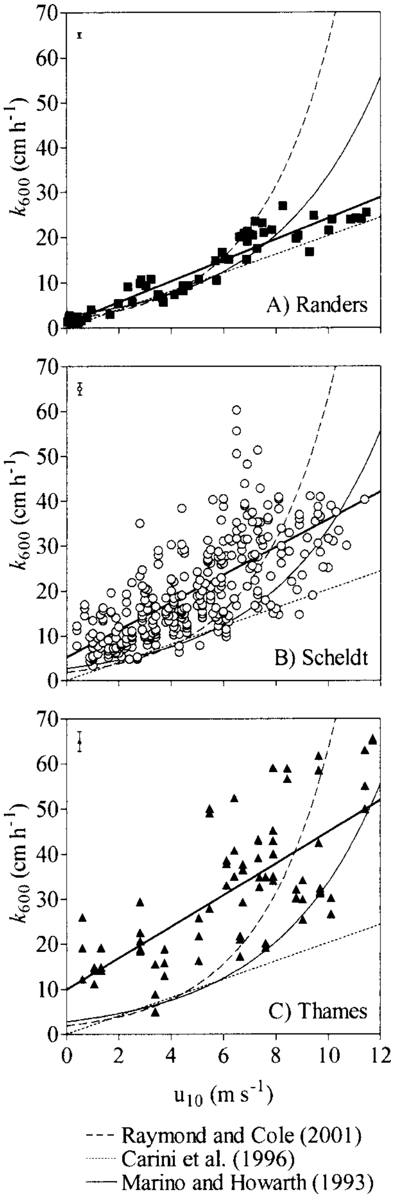

Fig. 2. Gas transfer velocity of CO_2 (k_{600}, cm h^{-1}) as a function of wind speed at 10 m height (u_{10}, m s^{-1}) in the three studied estuaries and three published relationships. The error bars on the top left corner of the plot correspond, for each of the three estuaries, to the average uncertainty on k_{600} estimated using the individual standard error on the slope of the regression of pCO_2 in the floating chamber against time (from which the CO_2 flux was computed; *see the Materials and methods section*) and assuming an error on ΔpCO_2 of ±3%. The estimated uncertainty on k_{600} varies with wind speed; in the Thames and Scheldt it ranges from about ±1 to ±4 cm h^{-1} at, respectively, low and high wind speeds; in the Randers Fjord it ranges from about ±0.1 to ±1.4 cm h^{-1} at, respectively, low and high wind speeds. The solid bold line corresponds to model 1 regression functions (Table 3). The Raymond and Cole (2001) relationship (k_{600} = 1.91 exp [$0.35u_{10}$]) is based on a compilation of published k_{600} values in various rivers and estuaries and obtained using different methodologies (floating chamber, natural tracers [CFC, ^{222}Rn] and purposeful tracer [SF_6]). The Carini et al. (1996) relationship ($k_{600} = 0.045 + 2.0277u_{10}$) is based on a SF_6 release experiment in the Parker River estuary. The Marino and Howarth

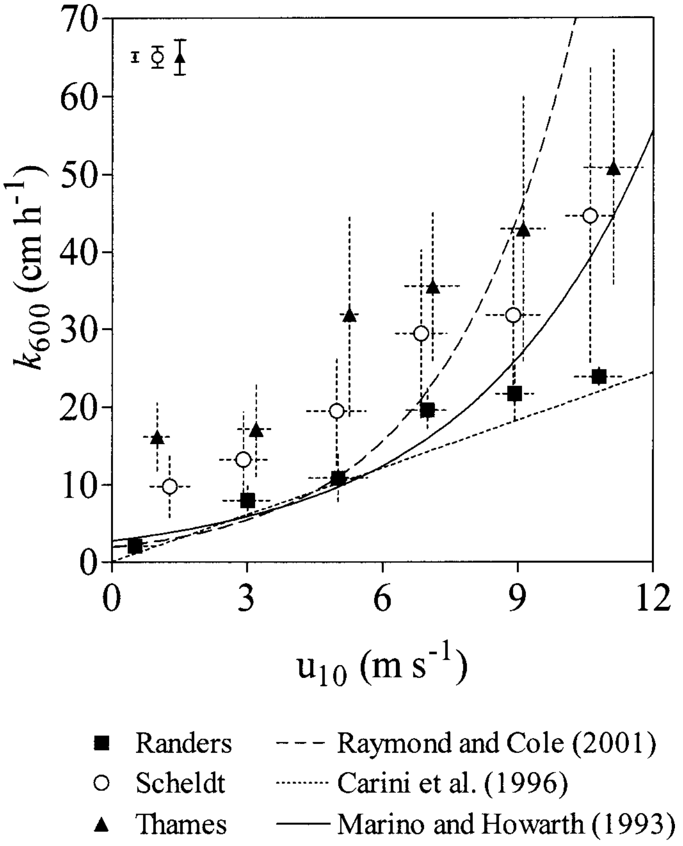

Fig. 3. Gas transfer velocity of CO_2 (k_{600}, cm h^{-1}) as a function of wind speed at 10 m height (u_{10}, m s^{-1}) in the three studied estuaries and three published relationships. The data were averaged over wind speed bins of 2 m s^{-1}. Standard deviations are shown by the horizontal and vertical dotted lines for the bin averages of u_{10} and k_{600}, respectively. The error bars on the top left corner of the plot correspond, for each of the three estuaries, to the average uncertainty on the k_{600} (refer to legend of Fig. 2 for details). The long-dashed line corresponds to the Raymond and Cole (2001) relationship, the short-dashed line corresponds to the Carini et al. (1996) relationship, and the solid line corresponds to the Marino and Howarth (1993) relationship (refer to legend of Fig. 2 for details).

speed is observed, although in the macrotidal Scheldt and Thames estuaries, data show higher scatter than the microtidal Randers Fjord. Note that the average estimated uncertainty on the k_{600} values (error bars on top left corner of plots in Fig. 2) is lower than the data scatter. For wind speeds below 6 m s^{-1}, the k_{600} values in the Randers Fjord follow published parameterizations in estuaries of k as a function of wind speed. For wind speed above 6 m s^{-1}, the k_{600} values in the Randers roughly follow the Carini et al. (1996) pa-

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←

(1993) relationship (k_{600} = 0.94 exp]$1.09 + 0.249u_{10}$]) is based on floating chamber oxygen measurements in the tidal freshwater portion of the Hudson River estuary. The latter two relationships were developed for oxygen and are expressed as k_{600} using the Schmidt number formulations given by Wanninkhof (1992) and assuming a dependency of the gas transfer velocity proportional to $Sc^{-0.5}$.

Table 3. Linear regression functions between the gas transfer velocity of CO_2 (k_{600}, cm h^{-1}) and wind speed at 10-m height (u_{10}, m s^{-1}) in the three studied estuaries, based on unbinned and bin-averaged data (k_{600} data were averaged over wind speed bins of 2 m s^{-1}).*

	$k_{600} = a\ (\pm SE) + b\ (\pm SE)u_{10}$	r^2	p	n
Unbinned data				
Scheldt	$k_{600} = 3.8(\pm1.0) + 3.45(\pm0.19)u_{10}$	0.519	<0.0001	322
Thames	$k_{600} = 9.7(\pm3.2) + 3.64(\pm0.45)u_{10}$	0.471	<0.0001	76
Randers Fjord	$k_{600} = 1.2(\pm0.7) + 2.30(\pm0.11)u_{10}$	0.897	<0.0001	56
Bin-averaged data				
Scheldt	$k_{600} = 3.4(\pm2.4) + 3.60(\pm0.35)u_{10}$	0.963	0.0005	6
Thames	$k_{600} = 10.2(\pm2.4) + 3.62(\pm0.35)u_{10}$	0.965	0.0005	6
Randers Fjord	$k_{600} = 0.9(\pm1.5) + 2.30(\pm0.22)u_{10}$	0.965	0.0004	6

* These relationships are only valid for u_{10} spanning the range of values between 0 and 11 m s^{-1}. For unbinned data, the regression function was computed with model 1 least squares fit. For bin-averaged data, the regression function was computed with model 2 functional fit. For the Scheldt and Thames regression functions, the slopes are not statistically different ($p = 0.6299$ for unbinned data; $p = 0.9675$ for bin-averaged data) but the y-intercepts are statistically different ($p < 0.0001$ for unbinned data; $p = 0.0016$ for bin-averaged data). The slope of the regression function of the Randers Fjord is statistically different from those of the Scheldt ($p = 0.0016$ for unbinned data; $p = 0.0099$ for bin-averaged data) and the Thames ($p = 0.0086$ for unbinned data; $p = 0.0090$ for bin-averaged data).

rameterization. For wind speeds below 8 m s^{-1}, the lowest k_{600} values in the Scheldt and Thames for a given wind speed fall on the lines from published parameterizations. However, the highest k_{600} values at a given wind speed are about eight times higher than the observed minimal values. This suggests that at a given wind speed, a process other than wind stress increases k_{600} in the Scheldt and Thames. Figure 3 shows the averaged k_{600} over wind speed bins of 2 m s^{-1} versus wind speed in the three estuaries. The binned k_{600} values are highly variable from one estuary to another, and at a given wind speed the highest values are observed in the Thames and the lowest in the Randers Fjord. The ratio of binned k_{600} values between the estuaries varies with wind speed; at low wind speeds, k_{600} is about eight times higher and at high wind speeds about two times higher in the Thames than in the Randers Fjord.

The k_{600} was parameterized as a function of wind speed by linear regression in each of the three studied estuaries (Table 3). Although various parameterization functions have been used in literature (linear, e.g., Liss and Merlivat 1986; Carini et al. 1996; Kremer et al. 2003*a*; power law, e.g., Hartman and Hammond 1985; Wanninkhof 1992; Cole and Caraco 1998; Jacobs et al. 1999; Wanninkhof and McGillis 1999; Nightingale et al. 2000; McGillis et al. 2001; exponential, e.g., Marino and Howarth 1993; Raymond and Cole 2001; Kremer et al. 2003*a*), the linear model is clearly appropriate for Randers Fjord, and for the Scheldt and Thames estuaries the linear approximation is the best first approximation especially considering the scatter. Moreover, in wind tunnel experiments, k has been shown to vary linearly with wind speed between 2 and 13 m s^{-1} (Broecker and Siems 1984), the range of our data. In wind tunnel experiments, at wind speeds above 13 m s^{-1}, the slope of k versus wind speed increased because of presence of air bubbles from breaking waves. Kremer et al. (2003*a*) also showed that a linear relationship between k and wind speed provides the best data fit in Sage Lot Pond and Childs River estuaries (Waquoit Bay).

The model 2 regression functions of binned k_{600} and model 1 regression functions of unbinned k_{600} versus wind speed are highly significant in the three studied estuaries (Table 3). The slopes and y-intercepts of unbinned and binned k_{600} versus wind speed relationships in the three estuaries (model 1 and 2 functions, respectively) are not significantly different (Table 3). The slopes of the linear regression functions are similar in the Scheldt and the Thames and significantly higher than the one in the Randers Fjord. The y-intercept of the linear regression function in the Thames is higher than those of the Randers Fjord and the Scheldt.

Discussion

The differences of the y-intercept and slope of the linear regressions of k_{600} as a function of wind speed described in the previous section for the three studied estuaries are discussed in relation to the potential contribution of water currents to water turbulence and fetch limitation.

Contribution of water currents to k_{600}—In the macrotidal Scheldt and Thames estuaries k_{600} values showed high scatter, and at wind speeds below 8 m s^{-1} most k_{600} values are above the values predicted by published parameterizations (Fig. 2). In contrast, in the microtidal Randers Fjord k_{600} values showed much lesser scatter. This strongly suggests that, in the Scheldt and Thames, tidal currents, in addition to wind stress, significantly contribute to k_{600} and induce high variability depending on the tidal phase (maximum ebb or flow and tidal slacks).

In streams, the interaction of the gravity flow and bottom topography generates turbulence because of bottom shear that is frequently considered to be the main factor controlling the gas transfer velocity of sparingly soluble gases in these sheltered systems where wind is usually very low. This has led to various parameterizations of the gas transfer velocity as a function of water current and depth based on empirical or conceptual approaches, reviewed by Bansal (1973) and more recently by Melching and Flores (1999) and Gualtieri et al. (2002). In estuaries, the tidal current can be as high as the gravity flow in streams and, thus, could in theory contribute significantly to k_{600}. To our best knowledge, in estuaries, this has been investigated in the field by Hartman and Hammond (1984) in San Francisco Bay using floating chamber ^{222}Rn measurements and by Zappa et al. (2003) in Plum Island Sound using the gradient flux technique. Hartman and Hammond (1984) found no distinct evidence for the contribution of water currents to the gas transfer velocity. However, in this study water currents were estimated from tide tables and not actually measured. Moreover, the sampling period for each flux measurement was rather long (1 h) in comparison with the time-scale characteristic of tidal current variability. Zappa et al. (2003) carried out four k measurements under low winds (1.9 m s^{-1}) during half a tidal cycle and found a significant enhancement of k (up to 10 cm h^{-1}) related to water currents measured with an acoustic Doppler current profiler (ranging from 10 to 80 cm s^{-1}).

Water currents measurements concomitant to flux measurements were obtained during the two Randers Fjord cruises and the November 2002 Scheldt cruise. Although water currents are expected to contribute to water turbulence whatever the wind speed, their effect is best identified if the contribution to turbulence from wind stress is low ($u_{10} < 4$ m s^{-1}). In the Randers Fjord, water current concomitant to flux measurements at wind speeds below 4 m s^{-1} ranged from 1 to 38 cm s^{-1} (on average 11 ± 12 SD cm s^{-1}). So it is possible to compare quantitatively water currents to the corresponding k_{600} values. In contrast, during the November 2002 Scheldt cruise, current speeds were systematically high (ranging between 66 and 107 cm s^{-1}, on average 92 ± 15 SD cm s^{-1}) during the flux measurements carried out at wind speeds below 4 m s^{-1}. Hence, it is not possible to directly compare k_{600} and water currents.

The k_{600} data set of the Randers Fjord was filtered by rejecting data for wind speeds above 4 m s^{-1} and for nil water currents (Fig. 4). Coincidentally, the k_{600} data are grouped for two wind speed ranges between 0 and 1 m s^{-1} and between 2 and 4 m s^{-1} (Fig. 4A). Even at these low wind speeds, wind stress contributes to k_{600}, as shown by the comparison of the data group for wind speeds below 1 m s^{-1} (filled squares in Fig. 4A) and the data group for wind speed above 2 m s^{-1} and water currents below 10 cm s^{-1} (open squares in Fig. 4A). Thus, the groups of k_{600} data for the two wind speed ranges are treated separately in relation to water currents (Fig. 4B). For the data group for wind speed below 1 m s^{-1}, the range of water currents is low (1 to 8 cm s^{-1}) and no relationship between k_{600} and water current is apparent. However, for the data group of wind speeds between 2 and 4 m s^{-1}, the range of water currents is high (1 to 38 cm s^{-1}) and k_{600} is well related to water current (Fig. 4B). This clearly shows that water currents contribute to k_{600}.

In the Scheldt, a different approach than in the Randers Fjord was used; the contribution of water current to k_{600} was estimated based on the frequently referenced conceptual relationship of O'Connor and Dobbins (1958) that gives the oxygen reaeration rate (R in d^{-1}) according to

$$R = 0.439 w^{0.5} h^{-1.5} \qquad (2)$$

where w is the water current in centimeters per second and h is the depth in meters.

The oxygen reaeration rate given in Eq. 2 can be expressed as the gas transfer velocity ($k = Rh$) and normalized

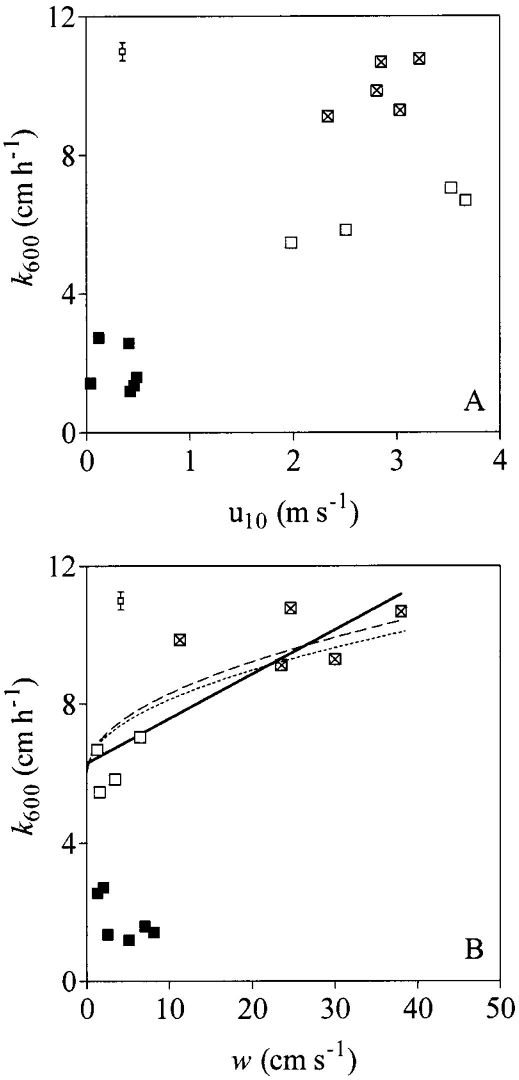

Fig. 4. The gas transfer velocity of CO_2 (k_{600}, cm h^{-1}) in the Randers Fjord as a function of (A) wind speed at 10 m height (u_{10}, m s^{-1}) less than 4 m s^{-1} and (B) non-nil water current (w, cm s^{-1}). The error bars on top left corner of the plots correspond to the average uncertainty on k_{600} (refer to legend of Fig. 2 for details). Filled squares correspond to data below a wind speed of 1 m s^{-1}. For clarity in the data interpretation and discussion, data for wind speeds above 2 m s^{-1} were separated for water currents above (crossed squares) and below (open squares) 10 cm s^{-1}. The short-dashed line corresponds to the k_{600} predicted from the conceptual relationship of O'Connor and Dobbins (1958) to which was added 6.1 cm h^{-1} (a depth 7 m was used in the computation, corresponding to the average value in the navigation channel, where measurements were carried out). The value of 6.1 cm h^{-1} is the average value of the two k_{600} values observed at the lowest (nearly zero) water currents and roughly accounts for the effect of wind speed on k_{600} evident from panel A. The solid line corresponds to the model 1 linear regression ($k_{600} = 6.3$ [±1.1 SE] + 0.13 [±0.03 SE] w, $r^2 = 0.732$, $p = 0.0033$, $n = 9$) between all the observed k_{600} for the wind speed range between 2 and 4 m s^{-1} and water current. The long-dashed line corresponds to a power law function ($k_{600} = 1.87$ [±0.03 SE] $w^{0.5} h^{-0.5}$, $r^2 = 0.725$, $n = 9$) that accounts for w and depth (h, m) in the same fashion as the O'Connor and Dobbins (1958) relationship ($k_{600} = 1.719 w^{0.5} h^{-0.5}$), based on all the observed k_{600} for the wind speed range between 2 and 4 m s^{-1}.

to a Schmidt number of 600 using the formulations given by Wanninkhof (1992), assuming a dependency of k proportional to $Sc^{-0.5}$, with the result that

$$k_{600\mathrm{current}} = 1.719 w^{0.5} h^{-0.5} \qquad (3)$$

where $k_{600\mathrm{current}}$ is the gas transfer velocity of CO_2 in centimeters per hour, w is the water current in centimeters per second, and h is the depth in meters.

From the water current measurements concomitant to those of the CO_2 flux, the contribution of water current to the gas transfer velocity of CO_2 ($k_{600\mathrm{current}}$) was computed according to Eq. 3 and was removed from the observed k_{600} ($k_{600\mathrm{observed}}$). This gives in theory the contribution to k_{600} of wind speed alone ($k_{600\mathrm{wind}} = k_{600\mathrm{observed}} - k_{600\mathrm{current}}$), assuming that both contributions to water turbulence are additive. At low wind speeds, $k_{600\mathrm{wind}}$ is about three times lower than $k_{600\mathrm{observed}}$, which suggests that the contribution of water currents to water turbulence is substantial when wind stress is low (Fig. 5A). At high wind speeds, $k_{600\mathrm{wind}}$ is about 1.1 times lower than $k_{600\mathrm{observed}}$, in agreement with the theoretical analysis of Cerco (1989) that shows that the relative contribution of water currents to the gas transfer velocity decreases with increasing wind.

The y-intercept of the model 2 regression function of $k_{600\mathrm{wind}}$ against wind speed for the Scheldt is negative but close to zero (Table 4). This is most probably related to the poor constraint on the linear regression at low wind because only two measurements were obtained for wind speeds below 2 m s^{-1}. The other possible explanation is that the conceptual relationship of O'Connor and Dobbins (1958) overestimates the contribution of water currents to the gas transfer velocity. However, in the Randers Fjord, the curve of k_{600} as a function of w predicted by the O'Connor and Dobbins (1958) relationship (short-dashed line in Fig. 4B; Eq. 3) is close to the regression line of the observed k_{600} as a function of w (solid line in Fig. 4B; $k_{600} = 6.3 + 0.13w$) (Fig. 4B).

A power law function that accounts for w and h in the same fashion as the O'Connor and Dobbins (1958) relationship (short-dashed line in Fig. 4B; Eq. 3) was established from the observed k_{600} and w values (long-dashed line in Fig. 4B; $k_{600} = 1.87 w^{0.5} h^{-0.5}$), and both relationships are very similar (Fig. 4B). Zappa et al. (2003) also showed that the O'Connor and Dobbins (1958) relationship gives a good approximation of four k measurements based on the gradient flux technique during a tidal cycle in Plum Island Sound estuary under low wind conditions. Our results and those of Zappa et al. (2003) strongly suggest that the O'Connor and Dobbins (1958) relationship gives a fairly adequate estimation of the contribution of water currents to the gas transfer velocity in estuarine environments.

The same computations as those outlined above were carried out for the Randers Fjord (Fig. 5B and Table 4), and the y-intercepts of the linear regression function of $k_{600\mathrm{observed}}$ and $k_{600\mathrm{wind}}$ against wind speed are not significantly different. This suggests that the overall contribution of water currents to k_{600} is negligible in the microtidal Randers Fjord. Indeed, 78% of the observed water currents are below 10 cm s^{-1} (Fig. 6A) and, thus, the high water currents in Fig. 4B are exceptional values. Moreover, for water currents ranging from 0 to 10 cm s^{-1}, the expected increase of k_{600} is on average only of a factor of about 1.2, based on the linear regression function in Fig. 4B. Also, the k_{600} data of the Randers Fjord follow closely the relationship of Carini et al. (1996) for Parker River estuary (Figs. 2, 3, and 5B) that is also characterized by low tidal currents according to Raymond and Cole (2001).

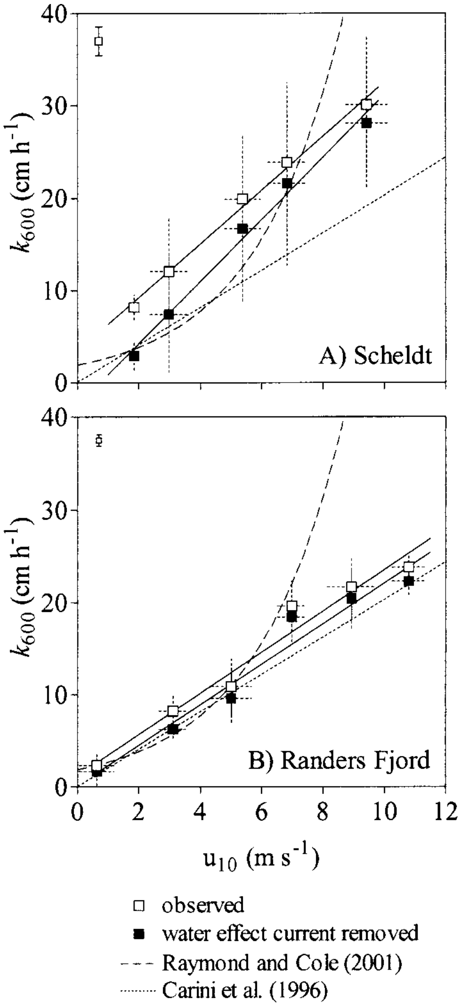

Fig. 5. Gas transfer velocity of CO_2 (k_{600}, cm h^{-1}) as a function of wind speed at 10 m height (u_{10}, m s^{-1}) for (A) the November 2002 Scheldt cruise and (B) for the two Randers Fjord cruises. The data were averaged over wind speed bins of 2 m s^{-1}. Standard deviations are shown by the horizontal and vertical dotted lines for the bin averages of u_{10} and k_{600}, respectively. The error bars on the top left corner of the plots correspond, for each of the two estuaries, to the average uncertainty on k_{600} (refer to legend of Fig. 2 for details). The open symbols correspond to the observed k_{600}. The filled symbols correspond to k_{600} from which the contribution of water currents was removed. The contribution of water currents to k_{600} was estimated from the conceptual relationship of O'Connor and Dobbins (1958), using water current measurements concomitant to the CO_2 flux measurements, and it was removed from individual k_{600} estimates before the data were bin averaged. Solid lines correspond to the model 2 regression functions developed in Table 4. The long-dashed line corresponds to the Raymond and Cole (2001) relationship, and the short-dashed line corresponds to the Carini et al. (1996) relationship (refer to legend of Fig. 2 for details).

Table 4. Regression functions between the gas transfer velocity of CO_2 (k_{600}, cm h^{-1}) and wind speed at 10-m height (u_{10}, m s^{-1}) in the Randers Fjord and the Scheldt (only the data from the November 2002 cruise).*

	$k_{600} = a(\pm SE) + b(\pm SE)u_{10}$	r^2	p	n
Observed k_{600}: unbinned data				
Scheldt	$k_{600} = 4.7(\pm 2.2) + 2.76(\pm 0.33)u_{10}$	0.897	<0.0001	112
Randers Fjord	$k_{600} = 1.2(\pm 0.7) + 2.30(\pm 0.11)u_{10}$	0.395	<0.0001	56
k_{600} without the contribution from water currents: unbinned data				
Scheldt	$k_{600} = -0.8(\pm 2.3) + 3.16(\pm 0.34)u_{10}$	0.898	<0.0001	112
Randers Fjord	$k_{600} = 0.1(\pm 0.6) + 2.26(\pm 0.10)u_{10}$	0.439	<0.0001	56
Observed k_{600}: binned data				
Scheldt	$k_{600} = 3.4(\pm 0.8) + 2.92(\pm 0.14)u_{10}$	0.993	0.0005	5
Randers Fjord	$k_{600} = 0.9(\pm 1.5) + 2.30(\pm 0.22)u_{10}$	0.963	0.0002	6
k_{600} without the contribution from water currents: binned data				
Scheldt	$k_{600} = -2.7(\pm 1.2) + 3.41(\pm 0.21)u_{10}$	0.989	0.0006	5
Randers Fjord	$k_{600} = -0.3(\pm 1.6) + 2.28(\pm 0.24)u_{10}$	0.959	0.0005	6

* For unbinned data, the regression function was computed with model 1 least-squares fit. For bin-averaged data, the regression function was computed with model 2 functional fit. The contribution of water currents to k_{600} was estimated from the conceptual relationship of O'Connor and Dobbins (1958), using water current measurements concomitant to those of air–water CO_2 fluxes. This contribution was removed from the observed individual k_{600}, and data were then averaged over wind speed bins of 2 m s^{-1} and the model 2 regression functions against u_{10} were recomputed (lower half of table). In the Scheldt, for the regression functions of the observed k_{600} and the k_{600} without the contribution from water currents, the slopes are not statistically different ($p = 0.3881$ for unbinned data; $p = 0.1059$ for binned data) but the *y*-intercepts are statistically different ($p = 0.0052$ for unbinned data; $p = 0.0028$ for binned data). In the Randers Fjord, for the regression functions of the observed k_{600} and the k_{600} without the contribution from water currents, the slopes ($p = 0.8015$ for unbinned data; $p = 0.9164$ for binned data) and the *y*-intercepts ($p = 0.0133$ for unbinned data; $p = 0.2263$ for binned data) are not statistically different.

In contrast, 67% of the observed water currents in the Scheldt estuary are above 10 cm s^{-1}, and the range of variation of the observed water currents is higher than in the Randers Fjord (Fig. 6B). This supports the idea that the difference in the *y*-intercept of the regression functions of k_{600} against wind speed between the Randers Fjord and the Scheldt (Table 3) is related to the contribution of water currents to k_{600} that is substantial in the Scheldt and negligible in the Randers Fjord. This is also consistent with the low *y*-intercept of the regression function of *k* as a function of wind speed reported by Kremer et al. (2003*a*) for Childs River and Sage Lot Pond estuaries (respectively, 1.9 and 0.8 cm h^{-1} normalized to a Sc of 600) that are close to the value in Randers Fjord. Indeed, Waquoit Bay is characterized by a low tidal amplitude (<0.5 m); thus, tidal currents can be assumed to be low in Childs River and Sage Lot Pond estuaries and, according to Kremer et al. (2003*a*), have a negligible effect on *k*. The high *y*-intercept of the regression functions of k_{600} against wind speed of the Thames (Table 3) is also assumed to be related to strong tidal currents, although no water current measurements are available to verify this hypothesis. The high tidal amplitude in the Thames (Table 1) suggests that tidal currents should be at least as strong as in the Scheldt.

Fetch limitation?—In addition to the differences in *y*-intercepts, the regression functions of k_{600} against wind speed of the Scheldt and the Thames have higher slopes compared to the one of the Randers Fjord (Table 3). This is not related to water currents because their contribution to k_{600} tends on the contrary to slightly decrease the slope (Fig. 5A; Table 4). This difference could be related to fetch limitation. Fetch is the distance over which the wind blows without significant deviation and determines (for a given wind speed) the intensity of water turbulence and wave height. The effect of fetch on *k* has been shown in wind tunnel experiments (Wanninkhof and Bliven 1991). Hartman and Hammond (1984) suggested fetch limitation to explain the differences of *k* values on the different sides of San Francisco Bay. Kremer et al. (2003*a*) have hypothesized that the lower slopes of *k*–wind linear relationships in Sage Lot Pond and Childs River compared to other estuaries could be related to fetch limitation. Also, Wanninkhof (1992) hypothesized that the difference between the slope of the linear regression functions of k_{600} (based on SF_6 evasion experiments) against wind speed in various lakes is related to their surface area.

Among the three studied estuaries, the Randers Fjord is shorter and narrower and has a smaller surface area than the Scheldt and Thames (Table 1). Thus, stronger fetch limitation could explain the lower slope of the linear regression function of k_{600} against wind in the Randers Fjord compared to the other two estuaries. In Fig. 7, the slopes of the regression functions of the three studied estuaries plus those investigated by Kremer et al. (2003*a*) are plotted on a semilogarithmic scale against their respective estuarine surface area. This clearly shows a significant effect of fetch limitation on *k* that induces a decrease of the slope of the *k* versus wind speed regression functions with increasing fetch limitation. The nonlinearity of the relationship suggests that the effect of fetch limitation is disproportionately stronger in small estuaries (<30 km^2). However, Fig. 7 should be interpreted with caution since besides the estuarine surface area, fetch limitation is expected to depend on the shape of the estuary (funnel, oval, narrow or wide linear channel) and on the relation between the direction of prevailing winds and the direction of main axis of the estuary (parallel or across).

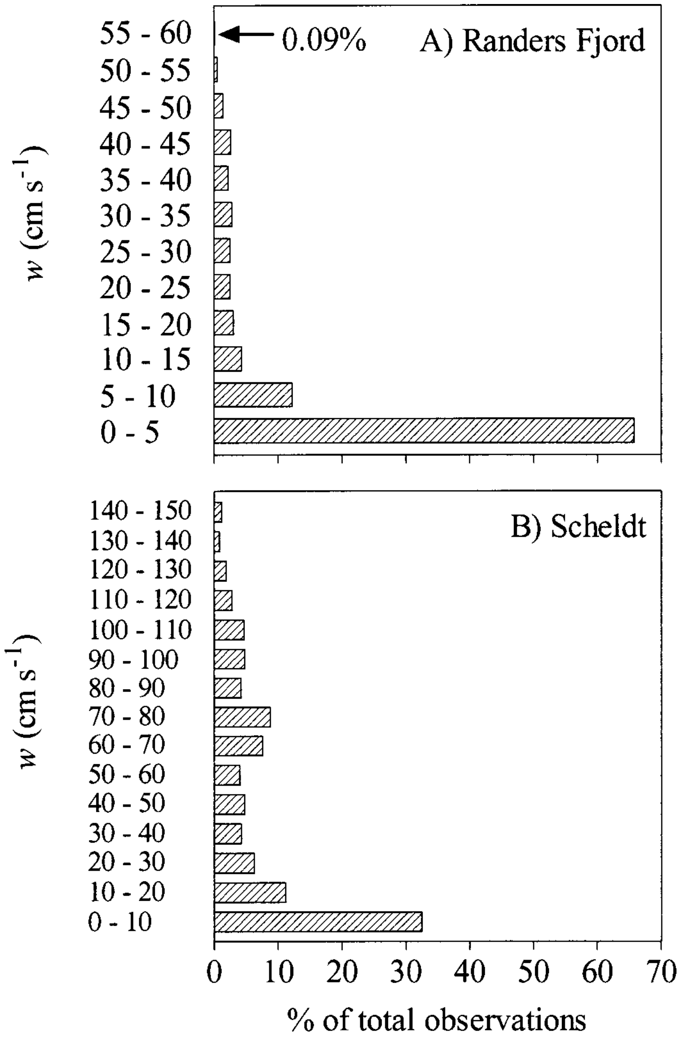

Fig. 6. Frequency distribution of water current (w, cm s^{-1}) measurements by (A) intervals of 5 cm s^{-1} in the Randers Fjord (total number of observations = 7,909) and by (B) intervals of 10 cm s^{-1} in the Scheldt (total number of observations = 2,278). During both Randers Fjord cruises, data were recorded every minute at three stations (56.46°N 10.04°E, 56.62°N 10.23°E, 56.61°N 10.30°E) that were occupied during 24 h. Data at the upstream station (56.46°N 10.04°E) were lost because of equipment failure during the April 2001 cruise. During the November 2002 Scheldt cruise, data were recorded every minute at four stations (51.13°N 4.31°E, 51.23°N 4.40°E, 51.41°N 4.04°E, 51.39°N 4.21°E) that were occupied during 24 h. Mean current speeds are 8 (±12 SD) and 44 (±40 SD) cm s^{-1} in the Randers Fjord and the Scheldt, respectively.

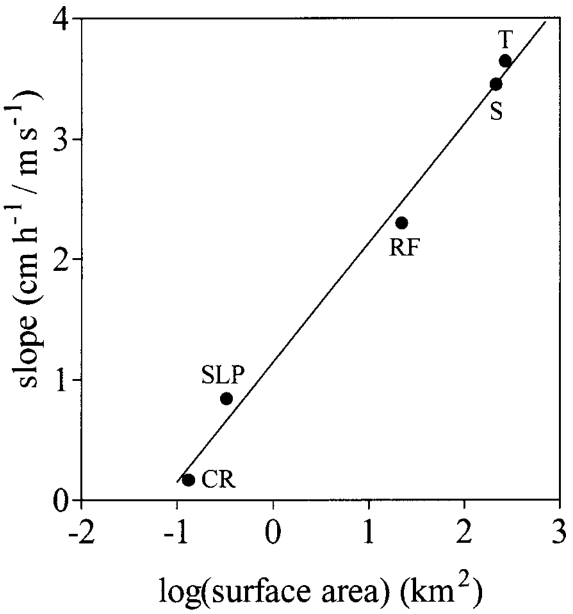

Fig. 7. Slope of the model 1 regression functions of k_{600} versus wind speed (Table 3) from the Thames (T), Scheldt (S), Randers Fjord (RF), Childs River (CR), and Sage Lot Pond (SLP) versus the logarithm of the estuarine surface area. The data from Childs River (1.3 km^2) and Sage Lot Pond (3.3 km^2) from Kremer et al. (2003*a*) were normalized to a Schmidt number of 600 using the formulations given by Wanninkhof (1992) and assuming a dependency of the gas transfer velocity proportional to Sc$^{-0.5}$. Solid line corresponds to model 1 regression function (slope = 1.14 (±0.09 SE) + 0.99 (±0.05 SE) log (surface area), $r^2 = 0.991$, $p = 0.0003$, $n = 5$).

When compared at the European regional level, the integrated air–water CO_2 fluxes in estuaries and open continental shelf are of the same order of magnitude but opposite in direction. Thus, more air–water CO_2 flux estimates are needed in worldwide estuaries to allow an evaluation of their significance in the CO_2 flux budget of the overall coastal ocean. The critical factor in the computation of the air–water CO_2 flux is the large uncertainty on the formulation of the gas transfer velocity. Based on a fairly large data set of air–water CO_2 fluxes, measured using the floating chamber method, in three European estuaries (Randers Fjord, Scheldt, and Thames), significant regression functions between k_{600} and wind speed were established. Based on these and in accordance with the conclusions of Kremer et al. (2003*a*), it appears that the formulation of k_{600} as a function of wind speed is site specific in estuarine environments. This implies that substantial errors in flux computations are incurred if generic *k*–wind relationships are employed in estuarine environments for the purpose of biogas air–water flux budgets and ecosystem metabolic studies. From one estuary to another, the differences in the *y*-intercepts of the linear relationships are due to tidal currents, whereas the differences in the slopes of the regression functions are related to fetch limitation. The contribution of tidal currents to k_{600} is significant in macrotidal estuaries such as the Scheldt and Thames but seems negligible in microtidal estuaries such as Randers Fjord, Childs River, and Sage Lot Pond. Based on our results and in accordance with those of Zappa et al. (2003), the O'Connor and Dobbins (1958) relationship originally developed for streams is appropriate to estimate the contribution of waters currents to *k* in estuarine environments. Finally, we suggest that in estuarine environments future research efforts should concentrate in the development of a physically more rigorous and probably multivariable formulation of the gas transfer velocity (including at least wind stress and water current effects on turbulence at the air–water interface), rather than a simple empirical formulation as a function of wind speed. To assist such theoretical work, more data on air–water CO_2 fluxes are also needed. Natural or purposeful tracer approaches give gas transfer velocity estimates that are on a time scale (day to week) that is larger than the one characteristic of tidal currents (minutes to hours). To resolve gas transfer velocity variability on short time scales, besides the floating chamber method, micrometeorological methods seem adequate. The earlier controversial drawbacks of these methods (Broecker et al. 1986) seem to a large extent resolved (Fairall et al. 2000; McGillis et al. 2001), and estuaries provide ideal settings for their application (low ship motion, high signal-to-noise ratio, i.e., very large fluxes and ΔpCO_2).

3.3 Le fjord de Randers

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Net ecosystem metabolism in a micro-tidal estuary (Randers Fjord, Denmark): evaluation of methods and interannual variability

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ABSTRACT

The metabolic performance of an estuary (Randers Fjord, Denmark) has been assessed based on two field campaigns in April and August 2001 and a number of approaches: (1) the O_2 incubation method, (2) the Response Surface Difference (RSD) method, (3) dissolved inorganic carbon (DIC) budgets and (4) Land-Ocean Interaction in the Coastal Zone (LOICZ) budgets.

Although each method has its own associated limitations and uncertainties, all approaches converged to consistent metabolic estimates, both in sign and magnitude and reveal that this system is near metabolic balance in spring and net heterotrophic in summer. In this shallow estuary (mean depth: 1.6 m), the benthic compartment was very active and represented 70 and 40% of the total gross primary production in April and August, respectively. Net ecosystem production (NEP) rates measured during this study are in the range of previously reported rates in estuaries. A long-term study of the metabolism of this ecosystem based on the LOICZ approach revealed a significant increase of annual NEP from 1991 to 2002.

KEYWORDS

ECOSYSTEM METABOLISM, ESTUARIES, PRIMARY PRODUCTION, RESPIRATION, RANDERS FJORD, OXYGEN, CARBON DYNAMICS

INTRODUCTION

The coastal zone, covering an area of 26 x 10^6 km^2 (7% of the surface of the global ocean), is one of the most biogeochemically active regions of the biosphere (Gattuso et al. 1998). Although it comprises 30-50% of calcium carbonate and about 80% of organic carbon accumulation of the whole ocean (Wollast & Mackenzie 1989, Morse & Mackenzie 1990, Wollast 1991, Milliman 1993, Smith & Hollibaugh 1993, Wollast 1998), there is no consensus whether the coastal ocean acts as a net source or sink for atmospheric CO_2. Two major reasons can explain this lack of consensus: (1) the net community production (NCP) and net calcification of the coastal zone are still poorly documented and (2) the wide physiographic and environmental diversity of coastal ecosystems complicates any upscaling procedure (Gazeau et al. in press).

Estuaries are particularly complex cases of coastal ecosystems, as they are inherently variable and dynamic with large temporal (from daily to seasonal timescales) and spatial gradients (Heip et al. 1995). Thus, to estimate the metabolic status of such systems a fully integrated method both in space and time is required. An ecosystem is deemed net autotrophic when production of organic matter by primary producers exceeds the consumption of this matter by heterotroph organisms. Such systems are potentially net sinks for atmospheric CO_2 although import of high partial pressure of CO_2 (pCO_2) such as in productive upwelling areas or estuaries can result in the release of CO_2 to the atmosphere. On the contrary, an ecosystem is heterotrophic when consumption exceeds primary production, leading generally to high pCO_2 and low oxygen (O_2) concentrations in the water column.

A wide range of techniques have been used to estimate the trophic status of coastal ecosystems. Each technique relies on one or several assumptions and covers different spatial and temporal scales. For instance, metabolic processes rates measurements based on incubation methods (mainly O_2 and ^{14}C) or open water O_2 measurements (Odum 1956, Kemp & Boynton 1980, Howarth et al. 1992, Caffrey 2004) have been used on local scales in numerous studies but their extrapolation to larger areas remains problematic.

The direct measurement of CO_2 fluxes across the air-water interface has been only recently applied at large spatial and temporal scales in a number of coastal

ecosystems (Frankignoulle et al. 1998, Tsunogai et al. 1999, Cai et al. 2000, Raymond et al. 2000, Frankignoulle & Borges 2001b, Borges & Frankignoulle 2002).
Within the IGBP program, the Land Ocean Interaction in the Coastal Zone (LOICZ) stoichiometry budgeting approach has been applied to more than 170 sites and can provide system scale estimates (Gordon et al. 1996).

The EUROTROPH project (http://www.ulg.ac.be/oceanbio/eurotroph/) aims at determining the trophic status of three European coastal ecosystems (Randers Fjord, Scheldt estuary and Bay of Palma) using simultaneously different available techniques and to compare the estimates at several time scales. Here, we estimate, using a variety of methods, the metabolic status of the Randers Fjord (Denmark), during two field campaigns in 2001. The following methods were used and compared: integration and extrapolation of changes in O_2 during incubations, the RSD (Response Surface Difference) method, dissolved inorganic carbon (DIC) and LOICZ budgets. Moreover, the LOICZ budgeting procedure was applied on an annual scale from 1991 to 2002, based on an historical dataset collected by the Danish National Environmental Research Institute (NERI). To our knowledge, this is the first systematic comparison of these four approaches to asses the metabolic balance of a coastal ecosystem.

MATERIAL AND METHODS

Study area

Randers Fjord is the longest Danish estuary located on the East coast (Fig. 1). The river and fjord drain an area of 3260 km^2 and receive treated sewage water from 600,000 inhabitants. The estuary is 27 km long and covers an area of 23 km^2. The main freshwater input comes from the river Gudenå, which drains 80% of the catchment area and enters the innermost part of Randers Fjord (Nielsen et al. 2001). The mean annual water residence time within the estuary is ~13 d (Nielsen et al. 2001). A pycnocline is present throughout the year in almost the entire estuary (Nielsen et al. 1993). The top-layer of sediment varies from soft-mud with a high organic content (10-14%) in the inner part to fine/medium-sized silt with low organic content (1-2%) in the outer area (Nielsen et al. 2001). Seasonal anoxic conditions in bottom waters have been recorded in the innermost part of the estuary during summer (Sømod et al. 1999). In the 1970's, regulatory measures were implemented in order to decrease the loading of nutrients and organic carbon from point sources and cities. Additionally, villages with more than 200 inhabitants were required to build sewage treatment plants with C, N and P removal capabilities.

Oxygen incubations

Planktonic gross primary production (GPP) and community respiration (CR) were measured at several stations in the estuary (Fig. 1) during two cruises in April-May and August 2001 hereafter referred to Randers 1 and Randers 2, respectively. Samples were incubated *in situ* at 4 depths (5 replicates at each depth) from sunrise to sunset in both transparent and dark 60 ml biological oxygen demand (BOD) bottles. O_2 concentrations were measured before and after incubation using an automated Winkler titration technique with a potentiometric end-point detection. Analyses were performed with an Orion® redox electrode (9778-SC) and a custom built titrator. Reagents and standardizations were similar to those described by Knap et al. (1996). Hourly planktonic CR (expressed as a negative value) and net community production during the day (NCP_d) were estimated by regressing O_2 in the dark and transparent bottles against time. Hourly planktonic GPP was calculated as the difference between NCP_d and hourly CR.

Triplicate sediment cores (8 cm in diameter) were collected with a box corer at 6 stations along the estuary in the navigation channel. Additionally, 2 sets of triplicate sediment cores were collected manually at 3 stations located on the shallow banks (Fig. 1). For each sampling station, cores were incubated in the laboratory at *in situ* temperature under darkness for around 6 h and one set of bank cores was incubated under *in situ* light conditions for 3 to 6 h. Before the start of the incubations, the overlying water was removed and cores were filled with *in situ* water. Cores were closed with airtight lids and the overlying water was stirred during the whole incubation period. Water samples were collected with acid-washed syringes before and after incubation and O_2 concentrations were determined by the Winkler method using potentiometric end-point detection and a Mettler® titrator (DL21). Hourly benthic CR and GPP rates were calculated with the same method as that for the planktonic compartment outlined above.

At each station and incubation depth, samples were taken for chlorophyll *a* and nutrient analysis. For chlorophyll *a,* water was filtered through GF/F filters that were stored frozen until extraction and analysis by high-performance liquid chromatography (Barranguet et al. 1997). Automated colorimetric techniques were used for orthophosphate, nitrate, nitrite and ammonium (Van den Meersche et al. 2004).

Light penetration in the water column was measured using a LI-COR quantum LI-1935A and a LI-1400 datalogger twice during each incubation period. Surface irradiance was measured every 15 min during the first cruise using a LI-COR cosine corrected quantum sensor (LI-1925A) and a LI-1400 datalogger. Hourly surface irradiance data during the second cruise were provided by the Danish Institute of Agricultural Sciences at Folum, about 25 km from the city of Randers.

Benthic and planktonic primary production is strongly dependent on the available light intensity. Strong variations in surface light irradiance were observed during both campaigns (see Table 1) and a correction was therefore applied to compare results obtained under different light conditions. During both cruises, for each station, relationships between planktonic hourly GPP rates normalized per unit of chlorophyll *a*

(GPP_B, mmol O_2 mg Chl *a* h^{-1}) and daily light intensities (I, µmol m^{-2} s^{-1}) were established using the model of Platt et al. (1980).

$$GPP_B = GPP_{Bmax} [1 - \exp(-I/I_k)] \quad (1)$$

where GPP_{Bmax} is the maximal GPP rate normalized per unit of chlorophyll *a* (mmol O_2 mg Chl *a* h^{-1}), I is the irradiance at each incubation depth (µmol m^{-2} s^{-1}) and I_k is the saturation irradiance value (µmol m^{-2} s^{-1}).

As samples for benthic GPP measurements were taken at only one depth and incubations performed under a 0.2 m water height, such procedure was not applicable. Gargas (1970) estimated saturation irradiance (I_k) on an annual scale in sediments of Nivå bay (Oresund) and found values around 100 and 300 µmol m^{-2} s^{-1} in April and August respectively. Thus, for each station, we fixed this parameter and calculated GPP_{max} (mmol O_2 m^{-2} h^{-1}) values to fit our data using eq. (1) although benthic GPP rates were expressed in mmol O2 m^{-2} d^{-1} and not normalized per unit of chlorophyll *a*. Planktonic and benthic hourly GPP values were recalculated for each station assuming a mean daily surface irradiance for each campaign (486.3 and 486.2 µmol m^{-2} s^{-1} during Randers 1 and 2, respectively). Daily planktonic and benthic CR rates were calculated by multiplying the hourly rates by 24. Daily GPP rates were multiplied by the daylight duration (14 h and 15 h during Randers 1 and 2, respectively) to estimate daily planktonic and benthic GPP.

The fjord was divided in 2 boxes and 3 depth layers were considered (0-2 m, 0-4 m and 0-7 m, the latter corresponding to the navigation channel). The surface area and the percentage covered by each depth layer were estimated for each box using a digitized map (INT 1381) and Arcview 8.3 software package. Planktonic metabolic rates were integrated and both benthic and planktonic rates were extrapolated according to these bathymetric profiles. Benthic GPP was assumed to be nil in the deep inner box of the estuary that mainly consists of the navigation channel (7 m deep) with a negligible surface area covered by banks.

Planktonic and benthic daily NCP rates were calculated as the sum of daily GPP and CR and the net ecosystem production (NEP) of each box was estimated by summing NCP rates in both compartments. As metabolic rates estimates in each box correspond to a mean value between several stations, associated standard errors (SE) are mentioned hereafter.

Carbonate dynamics and NEP estimates

During the Randers 1 cruise, pCO_2, total alkalinity (TA) and O_2 data were obtained at two stations that were occupied during 24 h (Sta. 2 and 4, respectively on 25-26 and 28-29 April 2001) and along a transect aboard the *Genetica* from the city of Randers to the mouth of the estuary (30 April 2001). During the Randers 2 cruise, the same variables were obtained at 3 stations occupied during 24 h (Sta. 2, 4 and 6, respectively on 23-24, 27-28 and 20-21 August 2001) and along 2 transects aboard the *Tyrfing* from the city of Randers to the mouth of the estuary on 30 and 31 August 2001. Samples for TA and O_2 were collected hourly during the 24 h cycles and each 2 salinity units during the shipboard transects. Samples for TA determination were filtered on GF/F filters.

pCO_2 was measured by equilibration using the Floating Equilibrator System (FES) described by Frankignoulle et al. (2003). Briefly, the FES is a buoy containing an equilibrator, a non-dispersive infra-red gas analyser (IRGA), water and air temperature probes, an anemometer, a data logger (1 min recording interval) as well as air and water pumps. During the 24 h cycles, the FES was deployed and anchored before 12:00 UT. For the shipboard transects, it was adapted for underway measurements from the subsurface water supply of the ship. The IRGA (LI-COR 6262) was calibrated daily using pure nitrogen and 3 gas standards with a CO_2 molar fraction of 365, 810 and 4000 ppm. All gases were supplied by Air Liquide, Belgium. The estimated accuracy of the pCO_2 measurements is ± 3 ppm. TA was measured by Gran electro-titration on 100 ml samples with a reproducibility of ± 2 $\mu mol\ kg^{-1}$ and an estimated accuracy of ± 3 $\mu mol\ kg^{-1}$. DIC was computed from pCO_2 and TA using the thermodynamic constants of Mehrbach et al. (1973); the accuracy is ± 5 $\mu mol\ kg^{-1}$ (for further details refer to Frankignoulle & Borges 2001a). O_2 was measured by the Winkler method using a potentiometric end-point determination, with an estimated accuracy of ± 2 $\mu mol\ kg^{-1}$.

Apparent oxygen utilisation (AOU) was calculated using the O_2 saturation computed according to Benson and Krause (1984). Salinity was measured with a portable salinometer (Orion® 125) with a precision of ± 0.1.

NEP estimates at estuarine scale

A mass balance of DIC in the mixed layer was constructed using estimates of fluvial DIC input, output of DIC to the Baltic Sea and air-water flux of CO_2. NEP was computed to balance the budget. The fluvial DIC input (FI_{DIC} in mmol m^{-2} d^{-1}) was computed according to:

$$FI_{DIC} = \frac{\rho DIC_0 Q}{S} \qquad (2)$$

where DIC_0 is the mean value of DIC measured at Sta. 6 (mmol kg^{-1}), ρ is water density (kg m^{-3}), Q is the fresh water flow (m^3 d^{-1}) and S is the surface area of the Fjord (m^2). The output of DIC to the Baltic Sea (OBS_{DIC} in mmol m^{-2} d^{-1}) was computed according to:

$$OBS_{DIC} = \frac{\rho DIC_{AZE} Q}{S} \qquad (3)$$

where DIC_{AZE} is the Apparent Zero End-member of DIC (mmol kg^{-1}), ρ is water density (kg m^{-3}), Q is the fresh water flow (m^3 d^{-1}) and S is the surface area of the Fjord (m^2). DIC_{AZE} is the intercept at zero salinity of a line tangent to the observed curve of DIC against salinity in the lower estuary (Kaul & Froelich 1984). The intercept at zero salinity was computed by linear regression from DIC data at salinities above 9, since DIC shows a relatively conservative behaviour in the lower estuary.

The air-water CO_2 flux was computed according to:

$$F = \alpha\, k\, \Delta pCO_2 \qquad (4)$$

where F is the air-water CO_2 flux (mmol m^{-2} d^{-1}), α is the CO_2 solubility coefficient (mmol m^{-3} ppm^{-1}), k is the gas transfer velocity (m d^{-1}) and ΔpCO_2 is air-water gradient of CO_2 (pCO_{2air}- pCO_{2water} in ppm). A positive flux corresponds to a transfer of CO_2 from the atmosphere to the water (Notice that our convention differs from that in air-sea exchange literature).

The gas transfer velocity was computed according to a parameterization as a function of wind speed established from floating chamber interfacial CO_2 flux measurements carried out during the two cruises (Borges et al. in press):

$$k_{600} = 0.3 + 0.536u_{10} \qquad (5)$$

where k_{600} is the gas transfer velocity of CO_2 normalized to a Schmidt number (Sc) of 600 (m d^{-1}) and u_{10} is wind speed referenced at a height of 10 m (m s^{-1}).

k_{600} was converted to *in situ* temperature conditions assuming a k dependency proportional to $Sc^{-0.5}$. Sc was computed for a given salinity from the formulations for salinity 0 and 35 given by Wanninkhof (1992), and, assuming that Sc varies linearly with salinity.

Uncertainty on the DIC fluvial input was estimated assuming an analytical error on DIC_0 of ± 0.005 mmol kg^{-1} and an error on Q of ± 5%. Uncertainty on the DIC output to the Baltic Sea was estimated from the standard error on the y-intercept of the regression line of DIC versus salinity (DIC_{AZE}) and assuming an error on Q of ± 5%. Uncertainty on the CO_2 atmospheric flux was computed assuming an error on ΔpCO_2 of ± 3 ppm and an error on u_{10} of ± 10%.

NEP estimates at daily scale

The rates of metabolic processes in the mixed layer were computed from the DIC and AOU time courses during the 24 h cycles according to the following equation (example for DIC):

$$\Delta DIC = h\ \rho\ \frac{(DIC_{(2)} - \frac{F}{h\rho}\Delta t) - DIC_{(1)}}{\Delta t} \qquad (6)$$

where ΔDIC is the hourly DIC variation (mmol C m^{-2} h^{-1}), $DIC_{(1)}$ is DIC (mmol kg^{-1}) at time step 1 (t_1), $DIC_{(2)}$ is DIC at time step 2 (t_2), h is the mixed layer depth (2.5 m), ρ is water density (kg m^{-3}), Δt is t_2-t_1 (h), F is the atmospheric CO_2 flux (mmol m^{-2} h^{-1}) computed according to eq. (4) and (5) from ΔpCO_2 at t_1 and the average u_{10} between t_1 and t_2.

The average of day-time ΔDIC or ΔAOU values correspond to GPP + CR and the average of night-time ΔDIC or ΔAOU values correspond to CR. The integration at daily scale of hourly GPP and CR rates is the same as outlined for O_2 incubation method. The DIC and AOU data were fitted with polynomial curves to remove the variability related to analytical errors and potential variability related to water mass advection. SE associated with ΔDIC an ΔAOU averages were estimated and are mentioned hereafter.

Response surface difference (RSD) method

The RSD method developed by Swaney et al. (1999) is derived from the *in situ* diel O_2 approach applied to flowing waters. It is based on the comparison of O_2 concentrations at an initial time and station with O_2 concentrations at a second station downstream, after the time interval estimated for water to flow from the upstream to the downstream station (Odum 1956). In tidal estuarine systems, this procedure is difficult to apply because of the intrusion of marine waters and potentially subsequent water column stratification. Swaney et al. (1999) used in their method salinity as a conservative tracer to provide information on mixing and advection. This procedure is based on the hypothesis that the concentration of O_2 in an estuary varies linearly with depth, salinity and time, following the equation:

$$O_2 = b_0 + b_z z + b_s \mathrm{Sal} + b_t t + \varepsilon \qquad (7)$$

where O_2 is the observed O_2 concentration (mol m^{-3}), b_i is the rate of O_2 concentration variation associated with a unit change in each of the independent variables (z: depth, Sal: salinity and t: time), and ε represents the random component of O_2 concentration variation not explained by the independent variables.

Rates of metabolic parameters (NEP, GPP and CR) are estimated from the change of O_2 over time (b_t), corrected for air-water O_2 exchange. The latter was estimated using the same procedure than the one used for CO_2 air-water exchange (see above). During the Randers 1 cruise, 8 stations were investigated along the estuary (Sta. 1A, 2, 2A, 3, 4, 5, 5A and 6; see Fig. 1) at midday, sunset (1 May 2001) and sunrise (2 May 2001). Seven stations were investigated during Randers 2 (Sta. 2, 2A, 3, 4, 5, 5A and 6; see Fig. 1) at sunset (19 August 2001), sunrise, midday and sunset (20 August 2001). At each station, vertical profiles of O_2, temperature and salinity were made using an YSI 556 multiprobe. The O_2 sensor was calibrated in water-saturated air before each transect. Wind speed was measured with a hand-held anemometer.

SE associated with this method result mainly from the uncertainty of the regression of O_2 over time (eq. 7) and from averaging wind speeds values (i.e. uncertainty in air-water exchange).

LOICZ budgeting procedure

Stoichiometrically-linked water-salt-nutrient budgets were constructed using data collected during the two cruises as described by Gordon et al. (1996). A 2 box-2 layer model was considered, as strong vertical stratifications were observed in the fjord. The inner box covers the area from the freshwater zone (Sta. 6) to Sta. 5 and the outer part from Sta. 5 to the mouth of the estuary (Sta. 1A; see Fig. 1). A depth of the mixed layer of 2.5 m was used as outlined above. Data of freshwater flows were provided by the National Environmental Research Institute, Department of Freshwater Ecology, Denmark. Vertical profiles of salinity and nutrients (DIN and DIP) were measured as described above. Sta. 6 and 1 data were used as riverine and marine end-members respectively.

NEP (*p-r* in the LOICZ terminology) is calculated from the non-conservative fluxes of DIP in each box, assuming that these fluxes are only related to biological activity and following the equation:

$$\mathrm{NEP} = -\Delta\mathrm{DIP} \cdot (C{:}P)_{part} \qquad (8)$$

where NEP is the net ecosystem production in mmol C m^{-2} d^{-1}, ΔDIP is the non-conservative flux of DIP in mmol P m^{-2} d^{-1} and $(C{:}P)_{part}$ is the particulate *C:P* ratio. A value of 106:1 was used.

Budgets of DIN were also computed and the difference between nitrogen fixation and denitrification ($n_{\text{fix-denit}}$ in the LOICZ terminology) was calculated from the equation:

$$n_{\text{fix-denit}} = \Delta\mathrm{DIN} - \Delta\mathrm{DIP} \cdot (N{:}P)_{part} \qquad (9)$$

where $n_{\text{fix-denit}}$ is in mmol N m^{-2} d^{-1}, ΔDIN and ΔDIP are the non-conservative fluxes of nitrogen and phosphorus in mmol m^{-2} d^{-1} and $(N{:}P)_{part}$ is the particulate *N:P* ratio. A value of 16:1 was used.

Annual LOICZ budgets were also calculated for the years 1991 to 2002 using data of salinity, orthophosphate, nitrate, nitrite and ammonium concentrations extracted from the MADS database (National Environmental Research Institute, Denmark, http://www.dmu.dk/1_viden/2_Miljoe-tilstand/3_vand/4_mads/default_en.asp). Data for 2 stations in the estuary (corresponding to Sta. 2 and 5 in Fig. 1) and 1 station in the Kattegat (Sta. 1; see Fig. 1) were used. Data of freshwater flow and concentrations of

DIP and DIN in the river for the same period were provided by the National Environmental Research Institute, Department of Freshwater Ecology, Silkeborg, Denmark.

RESULTS

Oxygen incubations

Environmental characteristics at the sampling stations during both cruises are presented in Table 1 and Fig. 2. In April, the mean water temperature was 8.1 ± 1.0°C; it was lowest in the freshwater area (Sta. 6; 6.6°C) and highest at the mouth of the estuary (Sta. 1A; 9.9°C). In August, lowest water temperatures were observed in the mid-estuary (Sta. 4 and 4A) while highest values were observed in the inner area (Sta. 5), the mean value during this cruise was 18.5 ± 1.2°C. The water column was stratified during both cruises especially in the inner part of the estuary. In April, the light attenuation coefficient (*K*) was highest in the inner estuary where relatively high suspended particulate matter (SPM) concentrations were measured. In August, the most turbid waters were located in the mid-estuary. Large changes of mean surface irradiance were observed during both cruises. The total range was 183.5 to 737.8 µmol m^{-2} s^{-1}.

O_2 saturation was higher in April than in August (Fig. 2). The lowest saturation values were measured during both cruises in the inner estuary with a minimal value in August at the bottom of Sta. 6 (36.8%). O_2 super-saturations were only measured in the Kattegat (Sta. 1) in April. Chlorophyll *a* concentrations were similar in the outer estuary during Randers 1 and 2 with values lower than 3 mg m^{-3}. In the brackish area, values were higher in April than in August with a maximal concentration in surface at Sta. 5 (21 mg m^{-3}).

The DIN concentrations were higher in April than in August with a maximal value in the freshwater area (135 mmol N m^{-3}). It generally decreased seaward, except in August when surface concentration was higher in the inner part of the estuary (Sta. 5) than in the river, suggesting a DIN release in this area. The DIP concentrations were higher in August than in April and were highest in the mid-estuary (2.9 mmol P m^{-3}; Sta. 4).

Rates of planktonic community metabolism (GPP and CR) are shown in Fig. 3. It should be noted that in April incubations were not performed in the Kattegat (Sta. 1). Similar CR volumetric rates were observed in surface waters during Randers 1 and 2 ranging from -1.2 to -11 mmol O_2 m^{-3} d^{-1}, while higher rates were generally measured in bottom waters during the second cruise. Stronger variations were observed for GPP

volumetric rates during both cruises. In April, the highest rates were measured in the freshwater and inner parts of the estuary (max: 44 mmol O_2 m^{-3} d^{-1} at Sta. 5 at 0.5 m) while low values were observed in the outer and marine parts. In August, Sta. 4 and 4A presented high GPP volumetric rates (max: 80 mmol O_2 m^{-3} d^{-1} at Sta. 4a at 0.5 m).
It must be stressed that, in August, metabolic rates measured at Sta. 4 and 4a were not used to calculate the integrated value for the outer estuary given in Table 2. In fact, these stations were investigated following a precipitation event on 26 August 2001 which strongly modified the environmental characteristics: surface temperature was 2°C lower (Table 1) and DIP concentrations were almost twice the observed concentrations at stations sampled before that date. Thus, only results obtained at Sta. 2 were upscaled to the whole outer estuary in August.

In April, benthic GPP was highest in the banks along the outer part of the estuary (72 ± 32 mmol O_2 m^{-2} d^{-1}) while the highest planktonic GPP was measured in the inner area (46 mmol O_2 m^{-2} d^{-1}). For the whole estuary, benthic GPP represents almost 70% of the organic matter production during this period, but benthic CR was of the same order of magnitude and the benthic compartment was net heterotrophic in April. In contrast, the planktonic compartment was net autotrophic in April. Consequently NEP estimates reveal a slight net heterotrophy in the estuary in April although not significantly different from 0 (1 ± 30 mmol O_2 m^{-2} d^{-1}).

In August, planktonic GPP was higher than in April and CR rates more than doubled in the inner area. The planktonic compartment was net autotrophic (5 mmol O_2 m^{-2} d^{-1}). Benthic GPP decreased by half between the two campaigns and benthic CR was similar during both cruises. As a result, the benthic NCP was lower in August than in April (-20 ± 16 vs. -5 ± 28 mmol O_2 m^{-2} d^{-1}). The summertime NEP of the whole estuary was -15 ± 16 mmol O_2 m^{-2} d^{-1}.

Carbonate dynamics and NEP estimates

Carbonate dynamics

The distribution of pCO_2, DIC and TA during both Randers cruises is shown as a function of salinity in Fig. 4. pCO_2 was significantly lower in the inner estuary in April than in August (Fig. 4A). The large variability of pCO_2 (2243-3906 ppm) at salinity 0.2

in August was measured during a 24 h cycle. It is related to diel alternation between photosynthesis and respiration and is discussed in more detail below. TA and DIC show strong non conservative behaviour against salinity during both cruises, with a distinct increase at salinities from 0 to 9 (Fig. 4B and C).

NEP estimates at estuarine scale

The air-water CO_2 fluxes exhibited strong spatial variations during both cruises. The inner part of the estuary was a source of CO_2 during both cruises, -54 ± 31 and -146 ± 18 mmol C m^{-2} d^{-1} during, respectively, in April and August. The outer part of the estuary was a CO_2 sink in spring and a source in summer (+10 ± 23 and -7 ± 27 mmol C m^{-2} d^{-1}).

The strong precipitation event which prevented to use the O_2 incubation data obtained during Randers 2 (see above) also prevented the use of DIC and pCO_2 values obtained at Sta. 4 as well as at the end of the cruise (transect onboard the *Tyrfing* on 30-31 August 2001). The mixed layer DIC budget of the Randers Fjord during both cruises is shown in Table 3. A careful error analysis shows that this approach to compute NEP is prone to very large uncertainty. NEP computed using this method reveals a higher net heterotrophy during the second cruise with values of -10 ± 36 and -47 ± 15 mmol C m^{-2} d^{-1} in April and August, respectively.

NEP estimates at daily scale

During the 24 h cycles at Sta. 2 and 4 in April and August, the variations of DIC and AOU were related to the tidal advection of water masses of different salinities (not shown) and cannot be used to estimate the rates of metabolic processes. During the 24 h cycle at Sta. 6 (20-21 August, Randers 2) salinity was constant at 0.2 and water flow was always downstream. The time-course of DIC and AOU clearly follows the evolution expected from the diel succession of photosynthesis and respiration (Fig. 5).

High values of metabolic rates with strong associated errors were estimated and a positive NEP value was found using both methods (Fig. 5).

Response surface difference (RSD) method

The estimates of time-dependent rates of oxygen change (b_t) resulting from eq. (7) are compiled in Table 4. During both campaigns, b_t estimates were significantly different from 0 although r^2 values were higher in April than in August. Stronger O_2 decrease overnight (i.e. higher respiration) and lower O_2 increase during daylight (i.e. lower NCPd) were estimated in August than during the first cruise.

As the water column was always undersaturated in term of O_2, fluxes across the air-water interface were directed from the atmosphere to the water with highest transfer velocities (*k*) in April due to stronger wind speeds. Nevertheless, because of lower water column O_2 saturation during the second cruise (< 80% vs. > 90% during Randers 1), higher O_2 fluxes across the interface were estimated. Computation of metabolic parameters yields a GPP of 143 ± 33 mmol O_2 m^{-2} d^{-1} and a CR of -123 ± 24 mmol O_2 m^{-2} d^{-1} in April. NEP value during this cruise is estimated to 20 ± 57 mmol O_2 m^{-2} d^{-1}, which due to the high cumulated error, is not significantly different from 0. In August, GPP, CR and NEP were estimated to 128 ± 33, -191 ± 28 and -63 ± 61 mmol O_2 m^{-2} d^{-1}.

LOICZ budgets

Salinity, nutrients concentrations (DIP and DIN), water residence time, non-conservative fluxes of DIP and DIN, as well as derived NEP and ($n_{fix-denit}$) values are shown in Table 5 for each box budgeted. As seen above, DIP concentrations were higher during both campaigns in the inner deep compartment than in the inner upper compartment. Concentrations of DIN and DIP revealed antagonistic changes between the two cruises with higher DIP and lower DIN in summer than in spring. Freshwater flows averaged over each period of investigation were significantly higher in April than in August (3.1 vs. 1.9 x 10^6 m^3 d^{-1}; not shown in Table 6). During both campaigns, the water residence time (τ) was highest in the inner deep compartment with a maximal value in April (44 d) due to a high surface freshwater flow inhibiting vertical mixing. Non-conservative fluxes of DIP were extremely low in spring with a whole estuary net release of 0.007 mmol P m^{-2} d^{-1}. It is noteworthy that during this period the upper compartments were net sinks and the deeper compartments were net sources of DIP. Consequently, NEP calculations led to a net heterotrophy in deep sections and a net autotrophy in surface. In April, the estuary was roughly in metabolic balance (NEP = -0.8 mmol C m^{-2} d^{-1}). Moreover, $n_{fix-denit}$ values of -0.6 and -0.2 mmol N m^{-2} d^{-1} were calculated in the outer and inner estuary respectively, leading to a whole estuary rate of -0.3 mmol N m^{-2} d^{-1}. In August, a higher DIP release is observed (0.26 mmol P m^{-2} d^{-1}) leading to a strong net heterotrophy (-27 mmol C m^{-2} d^{-1}). Results of $n_{fix-denit}$ computations revealed a net DIN fixation in the inner part and a net DIN denitrification in the outer part (5 vs. -10 mmol N m^{-2} d^{-1}).

LOICZ annual budgets from 1991 to 2002 are presented in Fig. 6. A significant increase of the NEP is observed during this period, although annual net autotrophic conditions were only met once in 2000. According to these results, the Randers Fjord seems to act as a sink for organic matter and a source of atmospheric CO_2 on an annual scale. Results of $n_{fix-denit}$ computations showed an annual net DIN fixation in the estuary during all the considered period.

DISCUSSION

One of the goals of this study was to estimate ecosystem metabolism in an estuary using different approaches. Results obtained using each method are summarized in Table 6. Data should be interpreted with caution as the different methods do not estimate NEP in the estuary at the same spatial and temporal scales. The LOICZ and DIC budgets as well as the O_2 incubation estimates are based on local estimates (either metabolic rates or concentrations) which were upscaled to the whole estuary. The DIC budget provides estimates of NEP for the mixed layer only. The RSD method is based on several transects along the estuary at different periods of the day, it therefore provides estimates of NEP integrated across space and time.

Moreover, the different methods do not provide estimates expressed in the same unit, a conversion factor is needed to express the O_2-based rates in carbon units. In August, using results from the AOU and DIC diel cycles at Sta. 6 (Fig. 5), a gross photosynthetic quotient (PQ) and a respiratory quotient (RQ) of around 1.26 and 1, respectively, were calculated. This value of PQ is within the range of 1.0-1.36 given by Williams and Robertson (1991). A RQ of 1 corresponding to the oxidation of carbohydrates (Richardson 1929) is commonly used to convert mineralization rates into carbon units in estuaries (Hopkinson & Smith in press).

All approaches provided consistent metabolic estimates, both in sign and magnitude. Estimates of NEP in April suggest a slight heterotrophy but the errors associated with each method do not allow us to draw a statistically unambiguous conclusion on the metabolic status of the estuary at this time of the year. In August, estimates based on the O_2 incubations and LOICZ budgets were very similar (-28 and -27 mmol C m^{-2} d^{-1}) while DIC budgets provided a slightly lower NEP (-47 mmol C m^{-2} d^{-1}). In contrast to April, the RSD method provides a lower NEP (-89 mmol C m^{-2} d^{-1}) than the other methods. It is noteworthy that the results from Sta. 4 were removed from our calculations using the O_2 incubation, LOICZ and DIC methods while this station was sampled during the RSD transects. In order to compare consistently the results from the different methods, we estimated NEP using the RSD method without considering Sta. 4 profiles. The estimated NEP reaches a value of -36 ± 76 mmol C m^{-2} d^{-1}, closer to the values obtained using the other methods. Therefore, we believe that NEP results based on O_2 incubation, LOICZ and DIC methods are perhaps underestimated in August because the rates or concentrations from only one station (Sta. 2) were extrapolated to the whole outer estuary. The value of -89 mmol C m^{-2} d^{-1} based on the RSD method (using the full dataset) is closer to reality as it covers the entire estuary.

The metabolic rates estimated for the whole estuary obtained with the open water (RSD) and incubation approaches differ dramatically. The values of GPP and CR resulting from the RSD method are about twice higher than the ones estimated from the O_2 incubations method during both cruises. This discrepancy between open system and bottle incubations measurements has already been reported in several studies (Pomeroy 1960, Bender & Jordan 1970, Kemp & Boynton 1980, Howarth et al. 1992). Usually, open water techniques estimates provide estimates 1.5 to 3 times higher than incubation methods. These discrepancies can have several causes. First, the RSD method considers a linear relationship between oxygen, salinity, depth and time. Applied to our data, these regressions yield r^2 of around 0.6 and 0.3 in April and August respectively. This is an important source of uncertainty. It should be stressed that this method was developed for the partially mixed Hudson River while the Randers Fjord, as outlined above, is almost permanently stratified. Second, incubations eliminate the effects of mixing and turbulence which may have strong effects on both primary production and respiration (Kemp & Boynton 1980, Howarth et al. 1992).

The data collected in August at St. 6 allow the comparison of open water and incubation approaches for the estimation of metabolic rates at daily scale. NCP values were similar (Table 6) but GPP and CR estimates based on AOU/DIC 24 h cycles are one order of magnitude higher than those from the O_2 incubations. The discrepancy may be mainly due to the presence of extensive freshwater marshes upstream of Sta. 6, leading to a large contribution of benthic GPP and CR to the daily oscillations of DIC and AOU in the mixed layer during the 24 h cycle.

An important source of uncertainty in the RSD method as well as in the DIC budgets is the parameterization of the gas transfer velocity to compute the air-water O_2 and CO_2 fluxes, respectively. We recomputed the DIC budgets using the air-water CO_2 flux calculated from the gas transfer velocity parameterization of Raymond and Cole (2001) based on a compilation of gas tracer experiments in various estuaries. The corresponding NEP estimates are –12 ± 36 and –38 ± 12 mmol C m^{-2} d^{-1} for April and August, respectively. This corresponds to a change of -20% and +20% compared to the data shown in Table 6 which were estimated using the formulation of Borges et al. (in press). Moreover, O_2 fluxes across the air-water interface (FO_2) represented between 17 and 70% of the observed O_2 variation with time (b_t), and thus is an important source of error in the computation of metabolic rates using the RSD method. This illustrates that the evaluation of the gas transfer velocity is important in ecosystem metabolic studies based on the open water approach, especially in estuaries where parameterisations as a function of wind speed only have recently been shown to be site specific (Kremer et al. 2003, Borges et al. in press).

As mentioned above, the DIC budgeting procedure only gives an estimation of the mixed layer NEP. Estimating the NEP of the mixed layer based on the LOICZ approach yields to a value of 0.3 and -45 mmol C m^{-2} d^{-1} in April and August respectively, close to the ones estimated by the DIC budgets. The Apparent zero end-member (AZE) method used for the DIC budgets has been criticized (e.g. Regnier & Steefel 1999) because if there is a large and rapid change of freshwater DIC during a time interval shorter than the flushing time of the estuary, then a non-conservative behaviour can appear in the profile of DIC versus salinity that is unrelated to a real removal or production term. This holds true for macrotidal estuaries where the flushing time is of the order of months, but the Randers Fjord is characterized by a very short water residence time (~5 d in April and August).

The LOICZ procedure assumes that all non-conservative DIP fluxes in a system are only related to ecosystem gross primary production and respiration (Gordon et al. 1996). This assumption may not be valid in systems receiving high loads of SPM because adsorption and desorption of phosphorus to and from these particles (the so-called phosphorus buffer mechanism) can occur along the salinity gradient (Sharp et al. 1982, Edmond et al. 1985, Froelich 1988, Fox 1990, Zwolsman 1994). SPM concentrations in the Randers Fjord are much lower than those reported in the latter studies with values ranging from 1.5 to 43.1 g m^{-3} in April and 0.6 to 12.1 g m^{-3} in August. Thus, abiotic non-conservative fluxes are unlikely to play a significant role in this system.

Finally, another source of uncertainty for both DIC and LOICZ budgets is lateral inputs of DIP and DIC. A significant modification of water column characteristics was evidenced in August following a strong precipitation event while no concomitant freshwater flow increase was observed. This suggests that lateral inputs can be punctual sources of DIP and DIC variability in this system. Unfortunately, no data were available to us to test this hypothesis on larger time scales.

Planktonic GPP is highly variable in estuaries and mostly depends on physical parameters governing light availability such as residence time, turbidity and vertical mixing rather than on nutrient concentrations (Boynton et al. 1982, Heip et al. 1995). In European estuaries (see review of Gazeau et al. in press), planktonic GPP was found to range between 1.7 (Ems-Dollard estuary; Van Es 1977) and 153.3 mmol C m^{-2} d^{-1} in the highly productive Urdaibaï estuary (Revilla et al. 2002). The production of organic matter by chemoautotrophic bacteria such as nitrifiers, which are reported to be very active in eutrophic estuaries (Heip et al. 1995), was not measured during our study. Ignoring this oxygen consuming process may have lead to an overestimation of CR. Nitrification is unlikely to be a significant process in the water column because ammonium concentrations were low during both cruises (3.5 and 2.7 mmol m^{-3} in April and August respectively).

In the extensive review of Hopkinson & Smith (in press), planktonic CR rates in estuaries were found to range between -1.7 in the Gulf of Finland to -84 mmol C m^{-3} d^{-1} in the Fly River delta with a mean value of -19.6 mmol C m^{-3} d^{-1}. Rates measured during this study (-1.2 to -11.2 mmol C m^{-3} d^{-1} with a mean value of -5.8 mmol C m^{-3} d^{-1}) are thus in the lower end of the range reported by Hopkinson & Smith (in press).

In this shallow estuary, the benthic compartment plays a significant role on the production and mineralization of organic matter. Benthic GPP was 53 and 23 mmol C m^{-2} d^{-1} in April and August, respectively or 70 and 40% of the total GPP. This is not surprising since the shallowness of the estuary (average depth: 1.6 m) and the relatively low SPM concentrations (mean of 4 to 9 g m^{-3}) enable benthic primary production on a large portion of the estuary. These rates of benthic GPP are within the range of 16-72 mmol C m^{-2} d^{-1} given by Van Es (1982) and Colijn and de Jonge (1984) for intertidal flats in the Ems-Dollard estuary. Benthic CR amounted to -58 and -43 mmol C m^{-2} d^{-1}, within the range from -30.2 to -62.9 mmol C m^{-2} d^{-1} in Norsminde Fjord (Denmark; Andersen & Kristensen 1988). Benthic CR rates measured during this study (-17 to -69 mmol C m^{-2} d^{-1}) fall in the range of -3 to -115 mmol C m^{-2} d^{-1} of published benthic CR rates compiled by Hopkinson & Smith (in press).

In a recent paper, Caffrey (2004) reported annual NEP estimates based on the *in situ* diel O_2 method for 42 estuarine sites in the US. All sites are heterotrophic in term of carbon with NEP ranging from -11 to -278 mmol C m^{-2} d^{-1} and a mean value of -110 ± 66 mmol C m^{-2} d^{-1}. Using the O_2 incubation method, Smith & Kemp (1995) estimated a NEP in Chesapeake Bay ranging from -6 to 65 mmol C m^{-2} d^{-1}. Raymond et al. (2000) estimated an annual NEP in the York River estuary based on a DIC budget of -23 mmol C m^{-2} d^{-1}. Smith & Hollibaugh (1997) used a LOICZ budget to estimate the NEP in Tomales Bay and found an annual rate of -12 mmol C m^{-2} d^{-1}. NEP rates measured in the Randers Fjord using four methods during the two cruises fall within the range of these previous studies.

Averaging CO_2 fluxes estimated during the two cruises leads to a rough estimate of the annual emission of CO_2 from the Randers Fjord of -6 mmol C m^{-2} d^{-1}. Although this is a minimal estimate since the spring phytoplanktonic bloom does not last half of the year, it is below the range of CO_2 emission from nine macro-tidal European estuaries (-86 to -208 mmol C m^{-2} d^{-1}; Frankignoulle et al. 1998). This is probably related to the shorter water residence time in micro-tidal estuaries, such as the Randers Fjord, than in macro-tidal estuaries. This leads to a less efficient consumption of allochthonous organic carbon during the transit through the estuary and a lower generation of CO_2. Also, due to the stratified nature of micro-tidal estuaries (as opposed to the generally well mixed macro-tidal estuaries), the CO_2 produced by degradation processes below the pycnocline are not immediately available for exchange with the atmosphere. This could also explain the fact that a net sink for atmospheric CO_2 was observed in April while all approaches suggest that the estuary was either heterotrophic or nearly balanced. This illustrates that the metabolic status and air-water CO_2 fluxes can be temporally decoupled by physical features.

As mentioned before, all LOICZ budgets for the years 1991 to 2002 suggest that nitrogen fixation is higher than denitrification. This result seems unrealistic since the estuary receives high loads of DIN and the mean annual rate of benthic denitrification is 2.7 mmol N m^{-2} d^{-1} or 281 tN yr^{-1} (Nielsen et al. 2001). Our budgets only take into

account DIN inputs from the River Gudenå while Nielsen et al. (2001) also considered the relatively minor river Allingå as well as waste water discharge. The difference between their DIN input value and the one we used for the same year (1995) is calculated to 670 tN yr^{-1} and therefore can explain the artificial net DIN fixation given by our budget. Adding this input to our budget yields to a value of -0.5 mmol N m^{-2} d^{-1}. This value is in the range of previously reported rates for sites with "Steve Smith's ranking ≥ 2" (-5.2 to 2.6 mmol N m^{-2} d^{-1}) and roughly corresponds to the median rate (-0.56 mmol N m^{-2} d^{-1}) from the LOICZ environmental database (downloaded on 23 March 2004 from http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm).
There is also a difference of 31.5 tP yr^{-1} between the DIP input used in our budget for the year 1995 and the one used by Nielsen et al. (2001). Adding this extra input to the LOICZ budget leads to a higher NEP (-7 vs. -18 mmol C m^{-2} d^{-1}).
Unfortunately, nutrient loading from the river Allingå and from point sources such as factories and sewage treatment plants are not available to us for the whole investigated period (1991-2002). Therefore, we believe that these annual LOICZ budgets provide significantly underestimates of both DIP and DIN net retention in the estuary and must be viewed with caution. Nevertheless, if the underestimations over the investigated period are assumed constant, then Fig. 6 clearly shows an evolution of the metabolic balance of the Randers Fjord toward higher NEP in the 1990's. (from -21 mmol C m^{-2} d^{-1} in 1991 to -9 mmol C m^{-2} d^{-1}). These annual values fall within the range of reported NEP values estimated using the LOICZ budgeting procedure in 70 coastal sites with "Steve Smith's ranking ≥ 2" (-42 and 32 mmol C m^{-2} d^{-1}; downloaded on 20 May 2004 from the LOICZ environmental database http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm).

In the catchment area of the Randers Fjord, the construction of sewage treatment plants took place in the 1970's and 1980's. Andersen (1999) pointed out that, since 1974, phosphorus and organic matter loading from waste water treatment plants have been reduced by around 90% and nitrogen loading by about 50%. In the estuary itself, phosphorus decrease has been delayed due to the release of phosphorus from the sediment in lakes in the catchment area (Nielsen et al. 1993).

Although each method investigated during this study has its own limitations and associated uncertainties, consistent NEP estimates in this estuary have been produced during two field campaigns by all methods and showed that the Randers Fjord was near metabolic balance in spring and net heterotrophic in summer. As incubation techniques, as well as *in situ* diel methods such as RSD remain hard to apply on large spatial and temporal scales, this result suggests that indirect methods such as LOICZ or DIC budgets may be alternative confident ways to estimate the metabolic status of a coastal ecosystem. Within the frame of the EUROTROPH project, the LOICZ budgeting procedure will be applied to the Scheldt estuary in order to assess the validity of this method in very turbid areas.

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Table 1 Date, geographical location and characteristics of incubated stations during both cruises. I_0 is the average irradiance, K is the light attenuation coefficient and SPM is the concentration of suspended particulate matter during each incubation period.

	Sta.	Date	Longitude °E	Latitude °N	Depth (m)	Sal	Temp (°C)	I_0 (μmol m^{-2} s^{-1})	K (m^{-1})	SPM (*g* m^{-3})
Randers 1	1	25/04	10.44	56.61	0.5	21.4	7.0	205.3	-	1.9
					1.5	21.4	7.0			1.5
					3	21.4	7.0			3.7
					7	21.4	7.0			1.9
	1a	1/05	10.32	56.61	0.5	12.1	9.9	737.8	0.72	5.2
					1.5	12.3	9.9			3.9
					3	12.5	9.9			4.0
					6	19.6	9.0			5.3
	2	26/04	10.30	56.61	0.5	6.7	8.5	472.2	0.60	5.3
					1.5	6.8	8.5			5.3
					3	6.9	8.5			3.9
					7	29.5	7.7			6.5
	2a	28/04	10.26	56.58	0.5	4.9	8.8	454.9	0.64	43.1
					1.5	5.3	8.9			5.2
					3	14.5	8.5			5.8
					6	19.2	8.1			3.0
	5	29/04	10.21	56.47	0.5	1.4	9.1	678.2	1.13	9.7
					1.5	2.5	9.0			12.4
					3	14.2	8.3			8.0
					6	15.9	8.2			35.3
	6	22/04	10.04	56.46	0.5	0.2	7.0	723.2	1.28	10.2
					1	0.2	7.0			9.9
					1.5	0.2	7.0			9.6
					4	8.2	6.6			9.5
Randers 2	1	22/08	10.44	56.61	0.5	22.0	18.7	551.5	0.22	0.57
					3	23.0	18.4			0.57
					5	23.1	18.4			0.91
					7	28.1	15.9			12.10
	2	24/08	10.30	56.61	0.5	16.3	19.8	529.4	0.67	2.58
					1.5	18.3	19.8			3.20
					3	19.8	19.8			2.49
					7	21.8	19.6			2.37
	4	28/08	10.23	56.52	0.5	11.3	17.4	502.8	1.35	6.34
					1.5	11.6	17.4			6.10
					3	13.6	17.8			7.34
					5	19.8	18.1			5.05
	4a	30/08	10.23	56.52	0.5	6.9	17.2	508.9	1.30	5.34
					1.5	8.0	17.6			5.08
					3	13.2	17.1			4.53

Table 1 continued

	Sta.	Date	Longitude °E	Latitude °N	Depth (m)	Sal	Temp (°C)	I_0 (µmol m^{-2} s^{-1})	K (m^{-1})	SPM *(g m^{-3})*
Randers 1					6	20.2	16.6			9.42
	5	26/08	10.21	56.47	0.5	2.7	19.9	183.5	0.89	3.58
					1.5	8.7	20.3			3.82
					3	13.5	20.2			4.61
					6	16.1	20.0			8.20
	6	21/08	10.04	56.46	0.5	0.2	18.8	588.4	0.84	4.10
					1	0.2	18.8			4.46
					1.5	0.3	18.8			4.11
					3.5	11.4	18.0			4.86

Table 2 Integrated metabolic rates based on oxygen incubations during both cruises. Planktonic volumetric rates are depth-integrated. All rates are expressed in mmol O_2 m^{-2} d^{-1}. Numbers in parenthesis refer to the standard error associated with the rates averaging between stations (± SE). See Fig. 1 for definition of inner and outer areas.

	Area	Plankton			Benthos			**Whole ecosystem**
	(km^2)	GPP	CR	NCP	GPP	CR	NCP	**NEP**
April 2001								
River	-	34	-25	9	0	-20	-20	**-11**
Inner	6.3	46	-25	21	0	-26	-26	**-5**
Outer	16.7	17 (± 1)	-17 (± 1)	0 (± 2)	72 (± 32)	-69 (± 7)	3 (± 39)	**3 (± 41)**
Whole estuary	23	25 (± 1)	-19 (± 1)	6 (± 2)	53 (± 23)	-58 (± 5)	-5 (± 28)	**1 (± 30)**
Kattegat	-	-	-	-	-	-	-	**-**
August 2001								
River	-	44	-28	16	0	-29	-29	**-13**
Inner	6.3	70	-67	3	0	-17	-17	**-14**
Outer	16.7	26	-21	5	32 (± 12)	-53 (± 12)	-21 (± 24)	**-16 (± 24)**
Whole estuary	23	38	-33	5	23 (± 8)	-43 (± 8)	-20 (± 16)	**-15 (± 16)**
Kattegat	-	62	-31	31	0	-22	-22	**9**

Table 3 Dissolved inorganic carbon (DIC) budget for the mixed layer of the Randers Fjord in April and August. Net ecosystem production (NEP) was computed to balance the budget. Positive CO_2 atmospheric flux corresponds to a transfer of CO_2 from the atmosphere to the water. Numbers in parenthesis refer to associated standard errors (± SE).

mmol C m^{-2} d^{-1}	24-30 April	20-24 August
DIC fluvial input	283 (± 14)[a]	166 (± 9)[b]
DIC output to the Baltic Sea	-298 (± 21)[c]	-195 (± 13)[d]
CO_2 atmospheric flux	5 (± 1)[e]	-17 (± 7)[f]
NEP	**-10 (± 36)**	**-47 (± 15)**

[a] DIC_0 = 2.075 ± 0.005 mmol kg^{-1}; [b] DIC_0 = 2.063 ± 0.005 mmol kg^{-1}; [c] DIC_{AZE} = 2.205 ± 0.044 mmol kg^{-1}; [d] DIC_{AZE} = 2.389 ± 0.027 mmol kg^{-1}; [e] ΔpCO_2 = 29 ppm; [f] ΔpCO_2 = -348 ppm.

Table 4 Nightime and daytime parameters used for and resulting from the response surface difference (RSD) method, and derived metabolic parameters. O_2 sat: oxygen saturation (%); b_t: volumetric O_2 rate of change (mmol O_2 m^{-3} h^{-1}); r^2: determination coefficient; p: probability value; wind speed (m s^{-1}); k_{O2}: gas transfer velocities (m h^{-1}); F_{O2}: fluxes across the air-water interface (mmol O_2 m^{-2} h^{-1}); GPP: gross primary production; CR: community respiration; NEP: net ecosystem production. All metabolic rates are expressed in mmol O_2 m^{-2} d^{-1}. Numbers in parenthesis (± SE) refer to the standard errors associated with the calculation of each parameter.

Date	O_2 sat (± SE)	b_t estimate (± SE)	r^2	p	Wind speed (± SE)	k_{O2} (± SE)	F_{O2} (± SE)	**GPP (± SE)**	**CR (± SE)**	**NEP (± SE)**
April (Sta. 1A – 6)										
Nighttime	94 (± 2)	-2.747 (± 0.2465)	0.62	< 0.0001	5.4 (± 0.9)	0.11 (± 0.02)	0.7 (± 0.6)	**143** **(± 33)**	**-123** **(± 24)**	**20** **(± 57)**
Daytime	97 (± 1)	3.869 (± 0.4574)	0.66	< 0.0001	7.1 (± 0.7)	0.14 (± 0.01)	1.1 (± 0.7)			
August (Sta. 2 – 6)										
Nighttime	78 (± 3)	-3.561 (± 0.5544)	0.35	< 0.0001	1.9 (± 0.6)	0.06 (± 0.01)	2.3 (± 0.3)	**128** **(± 33)**	**-191** **(± 28)**	**-63** **(± 61)**
Daytime	79 (± 3)	1.601 (± 0.3983)	0.35	< 0.0001	1.6 (± 0.3)	0.05 (± 0.01)	2 (± 0.4)			

Table 5 Surface area, salinity and nutrient concentrations (dissolved inorganic phosphorus, DIP and dissolved inorganic nitrogen , DIN) in each budgeted box (see Fig. 1). Computed water residence times (τ), non conservative fluxes of DIP and DIN (ΔDIP and ΔDIN) as well as net ecosystem production (NEP) and net difference between DIN fixation and denitrification ($n_{fix-denit}$).

Compartment	Area (km^2)	Sal	DIP (mmol m^{-3})	DIN (mmol m^{-3})	τ (d)	ΔDIP (mmol P m^{-2} d^{-1})	ΔDIN (mmol N m^{-2} d^{-1})	NEP (mmol C m^{-2} d^{-1})	$n_{fix-denit}$ (mmol N m^{-2} d^{-1})
Randers 1									
River	-	0.2	0.20	129		-	-		-
Inner upper	6.3	2.0	0.20	110	8	-0.006	-0.6	0.62	-0.47
Inner deep	6.3	15.1	0.29	45	44	0.009	0.0	-0.93	-0.15
Outer upper	16.7	8.4	0.18	70	7	-0.001	-0.1	0.09	-0.07
Outer deep	3.9	20.7	0.14	34	10	0.043	0.3	-4.53	-0.42
Kattegat	-	21.4	0.05	2		-	-	-	-
Inner	**6.3**					**0.003**	**-0.6**	**-0.3**	**-0.6**
Outer	**16.7**					**0.009**	**0.0**	**-1.0**	**-0.2**
Whole estuary	**23**					**0.007**	**-0.2**	**-0.8**	**-0.3**
Randers 2									
River	-	0.2	1.46	59		-	-	-	-
Inner upper	6.3	5.7	1.83	67	9	-0.017	9.3	1.78	9.52
Inner deep	6.3	14.8	2.53	27	17	0.232	-1.1	-24.63	-4.85
Outer upper	16.7	18.1	1.98	13	3	0.638	-5.2	-67.60	-15.36
Outer deep	3.9	21.8	0.75	7	2	-1.556	-4.2	164.98	20.73
Kattegat	-	28.1	0.49	2		-	-	-	-
Inner	**6.3**					**0.216**	**8.1**	**-23**	**5**
Outer	**16.7**					**0.271**	**-6.1**	**-29**	**-10**
Whole estuary	**23**					**0.256**	**-2.2**	**-27**	**-6**

Table 6 Areal metabolic rates estimates during both cruises based on the four different methods. All metabolic parameters are in mmol C m^{-2} d^{-1}. Gross primary production (GPP) rates based on oxygen (O_2 incubations and RSD method) were converted in carbon unit assuming a photosynthetic quotient (PQ) of 1.3 while a respiratory quotient (RQ) of 1 was applied to convert community respiration (CR) rates. Net ecosystem production (NEP) is the sum of GPP and CR. Number in parenthesis represents the standard error (±SE) associated with each parameter estimation.

	April			August		
	GPP	CR	NEP	GPP	CR	NEP
Whole estuary estimates						
O_2 incubations	62 (± 19)	-77 (± 6)	-15 (± 25)	49 (± 8)	-76 (± 8)	-28 (± 16)
RSD	114 (± 26)	-123 (± 24)	-13 (± 50)	102 (± 27)	-191 (± 28)	-89 (± 55)
LOICZ budget	-	-	-1	-	-	-27
Mixed layer estimates						
DIC budget	-	-	-10 (± 36)	-	-	-47 (± 15)
River estimates (mixed layer)						
O_2 incubations				34	-12	22
DIC/AOU cycle				312 (± 54)	-301 (± 38)	11 (± 92)

Figure captions

Fig. 1. Map of the Randers Fjord and location of sampling stations in the navigation channel (open circles) and on the banks (full squares). Planktonic oxygen incubations were performed at Sta. 1, 1a, 2, 2a, 5 and 6 in April and at stations 1, 2, 4, 4a, 5 and 6 in August. Benthic oxygen incubations were performed in the navigation channel at Sta. 1, 2, 3, 4 and 5 and on the 3 bank stations during both cruises. See text for stations sampled for the Response Surface Difference (RSD) method as well as for dissolved inorganic carbon (DIC) and Land-Ocean in the Coastal Zone (LOICZ) budgets.

Fig. 2. Vertical profiles of oxygen saturation and of the concentrations of chlorophyll *a* (Chl *a*), dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) at each station where incubation of the planktonic community was carried out.

Fig. 3. Planktonic volumetric gross primary production (GPP) and community respiration (CR) rates measured in Apri1 (A) and August (B). Rates are in mmol O_2 m^{-3} d^{-1}.

Fig. 4. Distribution along the salinity gradient of the partial pressure of CO_2 (pCO_2; ppm), dissolved inorganic carbon (DIC; mmol kg^{-1}) and total alkalinity (TA; mmol kg^{-1}) compiled from the 24 h cycle measurements and ship-born transects during the Randers 1 and 2 cruises (24-30 April and 20-31 August 2001).

Fig. 5. Time-course of dissolved inorganic carbon (DIC*;* mmol kg^{-1}) and apparent oxygen utilisation (AOU*;* µmol kg^{-1}) during a 24 h cycle at Sta. 6 during the Randers 2 cruise (20-21 August 2001).Time is expressed in UT. Gross primary production (GPP), community respiration (CR) and net ecosystem production (NEP) rates computed from these 24 h cycles are expressed in mmol C m^{-2} d^{-1} (DIC cycle) and mmol O_2 m^{-2} d^{-1} (AOU cycle). Numbers in parenthesis refer to associated standard errors (± SE).

Fig. 6. Annual net ecosystem production (NEP) and $n_{fix-denit}$ rates computed using the LOICZ budgeting procedure from 1991 to 2002.

Fig. 1 – Gazeau et al.

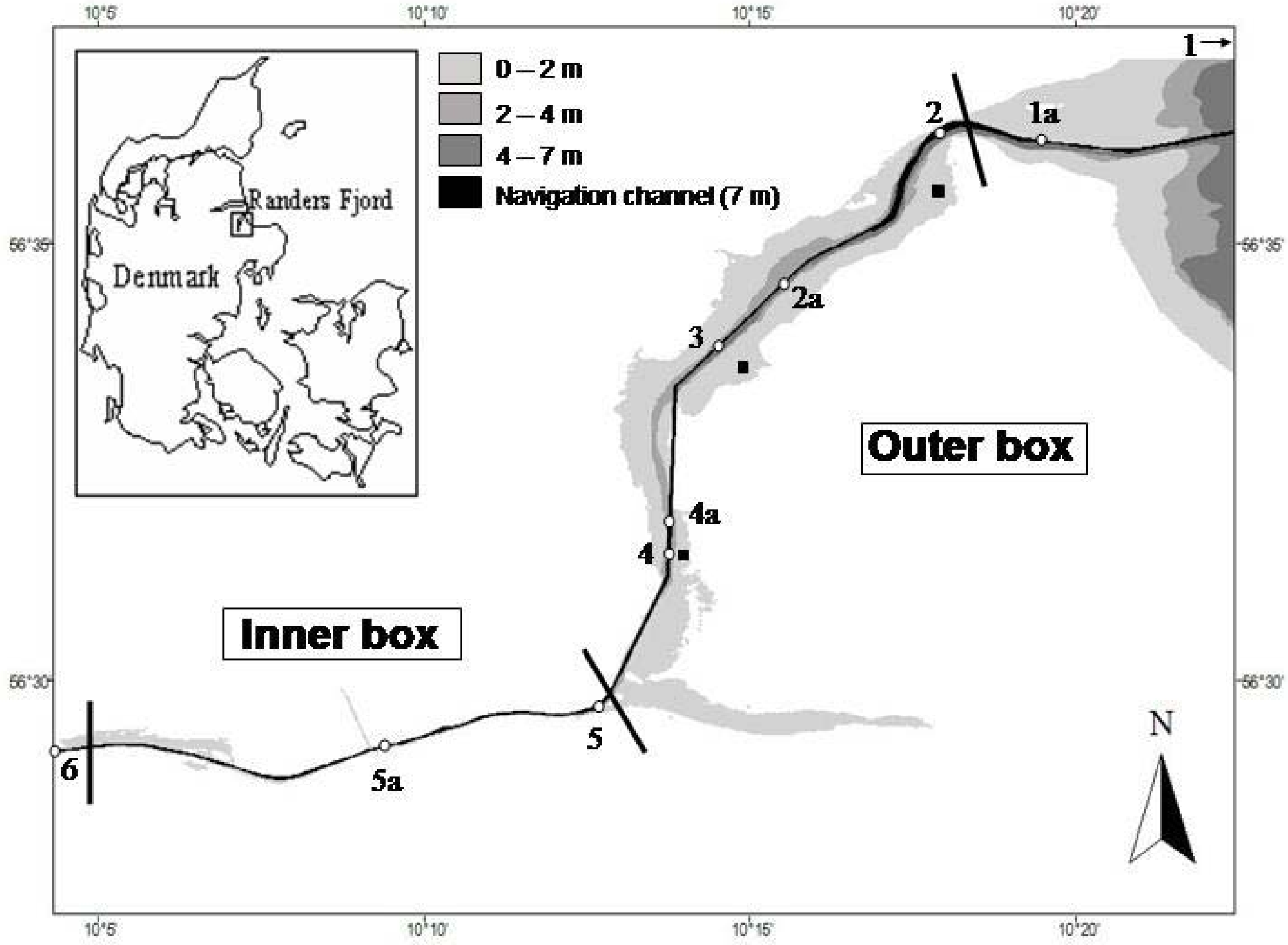


Fig. 2 – Gazeau et al.

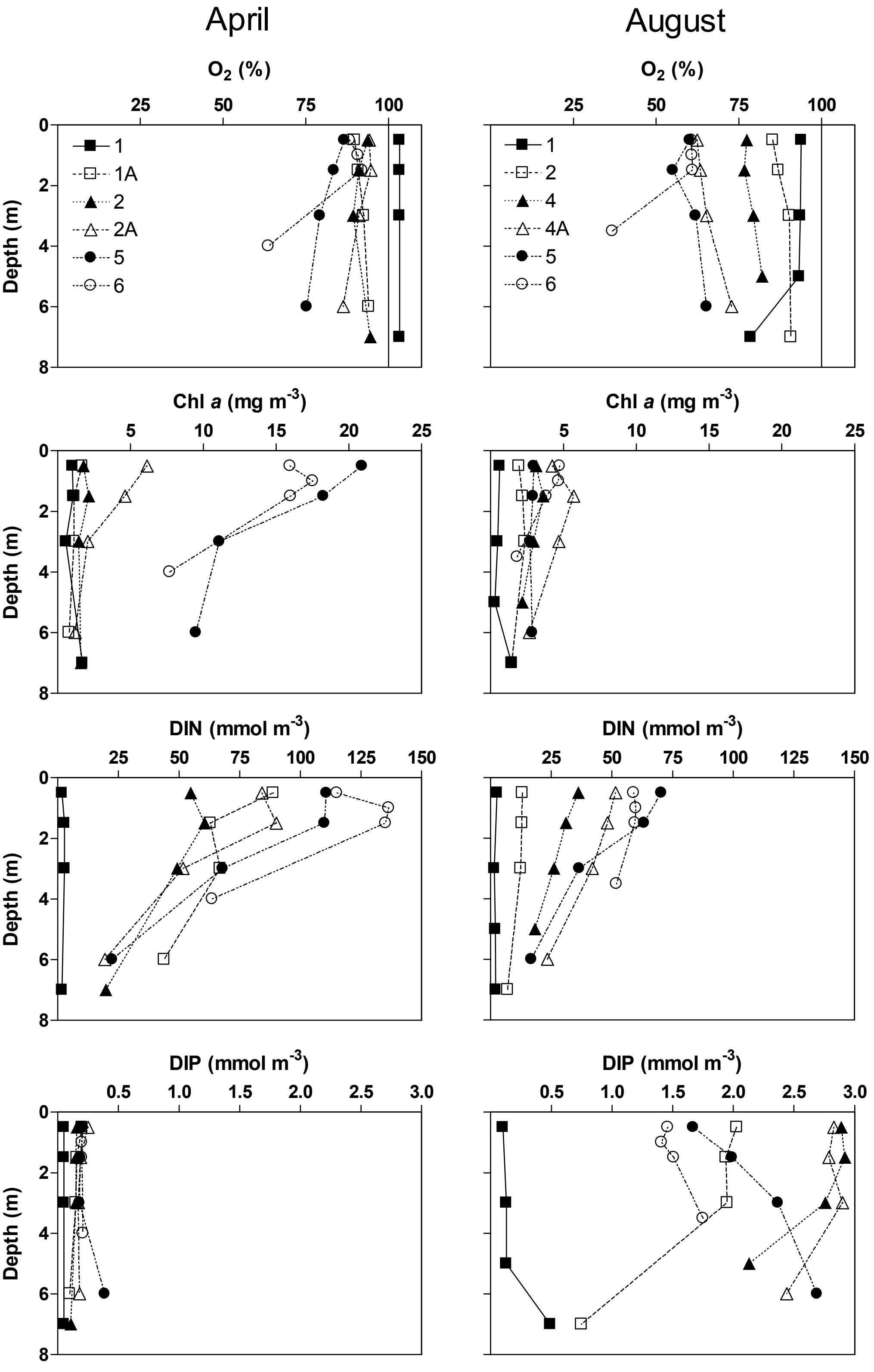


Fig. 3 – Gazeau et al.

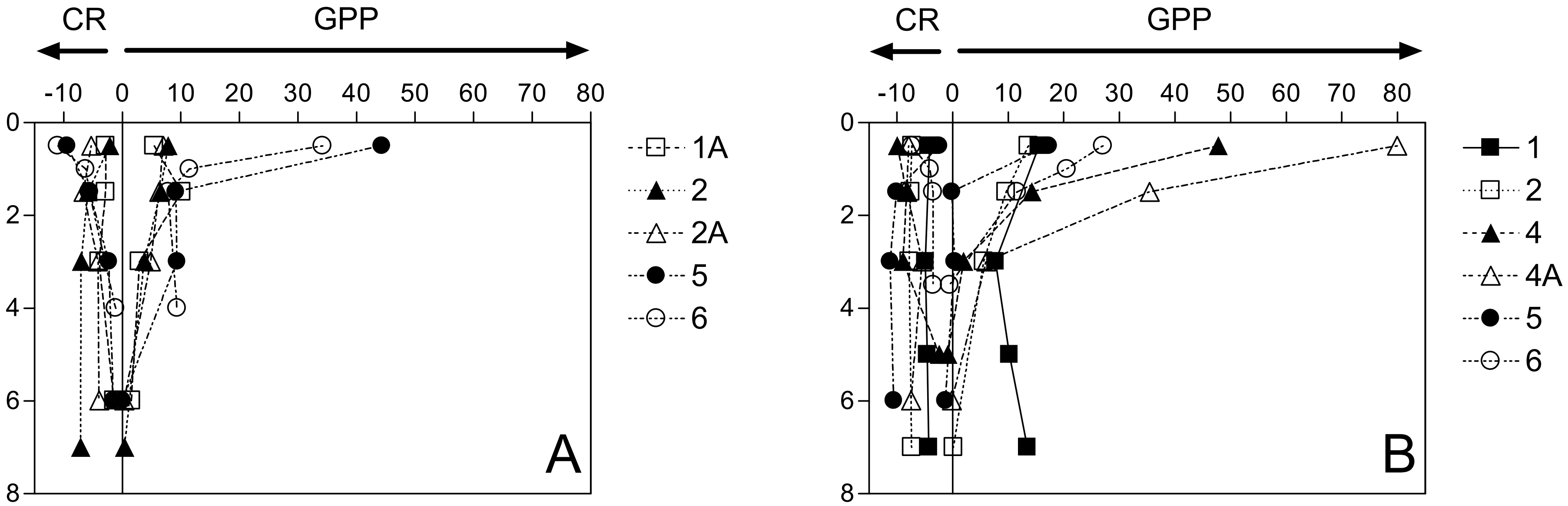


Fig. 4 – Gazeau et al.

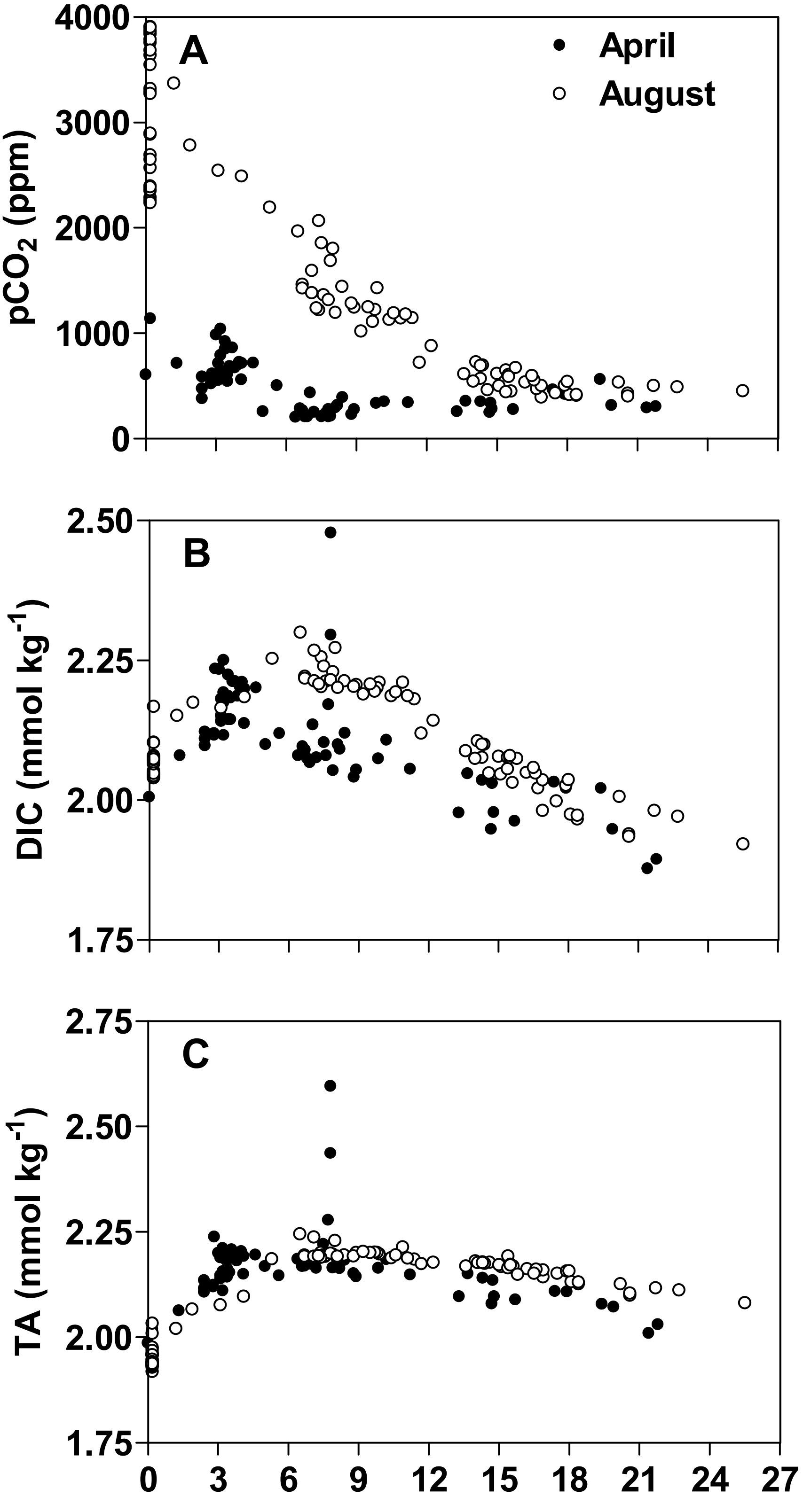


Fig. 5 – Gazeau et al.

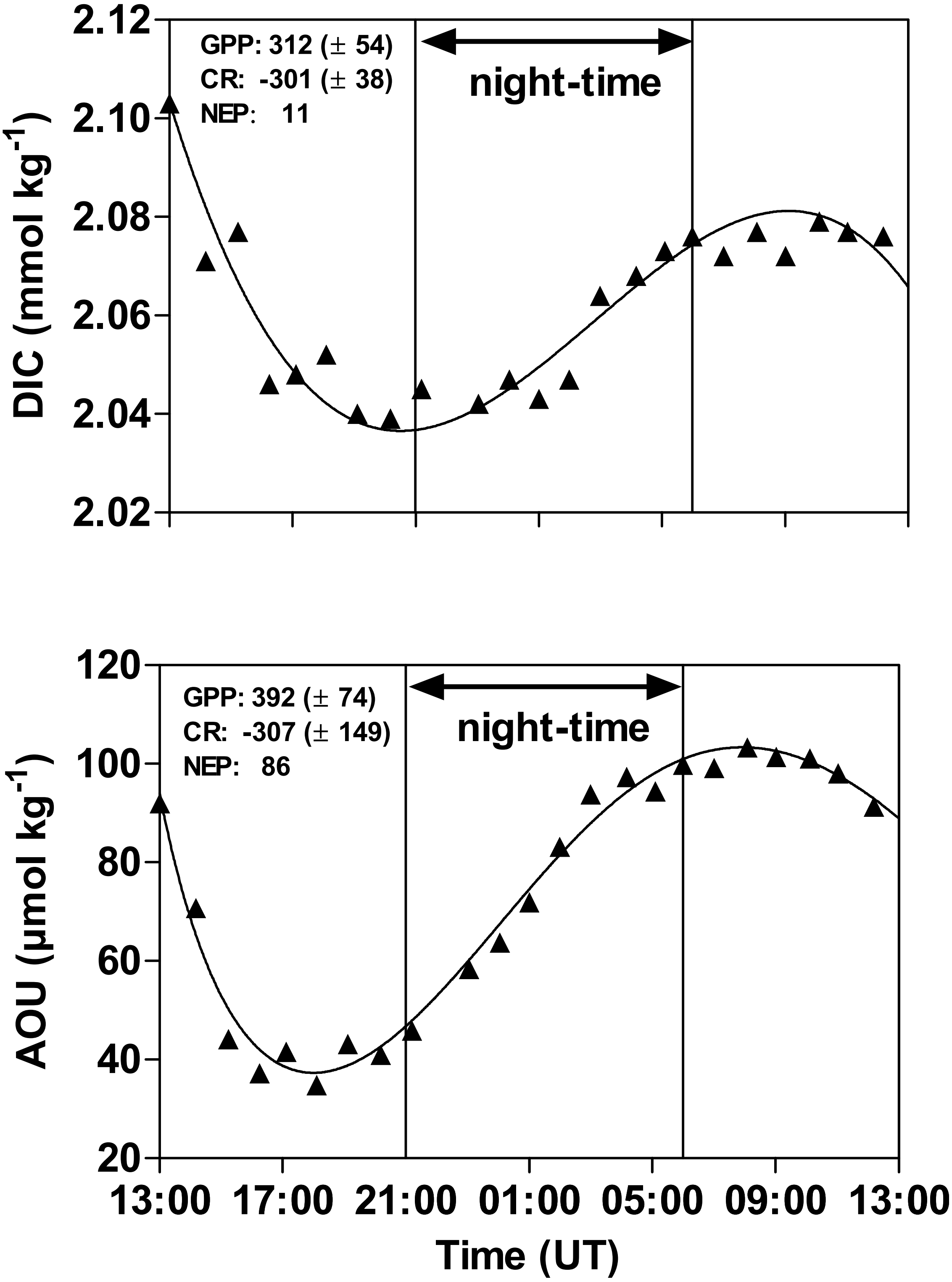
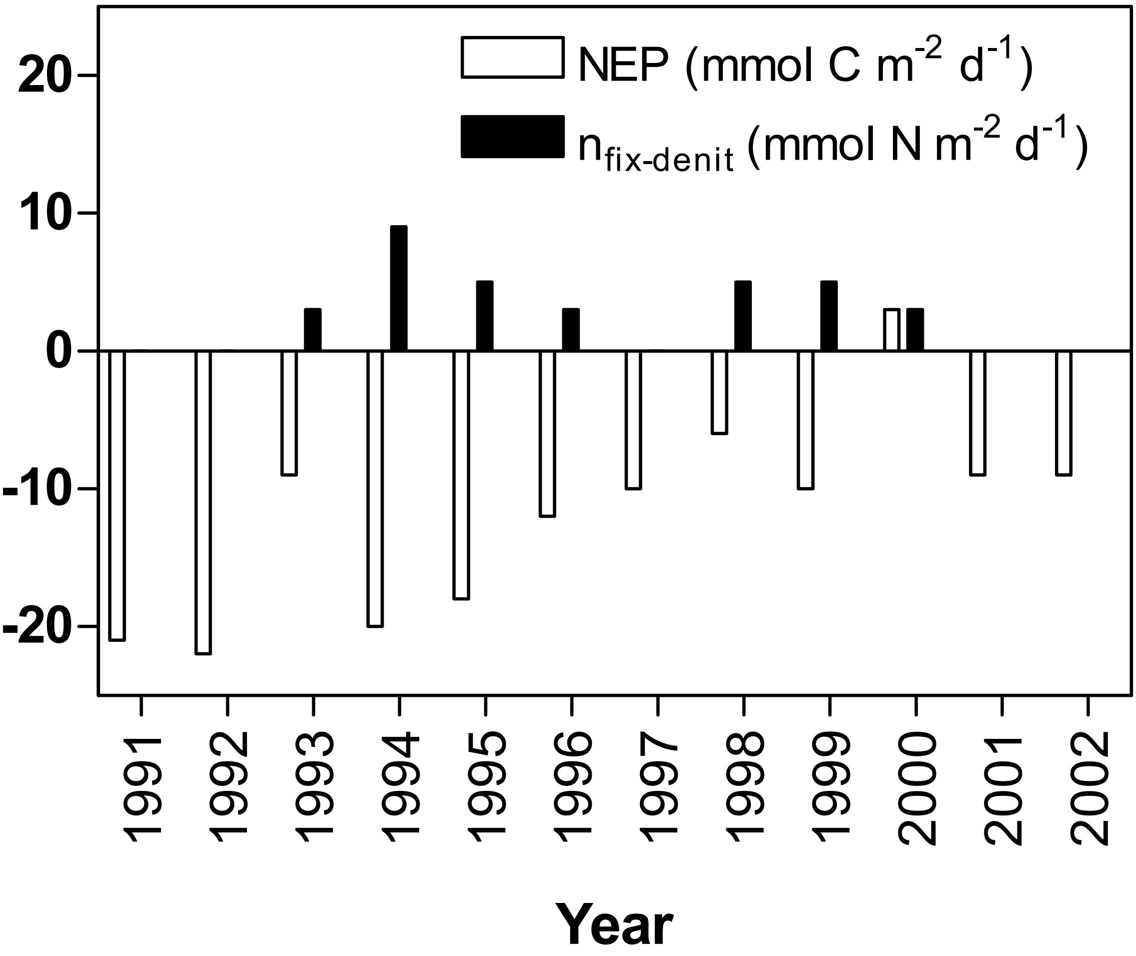


Fig. 6 – Gazeau et al.



3.4 L'estuaire de l'Escaut

Gazeau F., Gattuso J. -P., Middelburg J. J., Barrón C., Duarte C. M., Schiettecatte L. -S.,
Brion N., Pizay M. -D., Frankignoulle M. & Borges A. V.
Planctonic and whole-system metabolism in a nutrient-rich estuary (The Scheldt Estuary)
(soumis)
Limnology and Oceanography.

PLANKTONIC AND WHOLE SYSTEM METABOLISM IN A NUTRIENT-RICH ESTUARY (THE SCHELDT ESTUARY)

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Abstract

Planktonic gross primary production (GPP), community respiration (CR) and nitrification were measured monthly in the Scheldt estuary by the oxygen incubation method from January to December 2003 as well as in November 2002 and April 2003 with concomitant benthic subtidal CR measurements. Planktonic GPP rates were high in the freshwater area (92 mmol C m^{-2} d^{-1}) and decreased seaward (17-34 mmol C m^{-2} d^{-1}). Planktonic CR was significantly higher than subtidal benthic CR,was highest in the brackish area (max: -313 mmol C m^{-2} d^{-1} in October) and appears to be mainly driven by inputs of allochthonous organic matter rather than by local production. A significant decrease of nitrification is observed since the 1990's but this process still represents up to 31% of total organic matter production in the inner estuary.

Planktonic net community production (NCP) was most of the time negative in the estuary with values ranging from -300 to 165 mmol C m^{-2} d^{-1}. Whole estuary net ecosystem production (NEP) was investigated from June to December 2003 using the Land-Ocean Interaction in the Coastal Zone (LOICZ) budgeting procedure applied to dissolved inorganic phosphorus and carbon (DIP and DIC). While DIC budgets provided consistent NEP estimates with in situ measurements, DIP budgets failed to provide realistic estimates in the inner estuary where abiotic processes account for more than 50% of the DIP non-conservative flux. The same procedure applied to dissolved inorganic nitrogen (DIN) revealed that denitrification in this estuary did not significantly change since the 1980's.

Estuaries are highly dynamic systems with large seasonal and spatial gradients of biogeochemical compounds and processes (Heip et al. 1995). Linking land to the ocean, they are often greatly influenced by human activities, including enhanced organic matter and nutrient loadings. The balance between organic matter and nutrient loading is critical in determining the balance between autotrophy and heterotrophy (Kemp et al. 1997; Eyre and Mckee 2002).

An ecosystem is autotrophic when production of organic matter by primary producers exceeds the consumption of this matter by the overall community. Such systems are potentially net sinks for atmospheric CO_2 although air-sea CO_2 flux is also controlled by external inputs of dissolved inorganic carbon (DIC; upwelling, river inputs…), calcium carbonate ($CaCO_3$) precipitation and temperature thermodynamic effects. In contrast, an ecosystem is heterotrophic when organic matter consumption exceeds primary production, leading generally to high CO_2 partial pressures (pCO_2) and low oxygen (O_2) concentrations in the water column. Primary production is light-limited in many estuaries due to high turbidity driving these systems toward heterotrophy (Smith and Hollibaugh 1993; Gattuso et al. 1998).

Estuaries are generally oversaturated in CO_2 with respect to atmospheric equilibrium, with CO_2 fluxes ranging from 10 to 660 mmol C m^{-2} d^{-1} (Abril and Borges in press). Such emissions of CO_2 can have a significant impact on regional CO_2 budgets. For instance, European estuaries emit between 5 and 10% of present anthropogenic CO_2 emissions for Western Europe (Frankignoulle et al. 1998).

The Scheldt estuary (Belgium and The Netherlands; Fig. 1) is one of the most nutrient-rich estuaries in Europe (Wollast 1988), as a result of urban waste water drainage and runoff from agriculture. Indeed, the Scheldt river, its tributaries and the estuary drain a highly populated and industrialized area and therefore are subject to strong anthropogenic disturbances. It is one of the most studied coastal systems in Western Europe, and although several biogeochemical models or budgets have been reported and provide estimates of its metabolic status (Soetaert and Herman 1995b; Hellings et al. 2001; Vanderborght et al. 2002), no direct measurements have been carried out in the past.

A wide range of techniques have been used to estimate the trophic status of coastal sites. Each of them relies on one or several assumptions and covers different spatial and temporal scales. For instance, metabolic processes rates measurements based on incubation methods (mainly O_2 and ^{14}C) or open water O_2 measurements (Odum 1956; Kemp and Boynton 1980;

Howarth et al. 1992; Caffrey 2004) have been used in numerous studies. Within the IGBP program, the Land Ocean Interaction in the Coastal Zone (LOICZ; Gordon et al. 1996) stoichiometric budgeting approach has been applied to more than 200 coastal sites. This latter approach presents the capacity (1) to provide system scale estimates and (2) to be easily implemented as it is based on usually well studied parameters. As recommended by Gordon et al. (1996), dissolved inorganic phosphorus (DIP) is the main parameter used to compute net ecosystem production rates using the LOICZ budgeting procedure. Nevertheless, in turbid estuaries, processes of adsorption and desorption to and from suspended particles and/or sediment (Froelich 1988) can introduce a biais in the calculations. The use of DIC to compute the NEP suffers from the difficulty to estimate the other processes, besides primary production and respiration, which are likely to have an impact on DIC in coastal systems, such as CO_2 fluxes at the air-sea interface and $CaCO_3$ precipitation and dissolution (Gordon et al. 1996).

In this paper, we report, compare and discuss the metabolic status of the Scheldt estuary based on in situ measurements collected from November 2002 to December 2003 and on the LOICZ budgeting procedure applied to both DIP and DIC.

Finally, consecutive to strong summer depletions of O_2 and the severe associated fish and invertebrates mortality at the end of the 1970's (Heip 1988), the construction of wastewater treatment plants was initiated in the drainage basin of the Scheldt estuary. This resulted in a significant improvement of water quality in the river, its tributaries and the estuary over the past 20 years (Billen et al. submitted; Soetaert et al. submitted). The results collected in 2003 are compared to previous estimates of biogeochemical processes and their control by these environmental changes is discussed.

Material and methods

Study area - The river Scheldt, with a catchment area of 19500 km^2 (Heip 1989), is the most important freshwater source. Tidal exchange is, on average, 200 times higher than the freshwater input (Wollast 1988) and consequently the freshwater residence time is long, from 70 d in the upstream part of the estuary to 10-15 d in the most seaward area (Soetaert and Herman 1995a). Salinity ranges from about 0.5 at Temse to about 28 at the mouth of the estuary (Fig. 1). Due to strong tidal currents (up to 1.5 m s^{-1}), the water column is well mixed throughout the estuary (Wollast 1988). Turbidity is high in the entire upper estuary and phytoplankton is light limited rather than nutrient limited (Van Spaendonk et al. 1993; Kromkamp and Peene 1995). Intensive bacterial growth has been estimated and is among the highest reported in the literature (Goosen et al. 1995) and fuelled mainly by external subsidies (Boschker et al., 2004). These high bacterial production rates coupled with the long freshwater residence time lead to O_2 depletion and a large efflux of CO_2 to the atmosphere in the upper and middle estuary (Frankignoulle et al. 1996; Frankignoulle et al. 1998).

Planktonic metabolism - Planktonic gross primary production (GPP), community respiration (CR) and nitrification were measured at five and six stations in November 2002 and April 2003, respectively (Fig. 1A and Table 1) and monthly from January to December 2003 at five fixed salinities (±1): 0, 2, 10, 18 and 25. Figure 1A shows the average position of the stations corresponding to each salinity from the monthly surveys. Surface water samples (at least 3 replicates) were incubated in a 5-compartment on-deck incubator for at least 6 h in transparent 60 ml biological oxygen demand (BOD) bottles. Samples were kept at in situ temperature by flowing water and irradiance was controlled in each compartment with filters of shading capacity of 0, 81, 87, 92 and 100%. In order to avoid sedimentation of particulate material in samples, bottles were fixed on a rotating device (1 rpm).

Concentrations of dissolved O_2 were measured before and after incubation using an automated Winkler titration technique with a potentiometric end-point detection. Analyses were performed with an Orion redox electrode (9778-SC) and a custom built titrator from November 2002 to June 2003 and with a Mettler Toledo DL50 titrator and a Pt redox electrode for the rest of the study period. Reagents and standardizations were similar to those described by Knap et al. (1996). The O_2 consumption due to CR and nitrification (both expressed as negative values) was partitioned by incubating samples, in the dark compartment, with and without addition of the nitrification inhibitors N-serve (Nitrapyrine; 5 mg l^{-1}) and chlorate (10 mmol l^{-1}). In each compartment, hourly net community production during daylight (NCP_d) was estimated by regressing O_2 against time. Hourly planktonic GPP rates for each irradiance were calculated as:

$$GPP = NCPd - (CR + nitrification) \qquad (1)$$

Light attenuation in the water column was measured using LI-COR LI-193SA Spherical Quantum Sensor which was connected to a LI-COR LI-1400 datalogger. Surface irradiance data were obtained from the Netherlands Institute of Ecology (Yerseke, The Netherlands) using a LI-COR LI-190SA quantum sensor coupled to a LI-COR LI-1000 data logger.

The relationship of Platt et al. (1980) was fitted on the GPP data collected at the five irradiance levels (GPP/I or PI curves). Because of the duration of the incubations (usually less than 10 h) and to correct for the daily variability of surface irradiance, hourly GPP rates were recalculated using a mean daily surface irradiance for each month.

Hourly rates of CR and nitrification were converted to daily rates assuming no variation during the 24 h. Hourly rates of GPP were multiplied by the average day length for each month to estimate daily rates. Daily NCP was then calculated as the sum of daily GPP, CR and nitrification. The volumetric rates of CR and nitrification in November 2002 and April 2003 were depth-integrated at each station assuming no vertical variation and using PI curves to integrate GPP rates over the euphotic zone (0.1% of the surface irradiance). The volumetric rates measured during the monthly surveys were depth-integrated using a bathymetric study of the estuary carried out with the Arcview 8.3 software package. The estuary was divided in five boxes corresponding to the sampled salinities and each metabolic parameter was integrated with regard to the depth gradient in each box.

These oxygen based values were converted into carbon units by using a photosynthetic quotient (PQ) of 1.3, a respiratory quotient (RQ) of 1 and a nitrification O_2:C ratio of -14. This latter conversion factor was estimated from simultaneous N-serve-sensitive ^{14}C bicarbonate nitrification measurements (N. Brion, unpublished data) on four occasions in 2003.

At 17 fixed stations (hereafter referred to monitoring stations; Fig. 1B), samples were taken for nutrient and pigments analysis. For pigments, water was filtered through GF/F filters which were stored frozen pending extraction and analysis by high-performance liquid chromatography (Barranguet et al. 1998). Automated colorimetric techniques, as described by

Strickland and Parsons (1972), were used to measure concentrations of dissolved inorganic phosphorus (DIP), nitrate + nitrite (NO_x), ammonium (NH_4) and silicates (Si). Hereafter, dissolved inorganic nitrogen (DIN) refers to the sum of NH_4 and NO_x.

Total alkalinity (TA) and pH were measured at each of the five incubation stations from January to May as well as at each of the 17 monitoring stations from June to December. TA was measured by Gran electro-titration on 50 ml GF/F filtered samples with a reproducibility of ± 2 µmol kg-1 and an estimated accuracy of ± 3 µmol kg-1. pH was measured using a combined electrode (Metrohm) with a reproducibility of ± 0.004 pH units. Frankignoulle and Borges (2001) provide details on the pH calibration procedure and on pCO_2 and DIC computation from the pH and TA measurements. During the November 2002 and April 2003 cruises, surface pCO_2 was measured continuously by equilibration as described by Frankignoulle and Borges (2001). Surface O_2 was also measured continuously with an Oxyguard polarographic electrode calibrated against discrete Winkler samples.

Benthic metabolism - Triplicate sediment cores (5 cm in diameter) were collected with a box corer at 8 stations along the estuary in November 2002 and April 2003 (Table 1). Sediment cores, from each sampling station, were incubated in the laboratory at in situ temperature under darkness for about 6 h. Before starting the incubations, the overlying water was removed and cores were filled with collected bottom water. Cores were closed with airtight lids and overlying water was stirred during the whole incubation period. Before and after incubation, water samples were collected with acid-washed syringes and O_2 concentrations were determined by the Winkler method using a Mettler titrator (DL21). Daily benthic CR was calculated with the same method as the one described above for the planktonic compartment.

LOICZ budgeting procedure - Biogeochemical modelling according to Gordon et al. (1996) was applied to the Scheldt estuary based on salinity, DIP, DIN, DIC and pCO_2 data obtained at each monitoring station (Fig. 1B) from June to December 2003. As the water is well-mixed along the estuary throughout the year, a 3 box-1 layer model was considered: the inner, middle and outer estuary (Fig. 1A and B). Monitoring stations located near the freshwater tidal zone and stations located in the river plume (Fig. 1B) were used as the riverine and marine end-members respectively. The river plume data of DIC, DIN and DIP were collected during 5 cruises from June to December 2003 (Carbon, nitrogen and phosphorus cycling in the North Sea, CANOPY project; N. Brion, unpublished data). DIC was computed from measurements of TA and pCO_2, measured as described above. Colorimetric techniques were used for NH_4 and DIP while NO_x was measured using an AutoAnalyser (Technicon; Strickland and Parsons 1972).

Freshwater flow was provided by the Ministerie van de Vlaamse Gemeenschap, Belgium. Soetaert et al. (submitted) estimated that 32% of the total freshwater flow to the Scheldt estuary comes from lateral sources (12% from the Gent-Terneuzen channel, 10% from the Antwerpen harbour and 10% from diffuse sources and small canals). Wind speed data at Hansweert and Hoofdplaat were provided by Hydro Meteo Centrum Zeeland (http://www.hmcz.nl/). Precipitation data at Vlissingen (near mouth of the estuary) and Stabroek (near Antwerp) were provided by the Royal Netherlands Meteorological Institute and the Belgian Royal Meteorological Institute, respectively. Data of DIN and DIP in the Gent-Terneuzen channel (station Zelzate; 51.2° N 3.82°E) as well as at several stations in the Antwerpen harbour were provided by the Flemish Environment Agency, Belgium (http://www.vmm.be). DIC concentrations at these stations were estimated using an empirical DIC vs. O_{2sat} relationship established during the study period in the Scheldt estuary:

$$DIC = -21\ O_{2sat} + 4738 \qquad (r^2 = 0.88;\ P < 0.001) \qquad (2)$$

where DIC is expressed in mmol m^{-3} and O_{2sat} is the oxygen saturation (%).
No data of DIP, DIN and DIC loadings from diffuse sources and small canals were available for the year 2003. Representing 10% of the total water input, this source of nutrient was neglected in the present budget.

The net ecosystem production (NEP; p-r in the LOICZ terminology) was calculated from the non-conservative fluxes of DIP in each box, assuming that these fluxes are only related to biological activity, following the equation:

$$NEP = -\Delta DIP \times (C:P)_{part} \qquad (3)$$

where NEP is expressed in mmol C m^{-2} d^{-1}, ΔDIP is the non-conservative flux of DIP (mmol P m^{-2} d^{-1}) and $(C:P)_{part}$ is the particulate C:P ratio (a value of 106:1 was used).

NEP was also computed from a DIC budget (Gordon et al. 1996). The total non-conservative flux of DIC (ΔDIC_t) is computed according to:

$$\Delta DIC_t = \Delta DIC_o + \Delta DIC_g + \Delta DIC_c \qquad (4)$$

where ΔDIC_o, ΔDIC_g and ΔDIC_c are variations of DIC related to organic matter production (included nitrification) and mineralization (ΔDIC_o equals -NEP), flux of CO_2 across the air-water interface and precipitation or dissolution of $CaCO_3$, respectively. No information on this latter process is available, to our knowledge, in the saline estuary. Nevertheless, Hellings *et al.* (1999).reported that, in two intertidal areas located in the freshwater tidal estuary, the contribution of calcite dissolution to the DIC pool was relatively small. Therefore, this process was assumed negligible in the present study.

The air-water CO_2 flux was computed according to:

$$F = \alpha\, k\, \Delta pCO_2 \qquad (5)$$

where F is the air-water CO_2 flux (mmol m^{-2} d^{-1}), α is the CO_2 solubility coefficient (mmol m^{-3} ppm^{-1}), k is the gas transfer velocity (m d^{-1}) and ΔpCO_2 is air-water gradient of CO_2 (pCO_{2water} - pCO_{2air}, in ppm). Then, as a convention, a positive flux corresponds to a transfer of CO_2 from the water to the atmosphere. Therefore, in equation (4), ΔDIC_g equals $-F$.

To compute ΔpCO_2, we used monthly values of atmospheric CO_2 molar fraction from Weather Station Mike (66.00°N 2.00°E), representative of the open North Sea waters (from the National Oceanic and Atmospheric Administration / Climate Monitoring and Diagnostics Laboratory air samples network, available from the internet at http://www.cmdl.noaa.gov/) to which was added a value of 27 ppm that corresponds to the average observed increase of the atmospheric signal in the Scheldt (Borges et al. 2004a). The CO_2 molar fraction values were converted to partial pressure values in wet air using the procedure described in DOE (1994).

k was computed according to a parametrization as a function of wind speed, water current and depth established from 295 floating chamber interfacial CO_2 flux measurements carried out during the November 2002 and April 2003 cruises (Borges et al. 2004b):

$$k_{600(B)} = 0.24 + 0.4126 w^{0.5} h^{-0.5} + 0.619\, u_{10} \qquad (6)$$

where $k_{600(B)}$ is the gas transfer velocity of CO_2 normalized to a Schmidt number (Sc) of 600 in m d^{-1}, w is the water current (cm s^{-1}), h is the depth (m) and u_{10} is the wind speed (m s^{-1}) referenced at a height of 10 m.

k was also estimated using *k*-wind parametrization based on the compilation of *k* measurements in various estuaries derived from the mass balance of naturally occurring and purposeful tracers (Raymond and Cole 2001):

$$k_{600(R\&C)} = 0.38 \exp(0.3\, u_{10}) \qquad (7)$$

Monthly averages of $k_{600(B)}$ and $k_{600(C\&R)}$ were computed from hourly wind speed measurements and modelled water currents (as described in Borges et al. 2004b) at three reference stations representative of the three boxes (Fig. 1B). The $k_{600(B)}$ and $k_{600(C\&R)}$ values converted to in situ temperature conditions assuming a k dependency proportional to $Sc^{-0.5}$. Sc was computed for a given salinity from the formulations for salinity 0 and 35 given by Wanninkhof (1992), and assuming that Sc varies linearly with salinity.

Budgets of DIN were also computed and the difference between DIN fixation and denitrification ($n_{fix-denit}$ in the LOICZ terminology) was calculated, assuming that this latter corresponds to the fraction of the non-conservative DIN flux which is not associated to production and consumption of organic matter, from the equation:

$$n_{fix-denit} = \Delta DIN - \Delta DIC_o \text{ x } (N:C)_{part} \quad (8)$$

where ΔDIN is the non-conservative flux of nitrogen in mmol N m^{-2} d^{-1}, ΔDIC_o is equal to –NEP (see above, mmol C m^{-2} d^{-1}) and $(N:C)_{part}$ is the particulate N:C ratio (a value of 16:106 was used).

Results

Partial pressure of CO_2 and O_2 saturation during the November 2002 and April 2003 cruises - pCO_2 and O_2 saturation values recorded during surveys aboard the *RV Belgica* are shown against salinity in Figure 2. Very high pCO_2 values were recorded in the inner part of the estuary during both cruises with maximal values of 7821 and 6729 ppm in November 2002 and April 2003 respectively. These high pCO_2 values are well correlated in the inner estuary with low O_2 saturation values (1 and 5% in November and April respectively). pCO_2 values were always above atmospheric equilibrium in November 2002, while in April 2003, CO_2 was under-satured in the river plume area (minimal pCO_2 value of 198 ppm). O_2 super-saturations were measured in this area during both cruises with highest values in April (110 and 122 % in November and April respectively). It must be noted that the O_2 saturation increased significantly in the outer estuary and adjacent plume area from the start to the end of the April cruise. In November, a higher variability was observed in the upper estuary both for O_2 and pCO_2, especially around salinity 4 where distinctly lower pCO_2 and higher O_2 values than the general trend along the salinity gradient were observed (arrows in Figure 2). These data were observed at low tide during a 24 h cycle carried out at fixed station close to the extensive Saeftinghe salt marshes (located between stations 6 and 7 in Fig. 1A).

Community metabolism during the November 2002 and April 2003 cruises - Higher planktonic GPP were measured in April than in November with values increasing seaward and a maximal rate in the plume area (83.9 mmol O_2 m^{-2} d^{-1}; Fig. 3). The lowest GPP were measured during both cruises in the turbid inner estuary with minimal rates around salinity 3. High rates of planktonic CR and nitrification were found in the inner part with maximal values in November at salinity 3 where planktonic nitrification consumed approximately the same amount of O_2 as planktonic CR (-273 vs. -323 mmol O_2 m^{-2} d^{-1}). The rates of nitrification strongly decreased seaward, during both cruises, to reach minimal values of -1.6 and -2.1 mmol O_2 m^{-2} d^{-1} in November 2002 and April 2003 respectively. Planktonic CR was higher in April than in November in the middle and marine parts of the estuary despite lower water column temperatures. It should be noted that significantly higher GPP as well as particulate and dissolved organic matter concentrations were measured in April (data not shown).

Benthic CR was significantly lower than planktonic CR, with a maximal rate (-53 mmol O_2 m^{-2} d^{-1}) in November and April at salinity 0.4 and 0.7 respectively. As for planktonic CR, benthic CR strongly decreased seaward during both cruises.

Planktonic metabolism over an annual cycle - pCO_2, along the estuary, was lowest in winter and increased until the end of summer to reach a maximal value of 7784 ppm at salinity 2 in September (Fig. 4A). pCO_2 was always highest at the freshwater station except in summer when values strongly decreased to reach a minimal value in August (4781 ppm). Values were always above atmospheric equilibrium except in May at salinity 18.

O_2 saturation was higher in winter than in spring-summer, especially in the brackish part (salinity 2; Fig. 4B). The lowest O_2 saturations were measured, almost throughout the year, at salinity 2 than in the freshwater part. In summer, as noted for pCO_2, a strong increase of O_2 saturation was observed in the freshwater area. O_2 super-saturations were only measured in the marine part of the estuary (salinity 18) in May.

Since no sampling for nutrient and pigments concentrations were carried out at the freshwater incubated station (salinity 0), freshwater concentrations presented in the following section were collected at the less saline station during each monitoring survey (salinity between 0 and 1). Higher nutrient concentrations were measured in the freshwater part, dilution with low nutrient marine waters being observed seaward (Fig. 5). A large peak of NH_4 was observed in May at salinity 0 (308 mmol N m^{-3}; Fig. 5A). NH_4 concentration was highest in spring in the brackish part then decreased to reach minimal values in summer. Seaward, the highest concentrations were measured in winter, then concentrations decreased in early spring and were almost constant throughout the rest of the year. NO_x concentration was also highest in the freshwater and brackish parts with maximal values in winter (458 mmol N m^{-3} at salinity 0 in December; Fig. 5B) and minimal ones in summer (261 mmol N m^{-3} at salinity 2 in July). As for NH_4, seasonal changes were less marked in the mesohaline and marine parts of the estuary. DIP concentration was highest in the freshwater part during most of the year and decreased seaward (Fig. 5C). The seasonal cycle exhibited minimal values in winter - spring and maximal ones in summer - fall. As for the other nutrients, Si concentration was generally higher in the freshwater and brackish parts, except in August when it dropped to very low values (8.5 mmol Si m^{-3} in August at salinity 2; Fig. 5D).

The highest concentrations of chlorophyll *a* (chl *a*) were found in the freshwater area with maximal values in summer-fall (maximum in October: 110 mg m^{-3}; Fig. 6A). In the brackish part, a small peak was observed in June (30 mg m^{-3}) followed by a larger peak in September (73 mg m^{-3}). In the mesohaline and marine parts, a unique peak was observed in May (maximum: 30 mg m^{-3} at salinity 18). High concentrations of phaeopigments were measured in spring in the freshwater area (maximum: 51 mg m^{-3} in May; Fig. 6B), then values decreased in summer. In the brackish part, a peak was observed in May and highest concentrations were measured in late summer. Low phaeopigments concentrations were measured throughout the year in the mesohaline and marine part.

Integrated planktonic GPP, CR and nitrification rates are presented Figure 7. Planktonic GPP was high in the freshwater area in summer with a maximal value of 272 mmol C m^{-2} d^{-1} in August (Fig. 7A). Two peaks were observed in the brackish area (salinity 2): in June (50 mmol C m^{-2} d^{-1}) and August (102 mmol C m^{-2} d^{-1}). Seaward, the highest rates were observed in May and July at salinity 18 and 25 respectively. Averaged over the duration of the study (± SD), planktonic GPP rates were 92 (± 111), 25 (± 31), 17 (± 20), 30 (± 39) and 34 (± 41) mmol C m^{-2} d^{-1} at salinity 0, 2, 10, 18 and 25 respectively. Nitrification was always highest in the brackish part with a maximal value of 20 mmol C m^{-2} d^{-1} in May (Fig. 7B) and was related to high NH_4 concentrations (Fig. 5) in the freshwater area. A second peak was observed in October although no increase in NH_4 was observed at this time. Low nitrification activities were observed seaward with a minimal value in October at salinity 18 (0.2 mmol C m^{-2} d^{-1}). On average, annual nitrification represented 5, 31, 10, 4 and 3% of total organic production at salinity 0, 2, 10, 18 and 25. Planktonic CR was high especially in the freshwater and brackish parts (Fig. 7C). Maximal values were observed in May and October, well related to high phaeopigments (Fig. 6) and total organic carbon concentrations (data not shown). The highest rate was measured in October at salinity 2 (-313 mmol C m^{-2} d^{-1}). Planktonic NCP was negative during most of the year with lowest values in the brackish part (minimum in October: -300 mmol C m^{-2} d^{-1}; Fig. 7D). Positive NCP values were recorded in summer in the freshwater area (maximum in August; 165 mmol C m^{-2} d^{-1}). Seaward, positive NCP were also measured in April, July and August.

Whole system metabolism - Characteristics of the modelled boxes (surface area, mean depth and volume) as well as mean salinity, pCO2 and DIP, DIN, DIC concentrations are presented in Table 2. The whole estuary acts as a net source of DIP (0.16 mmol P m^{-2} d^{-1} or 462 tP yr^{-1}; Table

3) and as a net sink of DIN (3.3 mmol N m-2 d-1 or 4420 tN yr^{-1}). Almost 7.5 mmol C m^{-2} d^{-1} or 8530 tC yr^{-1} of DIC are also lost in the Scheldt estuary. NEP was estimated using three different approaches: LOICZ budgets based on DIP, DIC and in situ measurements.

NEP computations based on DIP budgets lead to an integrated negative NEP of -17 mmol C m^{-2} d^{-1}. It should be noted that these DIP budgets revealed an autotrophic status in the inner part with a NEP of 1 mmol C m^{-2} d^{-1}.

NEP computations based on DIC budgets lead to integrated negative NEP of respectively -52 and -132 mmol C m^{-2} d^{-1}, using the parametrizations of Raymond and Cole (2001) and Borges et al. (2004b) to estimate CO_2 fluxes across the air-water interface. CO_2 release to the atmosphere of 60 and 140 mmol C m^{-2} d^{-1} (68000 vs. 158000 tC yr-1) were estimated using these two formulations respectively.

NEP based on in situ incubations was estimated using planktonic metabolism results detailed in the previous section and published benthic metabolic rates (Middelburg et al. 1996; Barranguet et al. 1998). From June to December, our results suggested that the planktonic compartment was strongly heterotrophic with values of -103, -14 and -18 mmol C m^{-2} d^{-1} in the inner, middle and outer estuary respectively. Planktonic GPP, CR and nitrification rates in the inner area were estimated by averaging results obtained at salinities 2 and 10, in the middle and outer areas by using results obtained at salinity 18 and 25 respectively. Benthic CR estimated by Middelburg et al. (1996) at six intertidal stations in the area considered in the present study and based on CO_2 and CH_4 fluxes were used to estimate the rate of benthic mineralization in each box. Data of benthic CR collected during the November 2002 and April 2003 cruises (see above) showed that benthic CR at subtidal stations were almost 10-fold lower than planktonic CR, therefore we assumed that benthic mineralization only occurs on intertidal flats. The percentage of area covered by these flats was estimated by a bathymetry study in each box (40, 23 and 17% in the inner, middle and outer box respectively). Multiplying intertidal benthic CR rates measured by Middelburg et al. (1996) by the intertidal flats surface area leads to a benthic CR of -30, -16 and -12 mmol C m-2 d-1 in the inner, middle and outer estuary respectively. The same procedure was applied for benthic GPP estimated by Barranguet et al. (1998). Summing all these metabolic parameters leads to an estimation of the NEP in the estuary from June to December of -44 mmol C m-2 d-1.

Nfix-denit values of -20, -10 and -8 mmol N m^{-2} d^{-1} were calculated in the inner, middle and outer estuary respectively. These values were computed using NEP estimates based on Raymond and Cole (2001) formulation.

Discussion

Surface water pCO_2 did not change significantly since the period 1993-1996 (Frankignoulle et al. 1998). In 2003, pCO_2 ranged from 349 (May, outer estuary) to more than 10,000 ppm (or more than 25 times the atmospheric value; June, salinity 0). pCO_2 was generally higher in the freshwater part and decreased along the salinity gradient due to dilution with low pCO_2 marine waters and degassing at the air-water interface. O_2 concentrations did not follow a similar pattern as lower values were generally found in the inner estuary than in the freshwater zone. This discrepancy between pCO_2 and O_2 can be attributed to high nitrification rates found in the inner estuary as this process consumes more O_2 than it produces CO_2. Although O_2 conditions improved in the Scheldt estuary since the 1970's (Soetaert et al. submitted) due to a decrease of nitrification (see below), O_2 saturation was below 15% from May to November 2003 in the brackish part.

The O_2 and pCO_2 variability observed in November 2002 during a 24 h cycle near the extensive Saeftinghe salt marshes suggests than benthic processes on the salt marshes lead at high tide to a decrease of pCO_2 and an increase of O_2 due to net oxygen production, carbon fixation and enhanced air-sea water exchange. At low tide this water mass enriched in O_2 and impoverished in CO_2 mixes with the adjacent water of the channel, which explains the deviations observed from the general trends along the salinity gradient (Fig. 2). However, this is probably a transient feature that rapidly fades due to mixing since it has never been observed before from an available large data-set (31 cruises carried out from 1993 to 2000; Frankignoulle et al. 1996; Frankignoulle et al. 1998; Frankignoulle and Borges 2001; Borges et al. 2004a; Borges et al. 2004b; Boschker et al. in press).

Planktonic GPP rates measured in the present study are close to previous rates estimated in the 1990's by Kromkamp and Peene (1995) in the salinity mixing zone and by Muylaert (1999) in the tidal river (Fig. 8), showing no clear evolution over this time period. High rates were observed in the freshwater area (92 mmol C m^{-2} d^{-1}), decreasing towards the brackish part of the estuary (17-25 mmol C m^{-2} d^{-1}) to rise again towards the marine area (30-34 mmol C m^{-2} d^{-1}). As mentioned by van Spaendonk et al. (1993) and Kromkamp et al. (1995), nutrient concentrations in the Scheldt are high enough not to limit phytoplankton growth, although a significant decrease of silicates was observed in the freshwater and brackish parts in August and in the marine part in May coinciding with high GPP rates. In the freshwater and inner part of the estuary, GPP was highest in summer when irradiance and water temperature were also highest. Chl *a* and phaeopigments data showed that high loads of riverine phytoplankton were imported from March to May and degraded in the upper estuary when salinity increases. In summer, high chl *a* concentrations were still observed but phaeopigments concentrations dropped to low values indicating a much more active phytoplanktonic community in agreement with higher GPP. This is consistent with the findings of Muylaert et al. (2000) who studied the distribution and dynamics of phytoplankton communities in the inner and freshwater parts of the Scheldt estuary and found that salinity, irradiance and temperature were the main driving forces. Planktonic GPP rates measured in this estuary are in the range of published estuarine rates reviewed by Heip et al. (1995) and Gazeau et al. (2004) for European estuaries.

Planktonic CR rates were generally highest in the brackish area with maximal rates observed in May and October (-258 and -313 mmol C m^{-2} d^{-1}). These high rates are related to enhanced total organic carbon inputs during these 2 months (data not shown). Freshwater flow alone cannot explain these elevated organic matter loads, but daily precipitation data at Vlissingen (51.27 °N; 3.36 °E) and at Stabroek (51.19 °N; 4.21 °E) reveal that highest precipitations occurred in May and October (data not shown). Therefore, these peaks of planktonic CR might be explained by an increase of lateral organic matter inputs by water runoff inside the estuary and show that planktonic CR in the Scheldt estuary is mainly driven by inputs of allochtonous organic matter rather than by local production, consistent with the compound specific isotope data evidence presented by Boschker et al. (in press).

Hopkinson and Smith (in press) reviewed planktonic and benthic CR rates in 22 estuaries around the world and report planktonic CR between -1.7 in the Gulf of Finland to -84 mmol C m^{-3} d^{-1} in the Fly River delta with a arithmetic mean value of -17.8 mmol C m^{-3} d^{-1}. In the Scheldt estuary, we measured annually averaged planktonic CR rates ranging from -4.7 in the outer estuary to -19.1 mmol C m^{-3} d^{-1} in the inner part with a mean value in the whole estuary of -6.6 mmol C m^{-3} d^{-1}. This mean rate is close to the ones measured by Witek et al. (1999) in the Gulf of Gdánsk and Rudek and Cloern (1996) in San Francisco Bay.

Nitrification is maximal in the brackish part of the estuary and represents more than 30% of the total organic matter production in this area. In 1997-1998, de Bie et al. (2002) reported a mean rate over the whole estuary of 1.1 (range: 0 to 7.5) mmol C m^{-3} d^{-1} while we estimated a rate of 0.5 (range: 0 to 2.2) mmol C m^{-3} d^{-1}. Over the same time period, NH_4 concentrations in the estuary decreased from 90 to 60 mmol N m^{-3}. Therefore, it seems that the decrease in NH_4 loading in the Scheldt estuary induced a significant decrease of nitrification and led to improved O_2 conditions as reported by Soetaert et al. (submitted). Nevertheless, rates of nitrification measured in the Scheldt estuary in 2003 are still higher than or similar to the ones reported by Owens (1986) in the Tamar estuary (max: 0.8 mmol C m^{-3} d^{-1}), Berounsky and Nixon (1993) in Narragansett Bay (0 to 1.9 mmol C m^{-3} d^{-1}) and Brion et al. (2000) in the Seine river estuary (0.2 to 1.9 mmol C m^{-3} d^{-1}).

We report the first measurements of planktonic NCP in the Scheldt estuary which was only estimated through modelling by Soetaert and Herman (1995b). Rates measured along the salinity gradient in 2003 follow the same trend but measured data are significantly higher than those estimated by these authors (Fig. 8). Their model was calibrated on data gathered in the period 1980-1985 but it is difficult to conclude whether this difference results from an increase of the planktonic NCP over 20 years or from differences in methodology.

Estimates of NEP in the Scheldt estuary from June to December 2003 based on the LOICZ modelling procedure applied to DIC and using the parametrization of Raymond and Cole (2001) to estimate air-sea CO_2 fluxes, are consistent with in situ direct measurements for the same period (-52 vs. -44 mmol C m^{-2} d^{-1}). CO_2 fluxes over the investigated time-period were estimated using this relationship to 149, 56 and 20 mmol C m^{-2} d^{-1} in the inner, middle and outer area respectively. Hellings et al. (2001), in their DIC budget, estimated CO_2 fluxes in the inner area using the parametrization of Wanninkhof (1992) to compute *k* values from wind speed data and found an annual CO_2 efflux significantly lower than the one reported in the present study using the parametrization of Raymond and Cole (2001): 71 vs.149 mmol C m^{-2} d^{-1}. Moreover, these authors estimated the NEP in this zone to -73 mmol C m^{-2} d^{-1}, a value significantly higher than the one calculated in this study. Integrated over the entire estuary, a CO_2 flux to the atmosphere of 186 tC d^{-1} is estimated, lower than the estimate of 456 tC d^{-1} given by Frankignoulle et al. (1998). Vanderborght et al. (2002) estimated a CO_2 flux to the atmosphere for July 1996 of 225 tC d^{-1} using the coupled, networked, transport-reaction algorithm for strong tidal estuaries (CONTRASTE) model. This value is close to the one estimated in the present study for July 2003 (214 tC d^{-1}).

As mentioned above, NEP estimates based on the LOICZ budgeting procedure applied to DIC using the gas transfer velocity parametrization of Raymond and Cole (2001) is consistent with the NEP estimated from incubations while the use of Borges et al. (2004b) parametrization leads to a lower estimate. However, it does not allow to conclude on the validity of these parametrizations of the gas transfer velocity. Indeed, an error analysis on the NEP estimate associated to the computations of CO_2 fluxes was carried out assuming reasonable experimental errors on ΔpCO_2 and k_{600} of, respectively, ± 3% and ± 5 cm h^{-1}. The overall resulting error on NEP is ± 165, ± 33 and ± 12 mmol C m^{-2} d^{-1} for, respectively, the upper, middle and lower estuary. The error estimate on NEP is, as expected, strongly dependent on the spatial variations of ΔpCO_2. Thus, the lower bound of the NEP estimate based on the DIC budget using the Raymond and Cole (2001) parametrization (-103 mmol C m^{-2} d^{-1}) overlaps the higher bound of NEP estimate based on the DIC budget using the Borges et al. (2004b) parametrization (-71 mmol C m^{-2} d^{-1}). It is also possible that both DIC budgets underestimate the NEP. Some DIC input terms have been neglected or under-estimated. For instance, the lateral sources of DIC could be underestimated since they were computed from a relationship between O_2 and DIC established in the main channel of the estuary. Also, DIC diffuse inputs were not accounted for in the budget although diffusive inputs of total organic carbon had a major influence on metabolic processes in May and October during precipitation periods (see above). Finally, $CaCO_3$ dissolution was neglected in the budget, since to our best knowledge this process has not been quantified in the mixing region of the Scheldt, and we cannot exclude the possibility that this process could be significant. If both DIC budgest underestimate the NEP, the NEP value derived using the Borges et al. (2004b) gas transfer velocity parametrization could be consistent with the value from incubation measurements.

The annual NEP estimated in the Scheldt estuary by means of compiled in situ measurements (-42 mmol C m^{-2} d^{-1}) is in the lower range of previously reported LOICZ based rates with “Steve Smith’s ranking ≥ 2” (-42 and 32 mmol C m^{-2} d^{-1}; downloaded on 20 May 2004 from the LOICZ environmental database http://hercules.kgs.ukans.edu/hexacoral/envirodata/main.htm).

In a recent paper, Caffrey (2004) reported annual NEP estimates based on the in situ diel O_2 method for 42 estuarine sites in the US. All sites are heterotrophic in term of carbon with NEP ranging from -11 to -278 mmol C m^{-2} d^{-1} and a mean value of -110 ± 66 mmol C m^{-2} d^{-1}, lower than the one estimated in this study. It must be stressed that the in situ diel O_2 method does not take into account the O_2 consumption due to the nitrification process, which is likely to be an important process in estuarine systems, and can therefore underestimate NEP rates. The in situ diel O_2 method is also highly sensitive to the estimation of the exchange of O_2 across the air-water surface. This is particularly critical in estuaries where a simple parametrization of the gas transfer velocity as a function of wind speed has been shown to be site specific (Kremer et al. 2003; Borges et al. 2004a).

The LOICZ modelling procedure applied to DIP concentrations leads to a significant overestimation of NEP especially in the inner part of the estuary. It should be stressed that this method assumes that all non-conservative fluxes of DIP can be attributed to net uptake into organic matter during primary production or release from organic matter by respiration. The primary shortcoming of this method is that systems with high amounts of suspended mineral material may show evidence for DIP adsorption onto particulate materials or desorption from them (2001). High suspended matter concentrations are encountered in the inner Scheldt estuary (average over the investigated period: 74 ± 55 g m^{-3}) and processes of DIP sorption on these particles are likely (Zwolsman 1994). As the same procedure applied to DIC gave results very consistent with in situ measurements (see hereafter), we attributed the difference to DIP particle exchange processes and estimated the rate of net DIP sorption in the inner, middle and outer estuary to 1.3, 0.2 and 0.1 mmol P m^{-2} d^{-1}. Therefore, more than 50% of the non-conservative DIP flux in the inner area can be attributed to this net adsorption process. Unfortunately, no such estimates were found in the literature for comparative purposes.

Finally, the LOICZ approach applied to DIN from June to December 2003 provided an estimation of $n_{fix-denit}$ of -20, -10 and -8 mmol N m^{-2} d^{-1} in the inner, middle and outer estuary respectively, for a mean value in the whole estuary of -11 mmol N m^{-2} d^{-1} and, as NEP, far below the range (-5.2 to 2.6 mmol N m^{-2} d^{-1}) reported in the LOICZ environmental database. Assuming no N_2 fixation in this highly eutrophied estuary, a denitrification rate of -11 mmol N m^{-2} d^{-1} or -14900 tN yr^{-1} is estimated, lower than the rate reported by Billen et al. (1985) for the 1970’s (-20000 tN yr^{-1}) but consistent with the one provided by Soetaert and Herman (1995c) for the 1980’s (-15000 tN yr^{-1}). As mentioned by Soetaert et al. (submitted), it seems therefore that denitrification decreased from the 1970's to the 1980's in response to improved aeration, and decrease of NH_4 loadings and nitrification rates. Our results suggest that denitrification did not decrease significantly since the 1980's. Middelburg et al. (1995) reported denitrification rates on an intertidal flat in the Scheldt (station Doel) and found an annual average of -1.7 mmol N m^{-2} d^{-1}

for 1991. This is almost one order of magnitude lower than the rate estimated in this study for both the planktonic and benthic compartments. Since, according to Soetaert et al. (submitted), there is no evidence of water column denitrification since the beginning of the 1990's although DIN removal significantly increased during the last ten years, it is suggested that benthic denitrification increased significantly between 1991 and 2003. This may explain the discrepancy between our results and those of Middelburg et al. (1995) measured in 1991.

Finally, DIC, DIN and DIP inputs from lateral sources represented 18, 33 and 35% of the total inputs in the estuary. Inputs from diffuse sources as well as from small canals were not integrated in our models. Although representing only 10% of the total freshwater input in the estuary (Soetaert et al. submitted), this may have introduce a bias in the budgets output. We already discussed the limitation of the LOICZ budgeting procedure applied to DIP in this turbid estuary as well as the sensitivity to the parametrization of the gas transfer velocity when applied to DIC, it should be also mentioned that this procedure requires a perfect knowledge on the numerous potential sources of nutrients which are not always easy to sample.

This study confirmed that, due to high inputs of allochtonous organic matter, residence time and turbidity, the Scheldt estuary is a strongly heterotrophic system. Phytoplankton production is not nutrient-limited. Despite a significant decrease of nutrient inputs over the last decade, GPP values estimated in 2003 are very similar along the salinity gradient to rates measured in the 1990's. In contrast, a significant decrease of nitrification was observed in the past 6 years and is correlated with a decrease of the ammonium loading. Nevertheless, this process is still important and represents more than 30% around the maximum turbidity zone. As no previous direct CR or NEP estimates are available to compare with, no conclusion on the evolution of these parameters can be drawn.

Several approaches were tested to estimate the NEP in this estuary. We showed that the LOICZ method based on non-conservative DIP fluxes cannot be applied in this turbid system, as abiotic processes such as sorption and desorption from and to suspended particles and/or sediment can have a strong impact on these fluxes. The LOICZ method based on DIC using the parametrization of the gas transfer velocity of Raymond and Cole (2001) yielded NEP estimates consistent with estimates from incubations. Nevertheless, the present study also highlights that this method was subject to a relatively large uncertainty mainly related to the errors associated to the CO_2 fluxes estimates as well as the unknown influence of $CaCO_3$ on the carbon cycle in this system. Finally, the LOICZ approach applied to DIN suggests that the denitrification process did not change significantly since the 1980's despite a strong improvement of O_2 conditions in the estuary

Table 1. Sampling stations location and characteristics during the November 2002 and April 2003 cruises.

Cruise	Station number	Station name	Benthic/Planktonic	Lat (°N)	Long (°E)	Bottom depth (m)	Salinity	Temperature (°C)
November 2002	1	Oostende	Both	51.25	2.85	11	34	12.5
“	2	Vlissingen	Benthic	51.40	3.60	17.9	27.6	11
“	3	Terneuzen	Benthic	51.35	3.81	15.5	23.1	11
“	5	Hansweert	Both	51.41	4.04	16.6	19.7	11
“	7	Prosperpolder	Both	51.39	4.21	15.5	5.9	11.7
“	8	Doel	Benthic	51.35	4.25	14.4	4.9	12.4
“	10	Antwerpen	Both	51.23	4.40	14.8	1.9	12.2
“	11	Ruppel	Both	51.13	4.31	14.9	0.5	12
April 2003	1	Oostende	Both	51.23	2.84	11.6	30.3	7.8
“	2	Vlissingen	Benthic	51.40	3.60	22.4	25.40	7.7
“	3	Terneuzen	Benthic	51.35	3.81	11.5	20.55	8.2
“	4	Hoek van Ossenise	Planktonic	51.38	3.93	17	20.88	8
“	5	Hansweert	Benthic	51.41	4.04	15.3	18.43	8.1
“	6	Overloop	Planktonic	51.37	4.09	16.5	12.92	8.7
“	7	Prosperpolder	Benthic	51.39	4.21	14.2	12.00	9.3
“	8	Doel	Both	51.35	4.25	16.3	7.5	10.3
“	9	Oesterweel	Planktonic	51.24	4.37	14.6	2.88	10.8
“	10	Antwerpen	Benthic	51.23	4.40	12.5	2.28	10.7
“	11	Ruppel	Both	51.12	4.30	15.1	1	11.1

Table 2. Surface area, mean depth and volume of each estuarine box budgeted using the LOICZ procedure (in bold). Salinity and other environmental parameters in each budgeted box (in bold) as well as for the lateral inputs and in the freshwater and river plume areas. DIP, DIN, DIC and pCO_2 are respectively dissolved inorganic phosphorus, dissolved inorganic nitrogen, dissolved inorganic carbon and partial pressure of CO_2. Each value is an average of several stations (Fig. 1B) from June to December 2003 and numbers in parenthesis refer to the associated standard deviation (± SD).

Compartment	Freshwater flow (m^3 d^{-1})	Area (km^2)	Mean depth (m)	Volume (km^3)	Sal	DIP (mmol m^{-3})	DIN (mmol m^{-3})	DIC (mmol m^{-3})	pCO_2 (ppm)
River	5.62×10^6	-	-	-	1.1 ± 0.5	7.18 ± 0.51	397 ± 79	4670 ± 115	6185 ± 501
Gent-terneuzen channel	9.9×10^5	-	-	-	14	17.10	535	3314	-
Antwerpen harbour	8.26×10^5	-	-	-	4	5.58	295	3030	-
Inner		**54**	**8.8**	**475**	**7.9 ± 2.1**	**6.37 ± 0.60**	**298 ± 64**	**3898 ± 113**	**3850 ± 690**
Middle		**93**	**9.5**	**884**	**20.9 ± 2**	**5.24 ± 0.59**	**136 ± 21**	**3039 ± 97**	**1137 ± 319**
Outer		**113**	**12.9**	**1455**	**28.6 ± 1.1**	**2.88 ± 0.59**	**55 ± 10**	**2550 ± 73**	**682 ± 176**
River plume		-	-		32.3 ± 0.5	1.43 ± 0.33	19 ± 16	2333 ± 181	570 ± 136
Whole estuary		**260**	**9.7**	**2814**	-	**4.21 ± 1.6**	**121 ± 110**	**2931 ± 578**	**1360 ± 1496**

Table 3. Budgeting of nutrient fluxes, air-se CO_2 fluxes and net ecosystem production (NEP) of the Scheldt estuary for the period June to December 2003 using the LOICZ budgeting approach. ΔDIP, ΔDIN and ΔDIC (mmol m^{-2} d^{-1}) are the non-conservative fluxes of dissolved inorganic phosphorus, nitrogen and carbon. $F_{(B)}$ and $F_{(R\&C)}$ are the CO_2 fluxes (mmol C m^{-2} d^{-1}) at the air-water interface computed using the parametrization of the gas transfer coefficient of Borges et al. (2004b) and Raymond and Cole (2001), respectively. NEP (mmol C m^{-2} d^{-1}) was estimated from ΔDIP (NEP DIP), ΔDIC using $F_{(B)}$ and $F_{(R\&C)}$ (NEP $DIC_{(B)}$ and NEP $DIC_{(R\&C)}$ respectively), and direct processes measurements (NEP in situ). The difference between DIN fixation and denitrification ($n_{fix-denit}$; mmol N m^{-2} d^{-1}) was computed using NEP estimates based on the Raymond and Cole (2001) formulation.

Compartment	ΔDIP	ΔDIN	$ΔDIC_t$	$F_{(B)}$	$F_{(R\&C)}$	NEP DIP	NEP $DIC_{(B)}$	NEP $DIC_{(R\&C)}$	NEP in situ	$n_{fix-denit}$
Inner	-0.01	-0.8	-23	412	149	1	-396	-126	-121	-20
Middle	0.30	-2.4	-4	106	56	-31	-102	-53	-23	-10
Outer	0.12	-5.3	-4	38	20	-13	-31	-17	-24	-8
Whole estuary	**0.16**	**-3.3**	**-7.5**	**140**	**60**	**-17**	**-132**	**-52**	**-44**	**-11**

Figure captions

Fig. 1. A) Map of the Scheldt estuary showing the position of the stations where planktonic and benthic oxygen incubations were performed during the November 2002 and April 2003 cruises as well as the average position of each fixed salinity station during the annual study. B) Map of the Scheldt estuary showing the location of the monitoring stations as well as the river plume stations used in the LOICZ budgets. The location of the three meteorological stations from where wind speed measurements were obtained are also shown.

Fig. 2. A) Surface partial pressure of CO_2 and B) oxygen saturation along the salinity gradient during the November 2002 and April 2003 cruises. Solid lines correspond the atmospheric equilibrium.

Fig. 3. Metabolic performances measured in the Scheldt estuary during the November 2002 and April 2003 cruises, respectively. Planktonic gross primary production (GPP), community respiration (CR) and nitrification in A) November 2002 and B) April 2003. C) Benthic community respiration (CR) in subtidal stations during the same cruises. All rates are expressed in mmol O_2 m^{-2} d^{-1}.

Fig. 4. A) Surface partial pressure of CO_2 and B) oxygen saturation from January to December 2003 at fixed salinities (± 1) in the Scheldt estuary. Solid lines correspond the atmospheric equilibrium.

Fig. 5. Nutrient concentrations in surface waters from January to December 2003 at fixed salinities (± 1) in the Scheldt estuary. A) Ammonium (NH_4), B) Nitrate + Nitrite (NO_x), C) Orthophosphate (DIP) and D) Silicate (Si).

Fig. 6. A) Chlorophyll *a* (Chl *a*) and B) phaeopigments concentrations in surface waters from January to December 2003 at fixed salinities (± 1).

Fig. 7. Metabolic performances from January to December 2003 at fixed salinities (± 1) in the Scheldt estuary. D) Planktonic net community production (NCP) is the sum of A) phytoplankton gross primary production (GPP), B) nitrification and C) community respiration (CR). All rates are expressed in mmol C m^{-2} d^{-1}.

Fig. 8. Upper plot: comparison of annual phytoplankton gross primary production (GPP) rates measured in the Scheldt estuary in 2003 (black triangles) with previous measurements (Kromkamp and Peene 1995, open triangles, and Muylaert 1999 in the tidal river, open diamond). Lower plot: Comparison of annual planktonic net community production (NCP) rates measured during this study (full circles) with

the model-outputs of Soetaert and Herman (1995a; open circles). All rates are expressed in mmol C m^{-2} d^{-1}.

Fig 1 – Gazeau et al.

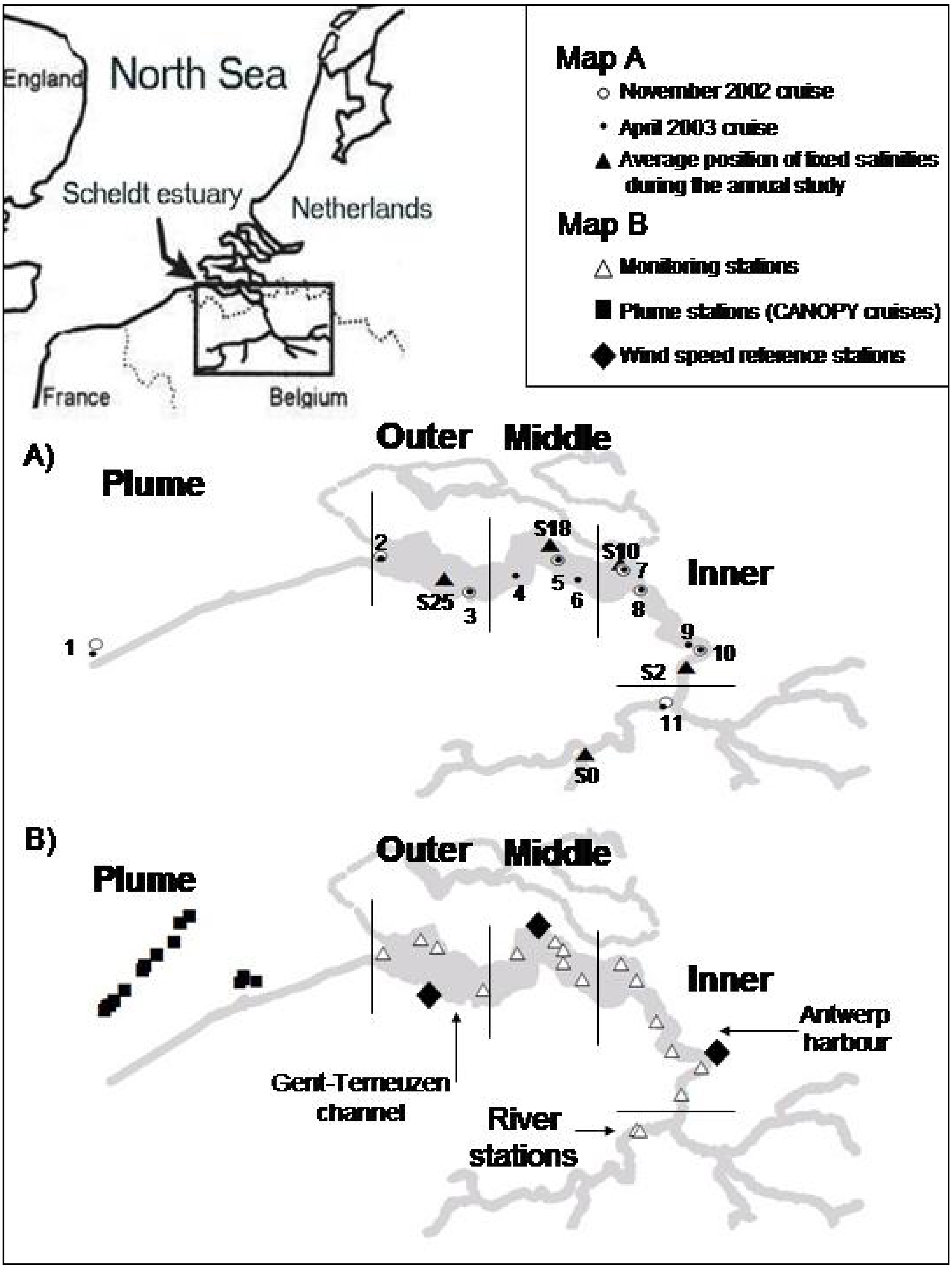


Fig 2 – Gazeau et al.

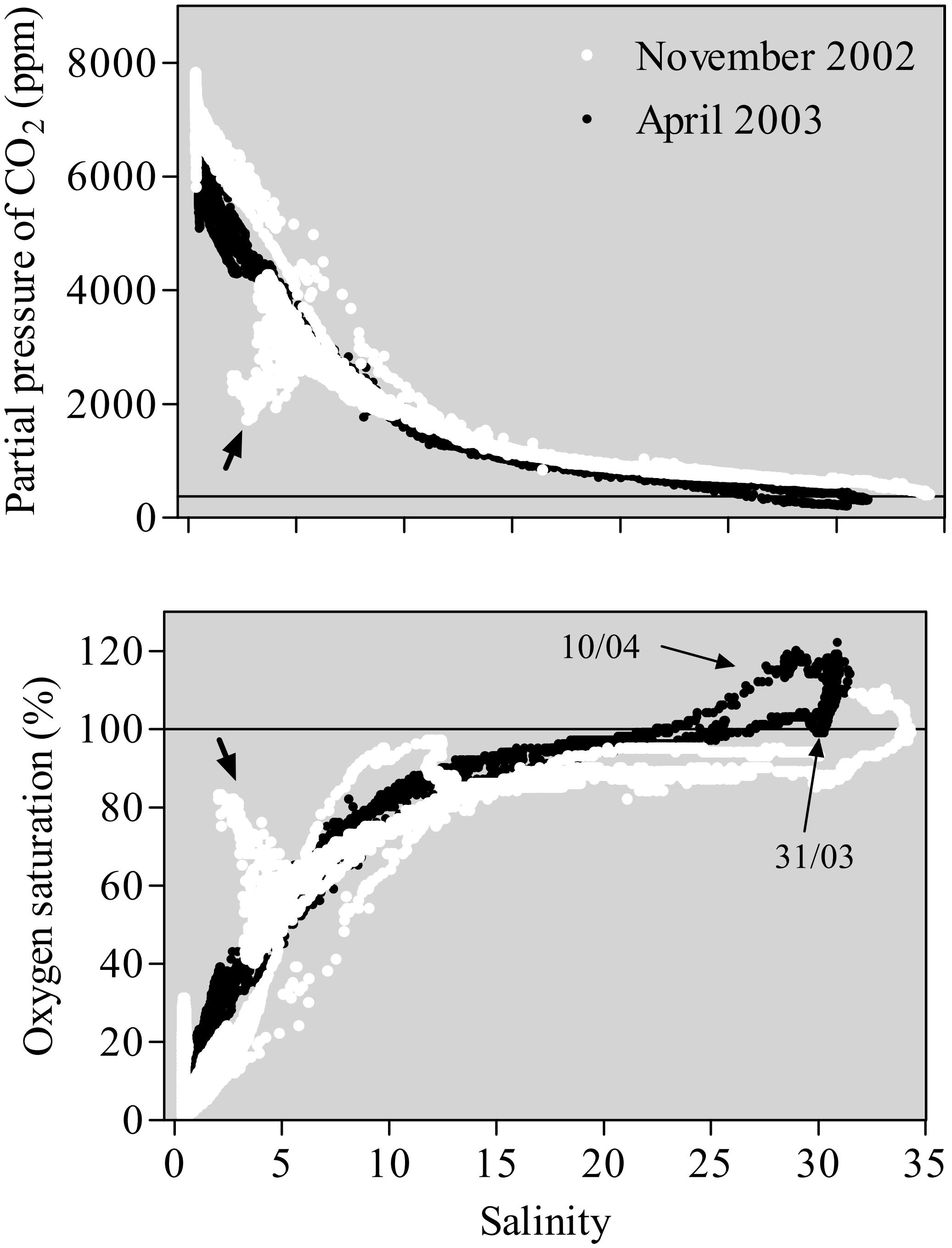


Fig 3 – Gazeau et al.

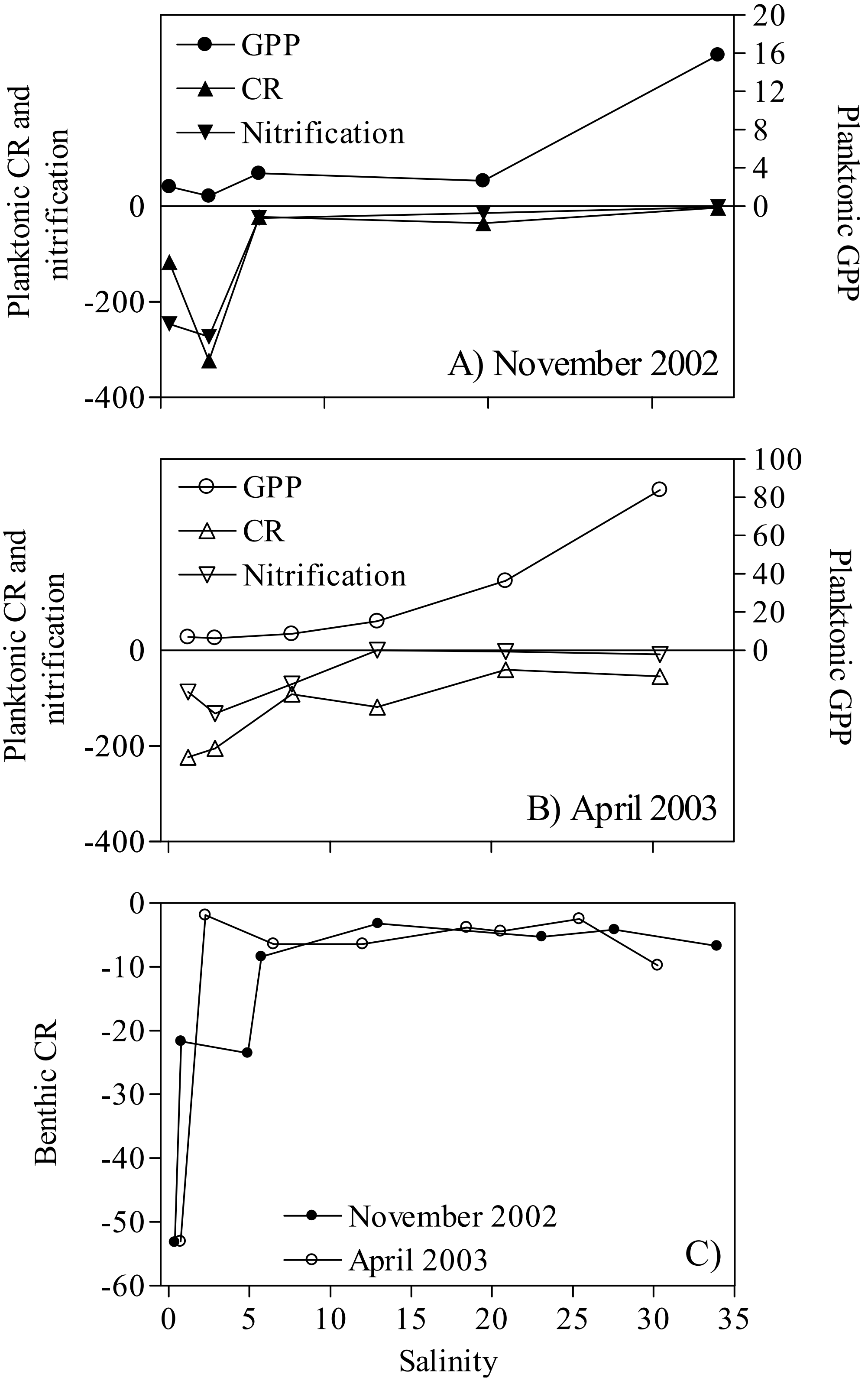


Fig 4 – Gazeau et al.

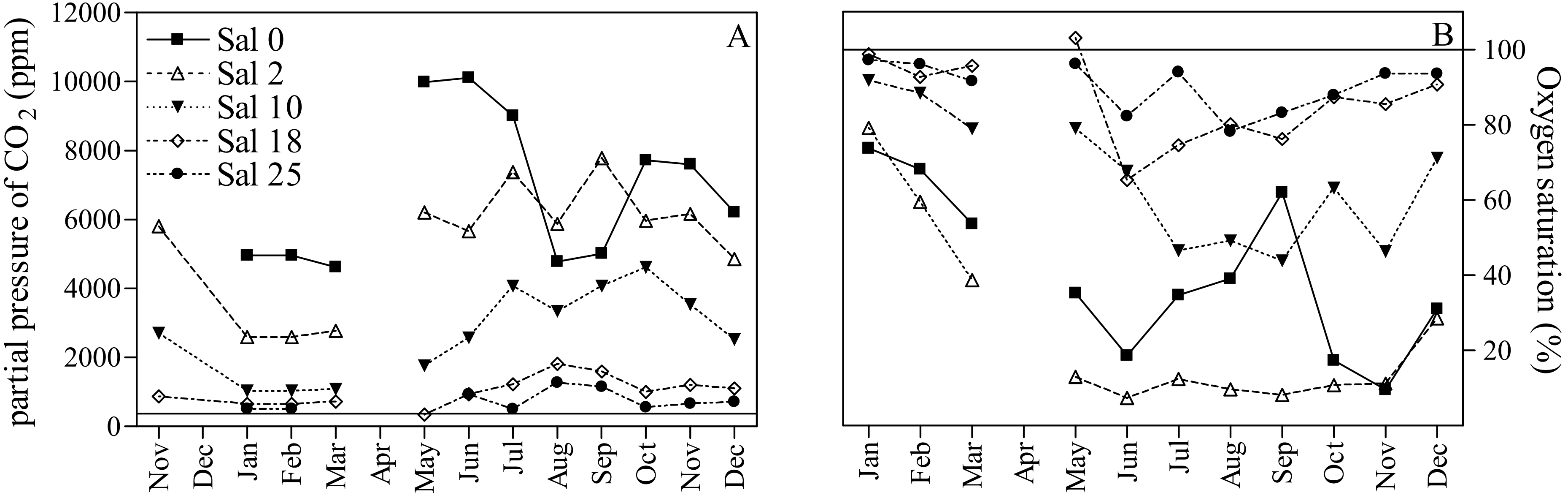


Fig. 5 – Gazeau et al.

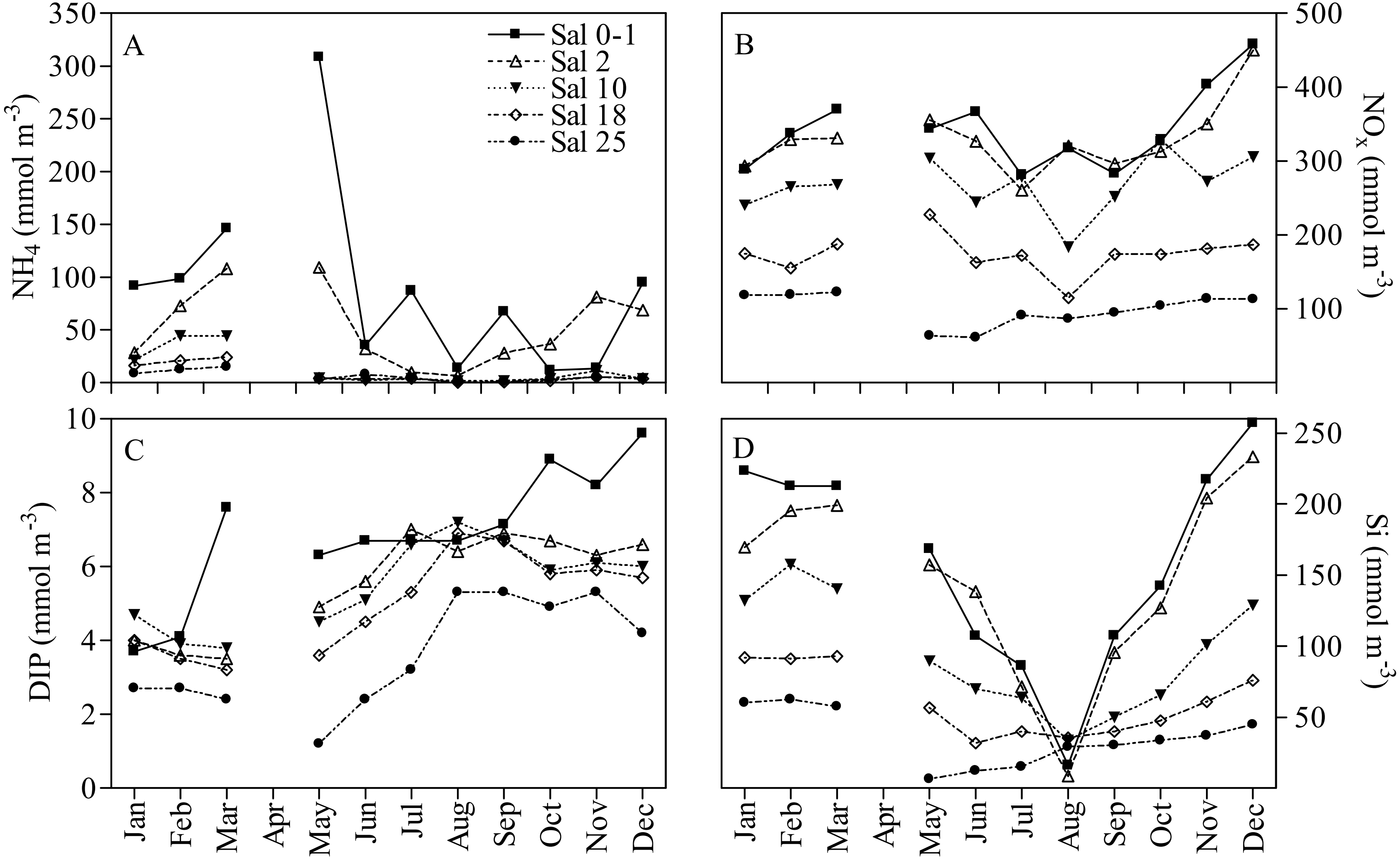


Fig 6 – Gazeau et al.

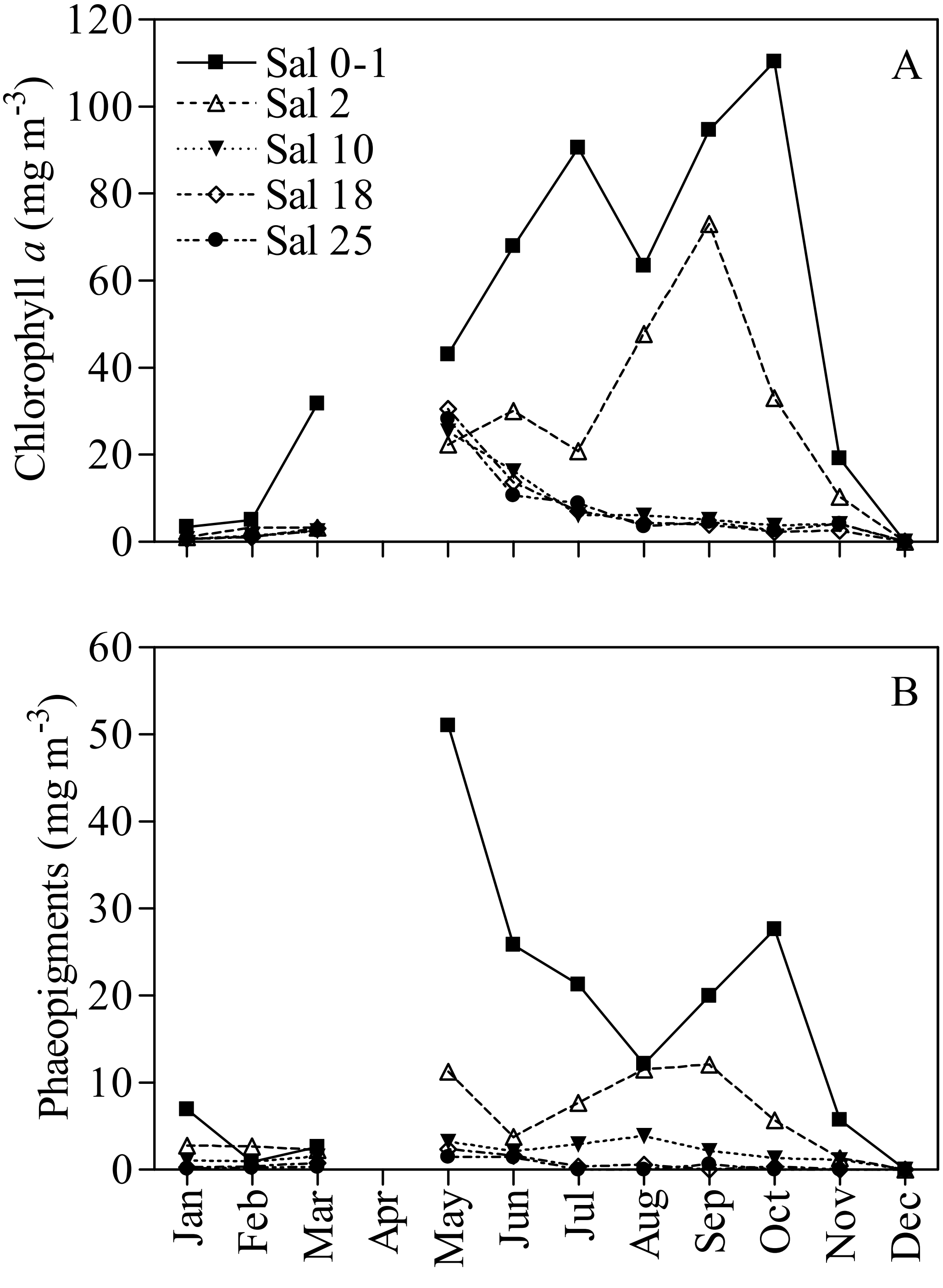


Fig 7 – Gazeau et al.

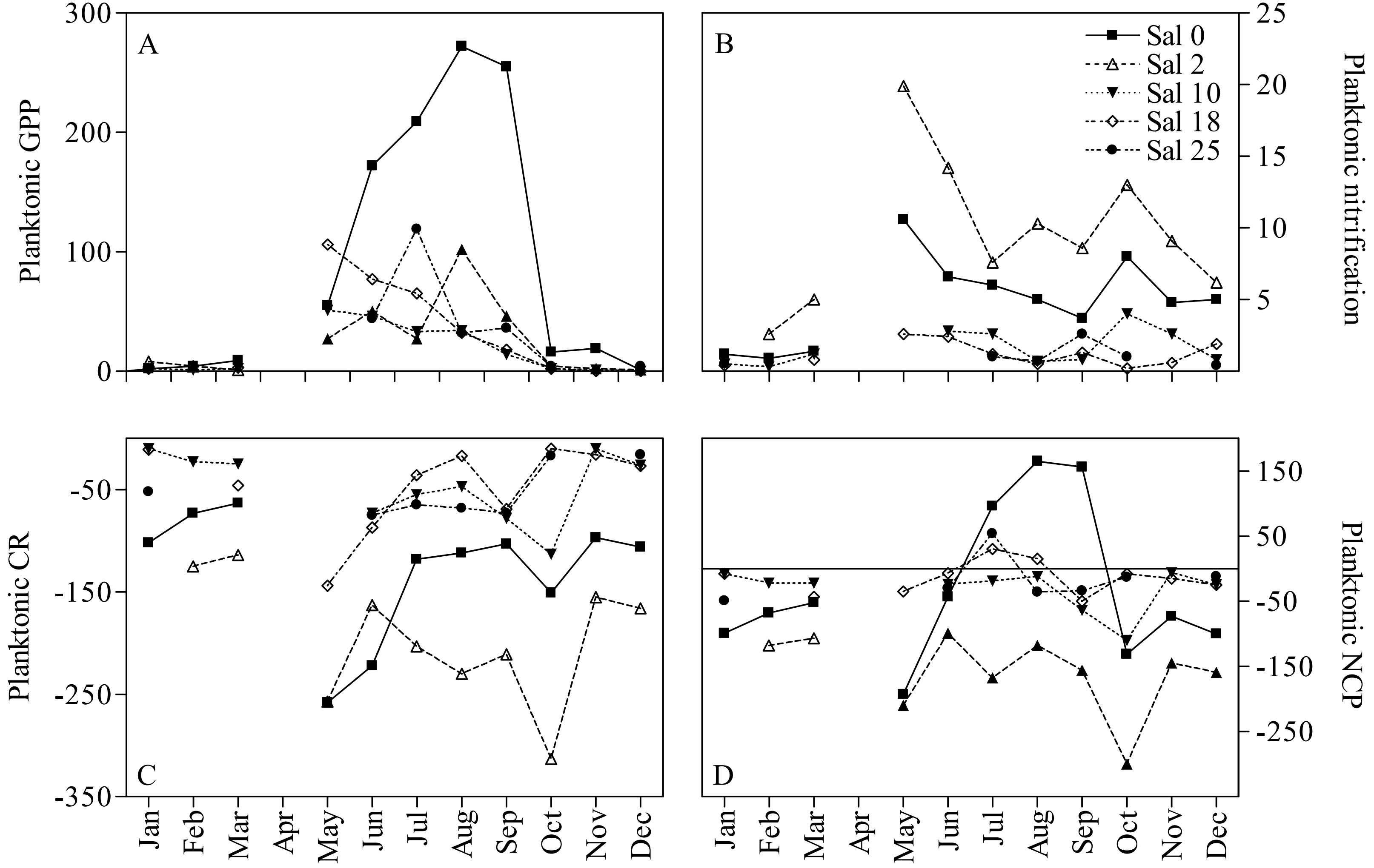
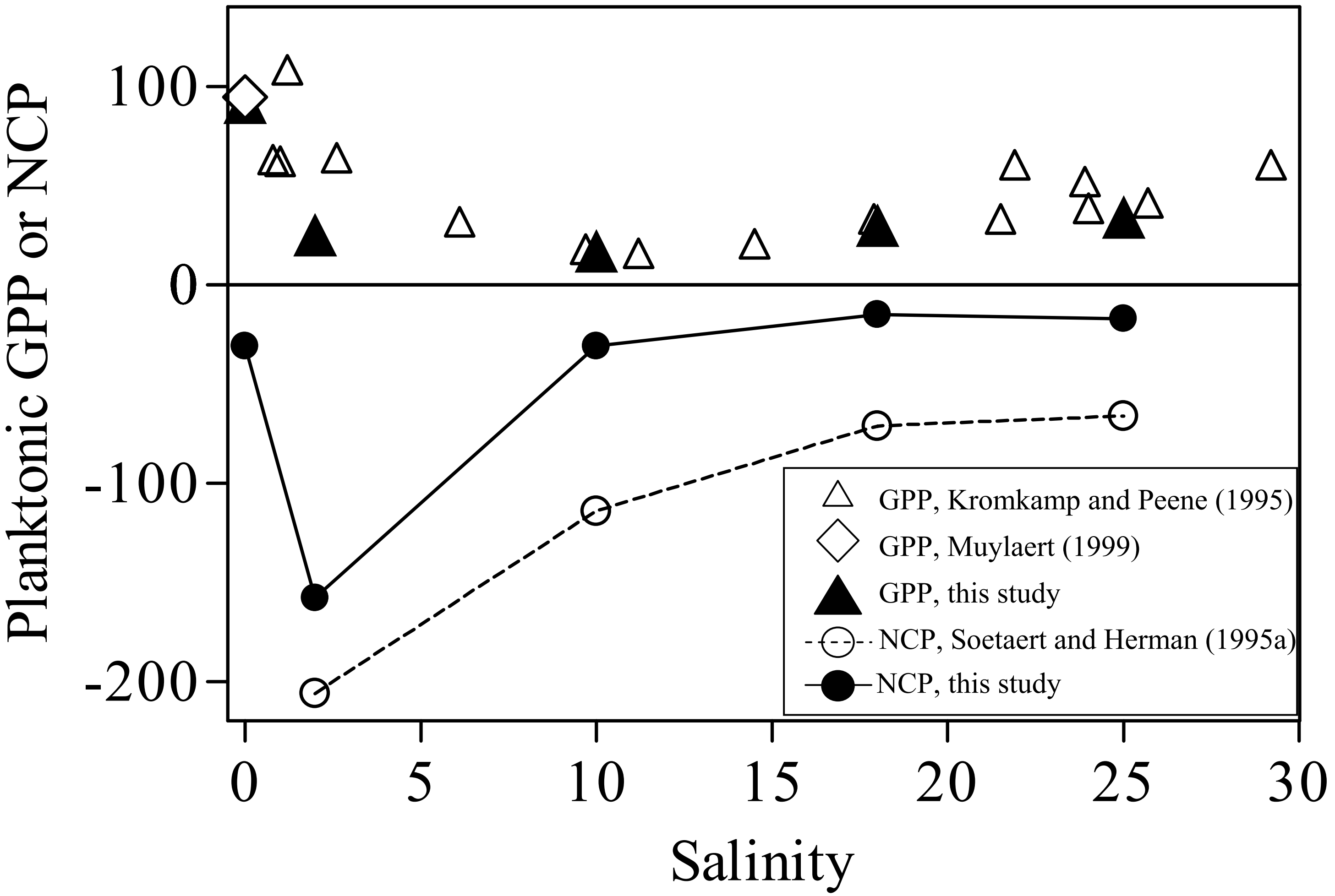


Fig 8 – Gazeau et al.



Chapitre 4

Synthèse

Dans ce chapitre, nous allons synthétisé les résultats obtenus concernant l'analyse bibliographique à l'échelle européenne, ainsi que les résultats acquis dans les trois sites étudiés. Les paramètres environnementaux seront comparés, dans ces trois sites, et reliés aux différences de métabolisme observées. Enfin, dans une dernière section, les avantages et inconvénients de toutes les méthodes utilisées dans cette étude seront présentés.

4.1 Le statut métabolique de la zone côtière européenne

L'étude bibliographique, menée au début de ce travail et présentée au chapitre 2, a permis de mettre à jour l'état de nos connaissances sur le fonctionnement des écosystèmes côtiers en Europe. Un total de 194 publications ont été analysées et 129 ont été introduites dans une base de données accessible à tous sur Internet (988 données; http://www.obs-vlfr.fr/eurotroph/index.php). Bien que la production primaire brute planctonique (GPP) soit le paramètre le mieux documenté dans notre base de données, de nombreuses lacunes ont été mises en évidence. Ces lacunes concernent la distribution spatiale des sites étudiés, par exemple très peu de mesures ont été effectuées dans le bassin Est méditerranéen ainsi que dans le nord de la mer Baltique et de la mer du nord. Toutefois, en divisant les trois régions étudiées (mer Baltique, mer du Nord/Atlantique et mer Méditerranée) en plusieurs sous-systèmes et en calculant des moyennes pondérées, nous avons très certainement limité de façon importante les effets de ce déséquilibre.

Un autre problème concerne l'estimation de la GPP phytoplanctonique dans la mesure où la majorité des mesures a été effectuée à partir de la méthode du ^{14}C. En ne prenant en compte que les mesures obtenues au cours d'incubations de durée inférieure à 6 h, nous avons opté pour l'utilisation de valeurs les plus proches possibles de GPP. Par ailleurs, la grande majorité des mesures ne concernent que la production particulaire. Or, il est à présent connu qu'une partie de la production phytoplanctonique est relarguée sous forme dissoute (exsudation, lyse cellulaire etc..) et ce spécialement dans les zones oligotrophes (Karl *et al.* 1998 ; Morán *et al.* 2002). Par exemple, une étude très récente (Sandberg *et al.* 2004) dans la mer et la baie de Bothnie (Baltique nord) a montré que la production dissoute représente presque 50 % de la production totale. Les valeurs annuelles estimées par ces auteurs sont, par conséquent, nettement plus importantes que les valeurs compilées dans notre base de données (6 vs. 4 mmol C m^{-2} j^{-1} dans la baie de Bothnie et 25 vs. 12 mmol C m^{-2} j^{-1} dans la mer de Bothnie). Il est fort probable que les estimations globales de GPP présentées dans le Tableau

1 soient sous-estimées du fait des problèmes liés à la méthode de ^{14}C. Afin de clarifier ce débat, il serait très intéressant dans le futur de reproduire ce travail à l'échelle européenne et mondiale en n'incluant que des mesures effectuées à partir de la méthode de l'O_2. Actuellement, le nombre de données est insuffisant pour cela.

Contrairement à la production planctonique, la GPP benthique est majoritairement mesurée à partir de la méthode de l'O_2 (chambres benthiques, microélectrodes etc…). Hormis une distribution spatiale peu homogène, le problème concernant ces mesures est que la plupart d'entre elles, pour des raisons pratiques évidentes, sont effectuées en zone intertidale. Or, il a été montré que la production microphytobenthique pourrait s'étendre jusqu'à des profondeurs supérieures à 20 m (Cahoon 1999). Pour être en mesure d'extrapoler la production microphytobenthique à toute la zone côtière (0-200 m), il convient donc de connaître la décroissance de la production avec la profondeur. Peu d'études se sont, jusqu'à maintenant, intéressées à ce problème. La méthode que nous avons employée n'est certainement pas parfaite car la relation liant la production à la profondeur n'est basée que sur quelques points. Ceci nous a néanmoins permis d'estimer, qu'à l'échelle de la zone côtière européenne, la production microphytobenthique est quasiment négligeable (Sédiment GPP; Tableau 1).

Localement, la production de matière organique par les macrophytes peut être importante et contribuer de manière significative à la dynamique du carbone dans ces systèmes. Toutefois, il nous a été impossible d'estimer cette contribution à l'échelle européenne. La raison majeure est, qu'à l'heure actuelle, il n'existe pas d'estimations de la surface occupée par les macrophytes en europe.

L'extrapolation des mesures de respiration (CR) benthique (uniquement sédiment) à l'échelle européenne souffre des mêmes problèmes et incertitudes que la GPP benthique, à savoir une distribution spatiale non homogène et peu d'études focalisant sur sa variation en fonction de la profondeur. L'estimation que nous avançons ici (17 mmol C m^{-2} j^{-1}) est proche de celle de Middelburg *et al.* (sous presse) pour la respiration sédimentaire au niveau mondial (19 mmol C m^{-2} j^{-1}).

La respiration planctonique en zone côtière est, sans aucun doute, le paramètre le moins bien documenté dans la littérature. Le peu de données disponibles, concernant presque uniquement la zone euphotique ne nous a pas permis d'extrapoler ce paramètre à l'échelle de l'Europe. Robinson et Williams (sous presse) estiment la respiration pélagique pour la zone côtière globale à 109 mmol C m^{-2} j^{-1}. Cette valeur semble très importante. Si nous appliquons les valeurs de GPP benthiques et planctoniques, estimées ici, à la zone côtière mondiale, ainsi que la CR benthique de Middelburg *et al.* (sous presse) et pélagique de Robinson et Williams (sous presse), la zone côtière dans sa globalité serait hétérotrophe avec une valeur de NEP de l'ordre de -80 mmol C m^{-2} j^{-1}. Ceci est en contradiction avec quelques études récentes montrant que la zone côtière serait autotrophe et une source de matière organique pour l'océan ouvert (Gattuso *et al.* 1998 ; Wollast 1998 ; Liu *et al.* 2000 ; Chen *et al.* 2003). De plus, considérant une surface de 26 x 10^6 km^2, cela revient à une consommation de matière organique allochtone de 760 Tmol C an^{-1}, soit environ vingt fois plus que l'apport de matière organique en provenance des rivières (estimé à 39 T mol an^{-1}; Meybeck 1982). Il est difficile de dire si cette incohérence provient d'une sous-estimation de GPP ou d'une surestimation de CR, ou éventuellement des deux.

Tableau 1 Paramètres métaboliques: production primaire brute (GPP), respiration communautaire (CR) et production nette au niveau de l'écosystème (NEP) extrapolés au plateau continental européen (en mmol C m^{-2} j^{-1}).

	Compartiment planctonique		Compartiment benthique			
Zone géographique	GPP	CR	Sédiment GPP	Sédiment CR	Macrophytes NPP	**NEP**
Mer Baltique	31	-	2	17	-	**?**
Mer du Nord/Atlantique	51	-	1	16	-	**?**
Mer Méditerranée	21	-	2.5	22	-	**?**
Europe	41	-	1.5	17	-	**?**

Dans cette étude, nous avions choisi de traiter les estuaires séparément car leurs caractéristiques sont très différentes de celles autres systèmes côtiers. Ce qui ressort de notre étude est la très grande variabilité des paramètres métaboliques dans ces systèmes, à l'exception de la GPP microphytobenthique. Toutefois, celle-ci, comme nous l'avions vu au niveau des plateaux continentaux, n'a été mesurée que dans des zones intertidales ou peu profondes. Ceci conforte l'idée selon laquelle la production primaire dans les estuaires n'est pas limitée par la disponibilité en sels nutritifs mais limitée par les paramètres gouvernant la disponibilité en lumière (profondeur de mélange, turbidité etc…). La respiration benthique estimée dans notre travail est de l'ordre de 60 mmol C m^{-2} j^{-1}, nettement supérieure à celle estimée par Hopkinson et Smith (sous presse) : 34 mmol C m^{-2} j^{-1}. Toutefois, il faut noter que notre estimation ne porte que sur une dizaine de valeurs et que ces estuaires, situés dans des régions fortement industrialisées et urbanisées, reçoivent d'importants apports en matière organique. Comme nous l'avons vu pour les plateaux continentaux, relativement peu d'études fournissent des données de respiration communautaire dans les estuaires. Enfin, la grande variabilité des paramètres métaboliques estuaires rend très difficile voire impossible toute extrapolation à une grande échelle. Nous suggérons donc que ces systèmes soient étudiés au cas par cas.

Tout comme les estuaires, d'autres types d'écosystèmes côtiers tels que les upwellings, les lagons, les plumes de dilution d'estuaires n'ont pas été intégrés dans le calcul des estimations présentées dans le Tableau 1. La raison est que ces systèmes possèdent des caractéristiques différentes de celles des plateaux continentaux et que le manque de données ainsi que le manque d'information concernant leur superficie au niveau européen interdit toute tentative d'extrapolation.

En conclusion, cette étude bibliographique montre que l'estimation de la balance métabolique de la zone côtière européenne à partir de données locales basées sur des méthodes d'incubations n'est actuellement pas envisageable. De nombreux points devront être éclaircis avant d'atteindre cet objectif :

- Que mesurons-nous exactement à partir de la méthode du ^{14}C ? Sous-estime t'elle la production primaire brute ? Si oui de combien?
- Quel est le devenir de la matière organique, spécialement en zone aphotique ?
- Quelle est la relation entre la production microphytobenthique et la profondeur ?
- Quelle est la surface représentée par les upwellings, lagons, herbiers de macrophytes ?

De plus, il faudrait une meilleure distribution spatiale des mesures en obtenant des données dans le bassin Est de la mer Méditerranée ainsi que dans le nord de la mer du Nord et de la mer Baltique.

Quantifier le statut métabolique de la zone côtière à partir d'incubations n'est pas chose aisée, cela nécessite évidemment beaucoup de temps au niveau de l'analyse ainsi qu'au niveau de l'extrapolation des résultats obtenus de petites à grandes échelle spatiales et temporelles. C'est pourquoi, il est très important de développer de nouvelles méthodes, intégratives, c'est-à-dire capable de fournir une estimation à de larges échelles spatio-temporelles.

Dans le cadre de ce travail, nous avons testé diverses méthodes existantes dans trois sites côtiers européens. Ces trois sites ont été choisis en fonction de leurs trois caractéristiques distinctes. Avant de synthétiser, à proprement parler, les résultats obtenus et de dresser un inventaire des avantages et inconvénients de chaque méthode, il nous paraît important de vérifier *a posteriori* si le choix de ces trois sites d'étude était judicieux.

4.2 Echelle locale : comparaison des trois sites d'étude

Les conditions environnementales

La Figure 1 compare ces sites au niveau de différents paramètres susceptibles d'avoir un impact sur leur statut trophique. Les valeurs présentées sont des moyennes des différentes stations étudiées (sur toute la colonne d'eau) pendant chaque campagne : Randers 1 (avril 2001), Randers 2 (août 2001), Palma 1 (mars 2002), Palma 2 (juin 2002), Escaut 1 (novembre 2002) et Escaut 2 (avril 2003). Il convient de souligner que les mêmes protocoles de prélèvement et d'analyse ont été utilisés durant ces campagnes

L'estuaire de l'Escaut est, de loin, le site le plus turbide et eutrophisé. Les concentrations moyennes en azote inorganique dissous (DIN) et phosphore inorganique dissous (DIP) sont en effet supérieures à 200 et 3 mmol m^{-3} respectivement.

De plus, la concentration en carbone organique total (TOC) y est également très importante particulièrement lors de la seconde campagne où elle est proche de 1000 mmol C m^{-3}. La concentration en matériel particulaire (SPM) limite sévèrement la pénétration lumineuse, si bien que la profondeur de la couche euphotique (Z_{eu} ; 0.1 % de l'irradiance de surface) est en moyenne de 3 m dans l'estuaire lors des deux campagnes. A l'opposé, la baie de Palma est un système méditerranéen oligotrophe (DIN < 0.5 mmol m^{-3} ; DIP ~ 0 ; TOC < 120 mmol C m^{-3}) où la disponibilité en lumière dans la colonne d'eau est relativement importante (Z_{eu} > 50 m). L'estuaire de Randers se situe entre ces deux systèmes : il est nettement moins turbide que l'Escaut avec une profondeur de la zone euphotique d'environ 7.5 m. Contrairement à la baie de Palma, la concentration en sels nutritifs n'est pas potentiellement limitante. Les concentrations en TOC, relativement constantes entre les deux campagnes sont de l'ordre de 400 mmol C m^{-3}. En toute logique, les plus faibles concentrations en O_2 et les plus fortes pCO_2 ont été rencontrées dans l'Escaut. La baie de Palma présente des saturations en O_2 et des pCO_2 proches de l'équilibre avec l'atmosphère. Il est à noter que la pCO_2 dans ce système est légèrement inférieure à la pCO_2 atmosphérique en mars et légèrement supérieure à celle-ci en juin.

Ces trois systèmes possèdent également des caractéristiques bathymétriques et hydrodynamiques très différentes. La baie de Palma est un système profond (profondeur moyenne ~ 30 m) où le temps de résidence de l'eau est faible (2 et 10 jours pendant les deux campagnes ; chapitre 3.1). L'estuaire de l'Escaut, d'une profondeur moyenne d'environ 8 m (estimée dans cette étude), est un estuaire macrotidal bien mélangé où le temps de résidence de l'eau douce est élevé (70 jours dans la partie amont et 10-15 jours dans la partie avale.

Soetaert & Herman 1995). Le fjord de Randers est très peu profond (1.6 m), stratifié de manière quasi permanente et le temps de résidence est en moyenne de 13 jours (Nielsen *et al.* 2001).

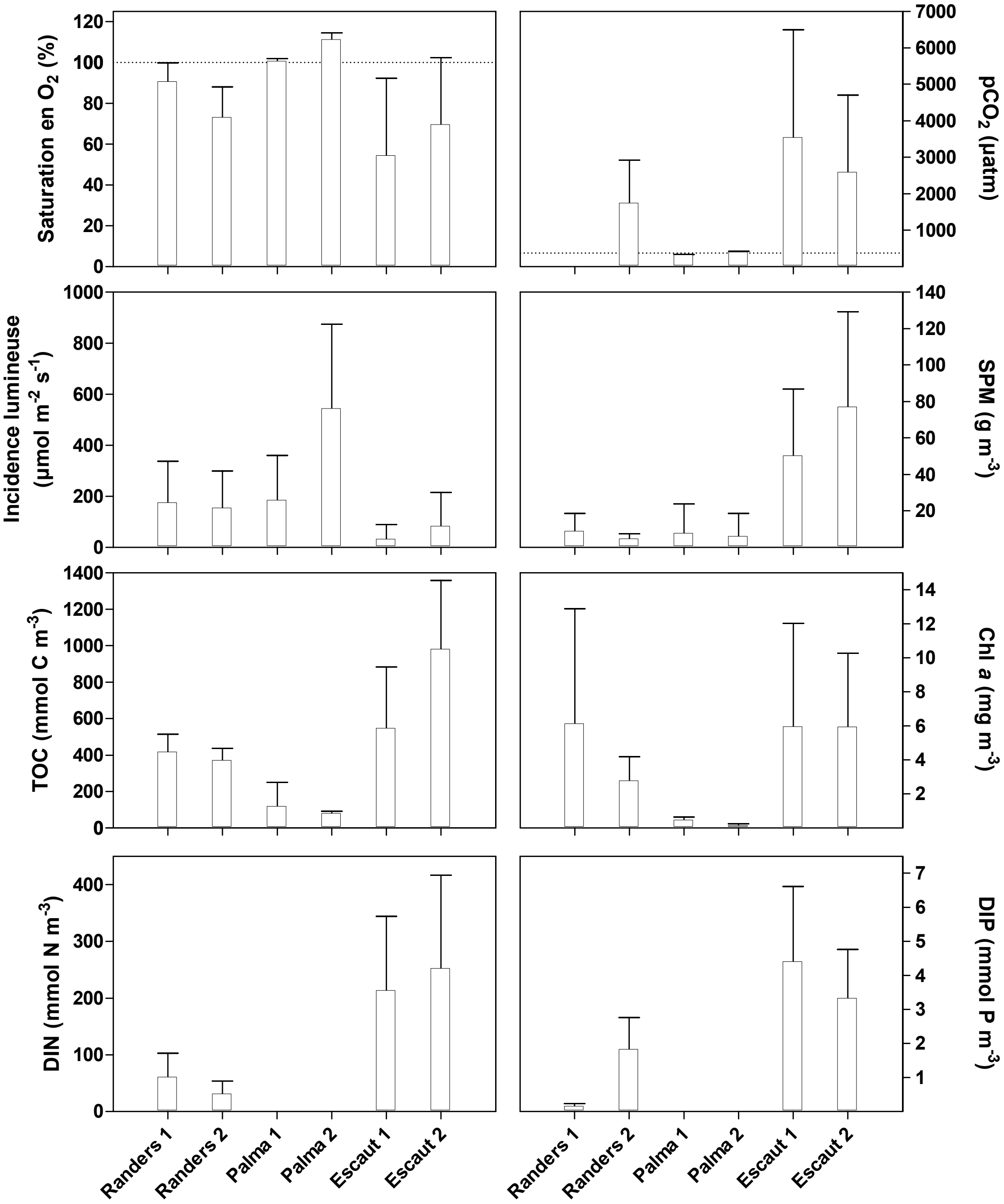


Figure 1 Paramètres environnementaux: saturation en O_2, pression partielle en CO_2 (pCO_2), incidence lumineuse et concentrations en matière en suspension (SPM), carbone organique total (TOC), chlorophylle *a* (chl *a*), azote inorganique dissous (DIN) et phosphore inorganique dissous (DIP) mesurés dans chaque site lors des six campagnes. Les valeurs présentées sont des moyennes pour chaque système pendant chaque campagne et les barres d'erreurs correspondent aux écart-types associés.

En conclusion, les trois sites présentent effectivement des caractéristiques environnementales bien distinctes, permettant une étude des relations entre celles-ci et les paramètres métaboliques mesurés.

Le compartiment planctonique

Les taux volumétriques horaires de GPP planctonique, de GPP planctonique normalisé par unité de chlorophylle *a* (GPP_B) et de CR planctonique obtenus au cours de chaque campagne sont présentés sur la Figure 2. Il convient d'ajouter que GPP et GPP_B sont les taux mesurés *in situ* non corrigés des variations d'irradiance (au contraire de ce qui a été fait pour chaque site).

Les GPP les plus fortes ont été mesurées dans le fjord de Randers. Toutefois, les communautés phytoplanctoniques les plus actives (GPP_B maximales) ont été rencontrées dans la baie de Palma. Ceci un point important à souligner car ces trois sites ne sont évidemment pas fermés et échangent de la matière avec l'environnement externe. Les estuaires de Randers et de l'Escaut reçoivent de fortes concentrations en chlorophylle en provenance soit de la rivière, soit du milieu externe (respectivement, du Kattegat et de la mer du Nord). Dans ces systèmes, les conditions de turbidité (particulièrement dans l'Escaut), ajoutées au stress cellulaire engendré par les forts gradients de salinité limitent la productivité (GPP_B) des communautés phytoplanctoniques. La stratification du fjord de Randers, qui limite les mouvements verticaux des cellules phytoplanctoniques, ainsi que les concentrations non limitantes en sels nutritifs permettent à ces cellules d'être légèrement productives. Cette légère productivité couplée à une forte biomasse donne des GPP relativement importantes.

Ce n'est pas le cas de l'Escaut où nous avons vu (chapitre 3.4) que la biomasse produite dans la rivière ou dans la mer du Nord se dégrade très rapidement en atteignant l'estuaire. La baie de Palma reçoit les apports de la Méditerranée occidentale, beaucoup moins chargés en biomasse phytoplanctonique. Bien que la productivité soit importante, le temps de résidence très court dans cette baie limite très certainement la formation de biomasse et ainsi la GPP dans ce système.

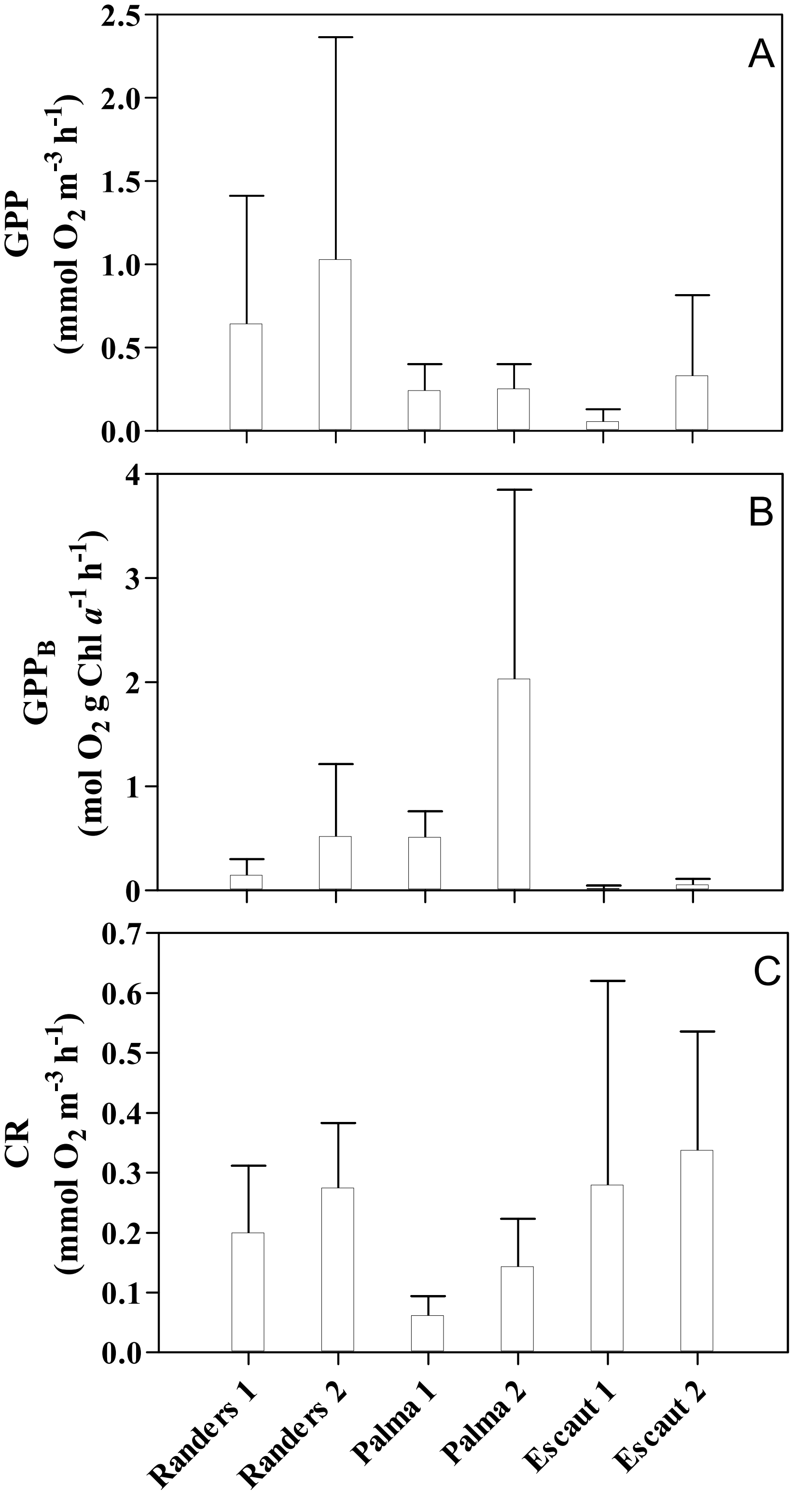


Figure 2 Production primaire brute (A; GPP), production primaire brute normalisé par unité de chlorophylle *a* (B; GPP_B) et respiration communautaire (C; CR) moyennes mesurées dans les trois sites d'étude lors des six campagnes. Les barres d'erreurs correspondent aux écart-types associés.

La Figure 3A montre la relation linéaire existant entre la GPP_B et la lumière. Bien que le r^2 de cette relation soit satisfaisant (0.95 ; $P < 0.001$), celle-ci est clairement biaisée par le fait qu'une seule mesure tire la relation vers les fortes valeurs, à savoir la seconde campagne dans la baie de Palma.

Les respiration communautaire (CR) est fort logiquement plus élevés dans l'estuaire de l'Escaut, toutefois, les différences existant au niveau de la concentration en TOC entre les 3 systèmes sont plus importantes que les différences observées au niveau de CR. Ces deux paramètres sont mis en relation sur la Figure 3B. Nous observons une relation de type logarithmique. Sur la Figure 3C, nous avons également mis en relation les valeurs journalières de CR et GPP. Au dessus de la droite 1:1, les paramètres mesurés dans le Randers et lors de la première campagne dans la baie de Palma suggèrent un statut autotrophe. A l'opposé, les taux de CR sont largement supérieurs aux taux de GPP dans l'Escaut suggérant un statut hétérotrophique. Lors de la seconde campagne à Palma, les stations étudiées sont proches de la balance métabolique. Nous observons également que GPP et CR à Randers et Palma sont liés de façon significative par une relation de type linéaire (pente égale à 2). Les mesures effectuées dans l'Escaut sortent très largement de cette relation, suggérant que la respiration dépend principalement des apports de matière organique allochtone plutôt que de la production locale.

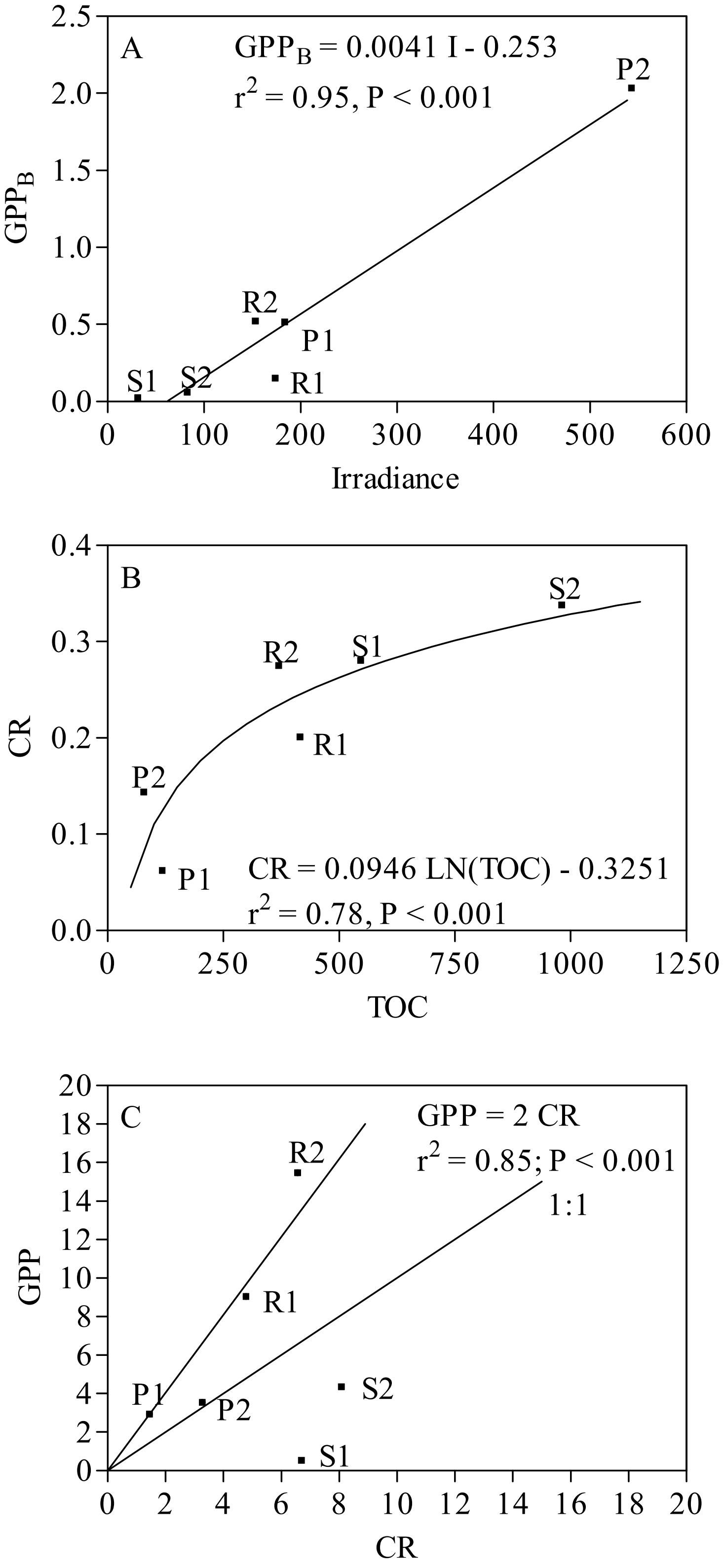


Figure 3 A) Relations entre A) GPP_B (mmol O_2 g Chla^{-1} h^{-1}) et l'intensité lumineuse (µmol m^{-2} s^{-1}), B) CR (mmol O_2 m^{-3} h^{-1}) et la concentration en TOC (mmol m^{-3}) et C) GPP journalière et CR journalière en mmol O_2 m^{-3} j^{-1}. R, P et S correspondent respectivement au fjord de Randers, à la baie de Palma et à l'estuaire de l'Escaut lors de chacune des 2 campagnes (1, 2) effectuées dans chaque système.

Afin de mieux visualiser les différences existant entre les trois sites étudiés, ainsi que les relations existant entre les paramètres métaboliques mesurés et les paramètres environnementaux, une analyse en composantes principales (ACP) a été réalisée en utilisant toutes les valeurs mesurées pendant chaque campagne (8 colonnes x 131 lignes). La pCO_2 n'ayant pas été estimée à chaque profondeur lors de la première campagne dans le fjord de Randers, celle-ci n'a pas été intégrée à l'analyse. De plus, nous avons choisi de différencier ici le POC (carbone organique particulaire) du DOC (carbone organique dissous). Les paramètres métaboliques mesurés (GPP, CR et GPP_B) ont été placés en variable illustrative sur le cercle de corrélation (Fig. 4). L'axe 1 représente plus de 55% de la variabilité observée. Les mesures effectuées dans les 3 sites se différencient bien sur cet axe avec de fortes concentrations en O_2, une bonne disponibilité en lumière et de faibles concentrations en sels nutritifs dans la baie de Palma (P). L'estuaire de l'Escaut (S) présente les caractéristiques inverses et le fjord de Randers (R) se situe approximativement entre ces deux systèmes comme nous l'avions avancé précédemment. Il faut noter également une variabilité beaucoup plus importante sur cet axe pour l'estuaire de l'Escaut.

Le second axe ne représente qu'environ 16% de la variabilité observée, principalement au niveau du POC et de la matière particulaire en suspension (SPM). Ici encore, la variabilité est nettement plus importante pour l'estuaire de l'Escaut que pour les deux autres sites.

Les mesures de GPP, GPP_B et CR planctoniques placées en variables illustratives sur le cercle de corrélation confirment ce que nous avons vu précédemment à savoir une forte relation entre la productivité (GPP_B) et la lumière (valeurs maximales à Palma en juin) et des CR liées à la concentrations en DOC et POC (maximales dans l'Escaut).

Ces considérations concernent uniquement les valeurs volumétriques des paramètres métaboliques. Pour chaque système, une étude bathymétrique a permis d'intégrer ces paramètres sur la colonne d'eau et de les extrapoler à la surface totale de chaque système.

Le Tableau 2 présente les valeurs intégrées de GPP, CR et NCP planctoniques estimées lors de chaque campagne et extrapolées à la surface totale des trois systèmes. Nous remarquons que la GPP est maximale à Palma lors de la première campagne (93 mmol O_2 m^{-2} j^{-1}) et minimale dans l'estuaire de l'Escaut en Novembre (4 mmol O_2 m^{-2} j^{-1}). Du fait de la profondeur relativement importante de la baie de Palma ainsi que d'une meilleure pénétration de la lumière, les faibles GPP volumétriques notées précédemment donnent une valeur intégrée approximativement égale à celles observées dans le fjord de Randers et dans l'estuaire de l'Escaut en avril. Intégrées également sur une relativement grande profondeur, les faibles CR volumétriques mesurées donnent des valeurs intégrées relativement fortes. Ceci souligne évidemment la difficulté d'extrapoler quelques mesures à une large échelle géographique et l'importance des données bathymétriques pour estimer convenablement le statut trophique d'un écosystème. Logiquement, les plus fortes hétérotrophies ont été rencontrées dans l'estuaire de l'Escaut (-52 et -26 mmol O_2 m^{-2} j^{-1} en novembre et avril respectivement) alors que le compartiment planctonique du fjord de Randers était légèrement autotrophe lors des deux campagnes (6 et 5 mmol O_2 m^{-2} j^{-1} en avril et août respectivement). Dans la baie de Palma, une forte autotrophie a été estimée (46 mmol O_2 m^{-2} j^{-1}) en mars lors du bloom phytoplanctonique printanier tandis que le compartiment planctonique s'est comporté comme un puits de matière organique en juin (-10 mmol O_2 m^{-2} j^{-1}).

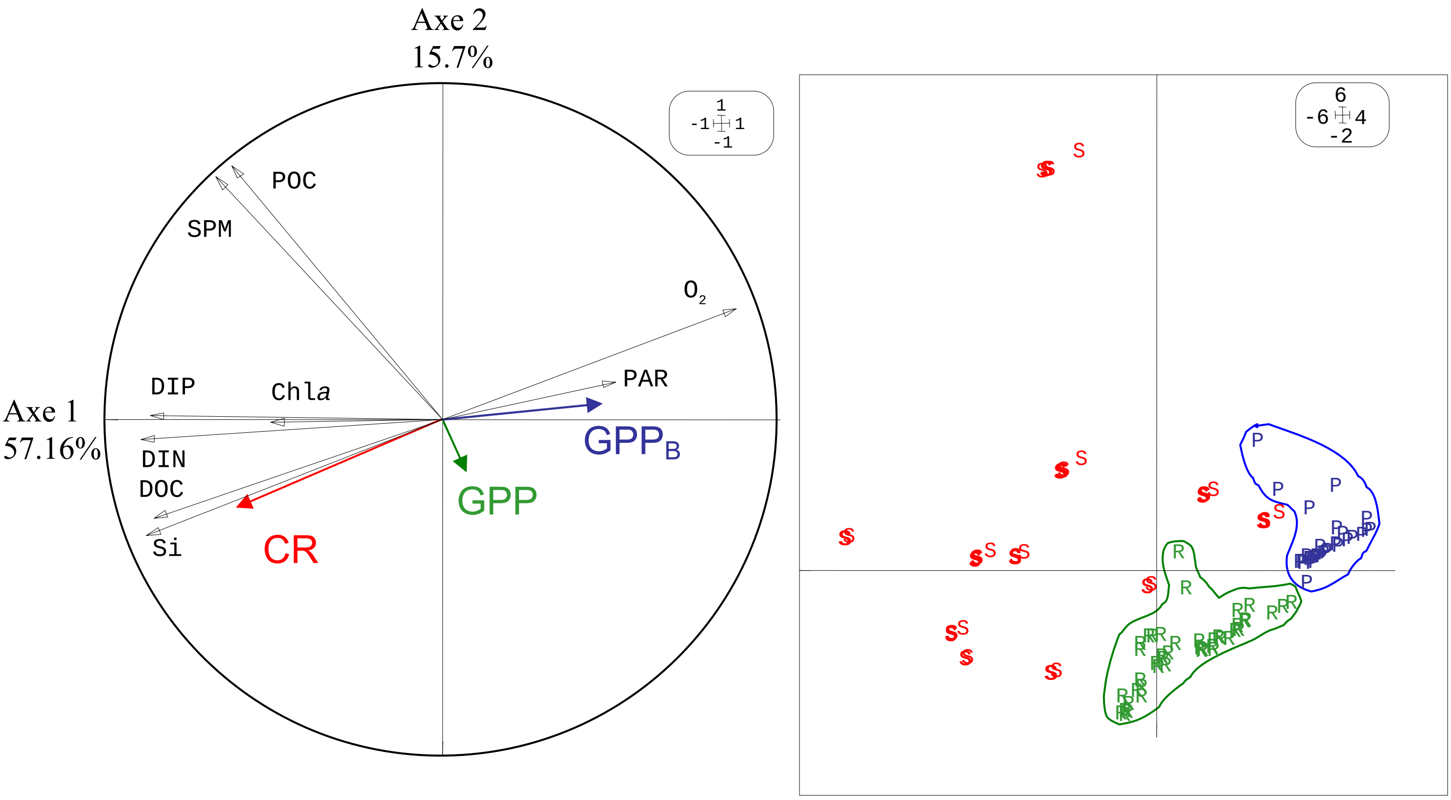


Figure 4 Analyse en composantes principales (ACP) établie à partir des paramètres environnementaux mesurés à toutes les stations lors des six campagnes (LxC : 131x8).

Tableau 2 Production primaire brute (GPP), respiration communautaire (CR) et production nette (NCP) planctoniques intégrées pour chacune des campagnes (toutes les valeurs sont en mmol O_2 m^{-2} j^{-1}).

	GPP	CR	NCP
Randers 1	25	-19	6
Randers 2	38	-33	5
Palma 1	93	-47	46
Palma 2	33	-43	-10
Escaut 1	4	-56	-52
Escaut 2	32	-58	-26

Le compartiment benthique

Les paramètres du métabolisme benthique mesurés lors de cette étude sont nettement plus difficiles à comparer. Premièrement, les productions microphytobenthiques n'ont pas été mesurées dans l'estuaire de l'Escaut. De plus, les mesures ont été effectuées sur des zones intertidales à Randers et dans des zones plus profondes à Palma et dans l'Escaut. Dans le Tableau 3 sont présentés les paramètres extrapolés à toute la surface de chaque système.

Le fjord de Randers est très peu profond (1.6 m en moyenne) et la faible turbidité permet une bonne pénétration de la lumière. Ainsi la lumière et la concentration non limitante en sels nutritifs permettent au microphytobenthos d'être très productif et de représenter 70 et 40 % de la production totale lors des deux campagnes. Toutefois, les forts taux de CR mesurés font que le compartiment benthique est hétérotrophe (-5 et -20 mmol O_2 m^{-2} j^{-1} en avril et août respectivement).

A Palma, les producteurs benthiques principaux sont les macrophytes (*Posidonia oceanica*) et le microphytobenthos est peu productif. *P. oceanica* occupe plus de 30 % de la surface de la baie et contribuent à 10 et ~50 % de la production de matière dans la baie, respectivement en mars et juin. Toutefois, les taux de CR mesurés étant importants, le compartiment benthique est proche de la balance métabolique lors des deux campagnes avec une tendance à l'autotrophie lors de la croissance des posidonies en juin. Un point très important à souligner ici : les NCP mesurées dans l'herbier de posidonies en surface (0-5 m) sont relativement fortes (30 et 38 mmol O_2 m^{-2} j^{-1} en mars et juin respectivement). Toutefois, en prenant en compte la décroissance de la production avec la profondeur ainsi que la surface occupée par les posidonies dans la baie de Palma, nous avons estimé que la production nette de l'herbier était relativement faible à l'échelle de la baie. Ceci souligne l'importance, comme nous l'avons vu dans la synthèse des données européennes (chapitre 4.1), d'étudier la croissance du microphytoplancton et des macrophytes sur un gradient de profondeur conséquent et d'avoir une connaissance satisfaisante de leur distribution à toutes les échelles spatiales. Une telle procédure n'a malheureusement pas été appliquée dans le fjord du Randers où la production n'a été mesurée qu'à une profondeur. Toutefois, nous avons cherché à limiter les erreurs d'extrapolation en construisant et intégrant des courbes PI (*production vs. irradiance*) à partir de données de la littérature.

Tableau 3 Production primaire brute (GPP), respiration communautaire (CR) et production nette (NCP) benthique (en mmol O_2 m^{-2} j^{-1}) mesurées dans les trois sites d'étude.

	GPP	CR	NCP
Randers 1 (intertidal)	53	-58	-5
Randers 2 (intertidal)	23	-43	-20
Palma 1			
Posidonia	37	-36	1
Sédiment	0.4	-1.8	-1.4
Total	12	-13	-1
Palma 2			
Posidonia	109	-83	26
Sédiment	11	-18	-7
Total	42	-39	3
Escaut 1 (subtidal)	-	-16	-16
Escaut 2 (subtidal)	-	-11	-11

Dans l'estuaire de l'Escaut, seuls les taux de CR ont été extrapolés à la surface totale de l'estuaire. Comme nous l'avons noté dans le chapitre 3.4, ces données sub-tidales sont nettement inférieures aux CR planctoniques. La profondeur de l'estuaire et le mélange vertical important font que la majorité de la matière organique est minéralisée dans la colonne d'eau, contrairement au fjord de Randers. En utilisant les données de Barranguet *et al.* (1998), une production microphytobenthique de 8 mmol C m^{-2} j^{-1} est calculée. Comparée à la valeur annuelle de GPP pélagique présentée au chapitre 3.4 (30 mmol C m^{-2} j^{-1}), cela correspond à une contribution du microphytobenthos à 20% de la production primaire brute totale.

En conclusion, le compartiment benthique est peu productif (en terme de production nette) dans les trois sites et se comporte comme un puits de matière organique, excepté en juin dans la baie de Palma où les posidonies fournissent une grande partie (~65%) de la matière organique nécessaire au compartiment planctonique. De plus, il ressort très nettement que l'importance du compartiment benthique au niveau des flux de matière diminue avec la profondeur, cette contribution benthique étant maximale dans le fjord de Randers car il est peu profond.

La production nette au niveau de l'écosystème (NEP)

Le Tableau 4 présente les GPP et CR totales ainsi que les NEP mesurées dans les trois sites étudiés. Il est à noter que la GPP microphytobenthique n'a pas été considérée pour l'estuaire de l'Escaut et que la CR subtidale dans ce site mesurée a été extrapolée à tout l'estuaire. L'absence de données intertidales durant ces campagnes nous interdit de statuer sur une possible sous- ou surestimation de la NEP pour ce système. Néanmoins, le système le plus hétérotrophe est logiquement l'estuaire de l'Escaut. Dans le chapitre 3.4, nous avons présenté une étude annuelle concernant ce système. En intégrant aux données planctoniques, des mesures de productions et de respirations benthiques (Middelburg *et al.* 1996 ; Barranguet *et al.* 1998), une NEP annuelle de l'ordre de -45 mmol C m^{-2} j^{-1} a été estimée. Un autre point important à soulever ici est l'unité différente des cette dernière valeur par rapport aux estimations présentées jusqu'ici, toutes basées sur la méthode de l'O_2. Dans la littérature, la NEP est indifféremment exprimée en O_2 ou en C. Toutefois, dans l'estuaire de l'Escaut, nous avons vu que la nitrification représentait plus de 30 % de la production de matière organique dans la zone amont. Ce processus de production, contrairement à la photosynthèse, consomme de l'O_2 au lieu d'en produire. La NEP exprimée en O_2 et présentée dans le Tableau 4 ne prend pas en compte ce processus alors que celui-ci est intégré à l'estimation annuelle présentée ci-dessus et exprimée en C. Ainsi, le même terme n'englobe pas les mêmes processus. De plus, il est à noter que nombre d'études ont montré que la méthode de l'O_2 sous-estimait de façon significative CR du fait des processus de minéralisation anaérobique, particulièrement en zone côtière (*respiratory quotient* : $RQ \neq 1$). Enfin, la quantité d'O_2 produite par la production d'une mole de carbone organique (*photosynthetic quotient* : $PQ \neq 1$) peut varier en fonction du substrat, ainsi accentuant la difficulté du passage entre les deux unités. Ces deux derniers points seront discutés de façon plus complète dans la prochaine section. Pour éviter toute confusion dans le cas où les deux unités ne soient pas comparables (comme par exemple dans l'estuaire de l'Escaut), il serait très bénéfique de clarifier la terminologie actuelle ou, au moins, de toujours spécifier la signification exacte des paramètres et unités utilisés.

Le schéma présenté en introduction ne représente pas tout à fait la réalité. En effet, le statut trophique d'un écosystème dépend évidemment des disponibilités en lumière, matière organique et sels nutritifs mais également d'autres paramètres secondaires tels que le temps de résidence, la bathymétrie, la stratification ou le mélange de la colonne d'eau. Le système le moins productif est certes l'estuaire de l'Escaut du fait de la forte turbidité et du fort gradient de salinité limitant la production locale ainsi que des importants apports de matière organique allochtone et du temps de résidence important favorisant la croissance bactérienne. Les deux autres systèmes ont été étudiés sur une échelle annuelle à l'aide de la méthode LOICZ pour le fjord de Randers (chapitre 3.3) et à partir d'incubations O_2 dans la baie de Palma (chapitre 3.1). Toutefois, nous avons vu que 1) les valeurs données par la méthode LOICZ pouvait être biaisées du fait de la sous-estimation des apports de matière (principalement d'origine latérale) et 2) le statut trophique de la baie de Palma n'a pas été estimé avec la même rigueur que lors des deux campagnes EUROTROPH en 2002. Au regard des résultats présentés ci-dessous, difficile de savoir, entre le fjord de Randers et la baie de Palma, lequel de ces systèmes est le plus productif sur une échelle annuelle.

Tableau 4 Production primaire brute (GPP) et respiration communautaire (CR) totales (benthiques + planctoniques) et production nette de l'écosystème (NEP) mesurées dans les trois sites d'étude. Toutes les valeurs sont exprimées en mmol O_2 m^{-2} j^{-1}.

	GPP	CR	NEP
Randers 1	78	-77	1
Randers 2	61	-76	-15
Palma 1	105	-60	45
Palma 2	75	-82	-7
Escaut 1	4	-72	-68
Escaut 2	32	-69	-37

Les données de GPP et CR estimées dans ces trois sites lors des six campagnes sont comparées aux données de la littérature compilées par Gattuso *et al.* (1998). Les points situés au dessus de la droite 1:1 (Fig. 5) révèlent un statut hétérotrophe alors que les points situés en dessous de cette droite révèlent un statut autotrophe. Les systèmes les plus productifs sont clairement les systèmes dominés par les macrophytes, les mangroves et les marais salants.

Cette comparaison (figure du bas pour laquelle seules les données des plateaux continentaux et des estuaires ont été considérées) montre que l'estuaire de l'Escaut présente un caractère très hétérotrophe, particulièrement lors de la première campagne alors que la baie de Palma lors de la première campagne est un des systèmes les plus productifs de cette comparaison de données. Ce système dominé par des macrophytes est toutefois nettement moins productif que ceux rapportés par Gattuso *et al.* (1998) pour des écosystèmes de ce type. Il est important de souligner que nos estimations de GPP et CR dans ce système prennent en compte la décroissance de la production des *posidonies* dans cette baie relativement profonde et qu'ainsi les données présentées sont extrapolées à toute la baie. Les données présentées par Gattuso *et al.* (1998) concernent principalement des sites peu profonds pour lesquels les mesures n'ont été effectuées presque uniquement en surface. Il est à noter que la compilation de Gattuso *et al.* (1998) ne concerne que des données annuelles que nous comparons ici à des données ponctuelles. Les données annuelles estimées dans l'estuaire de l'Escaut sont également présentées sur ce graphique. Nous observons que les caractéristiques métaboliques de cet estuaire sont proches de celles de Jassby *et al.* (1993) dans la baie nord de San Francisco et de Collins (1978) près de Southampton.

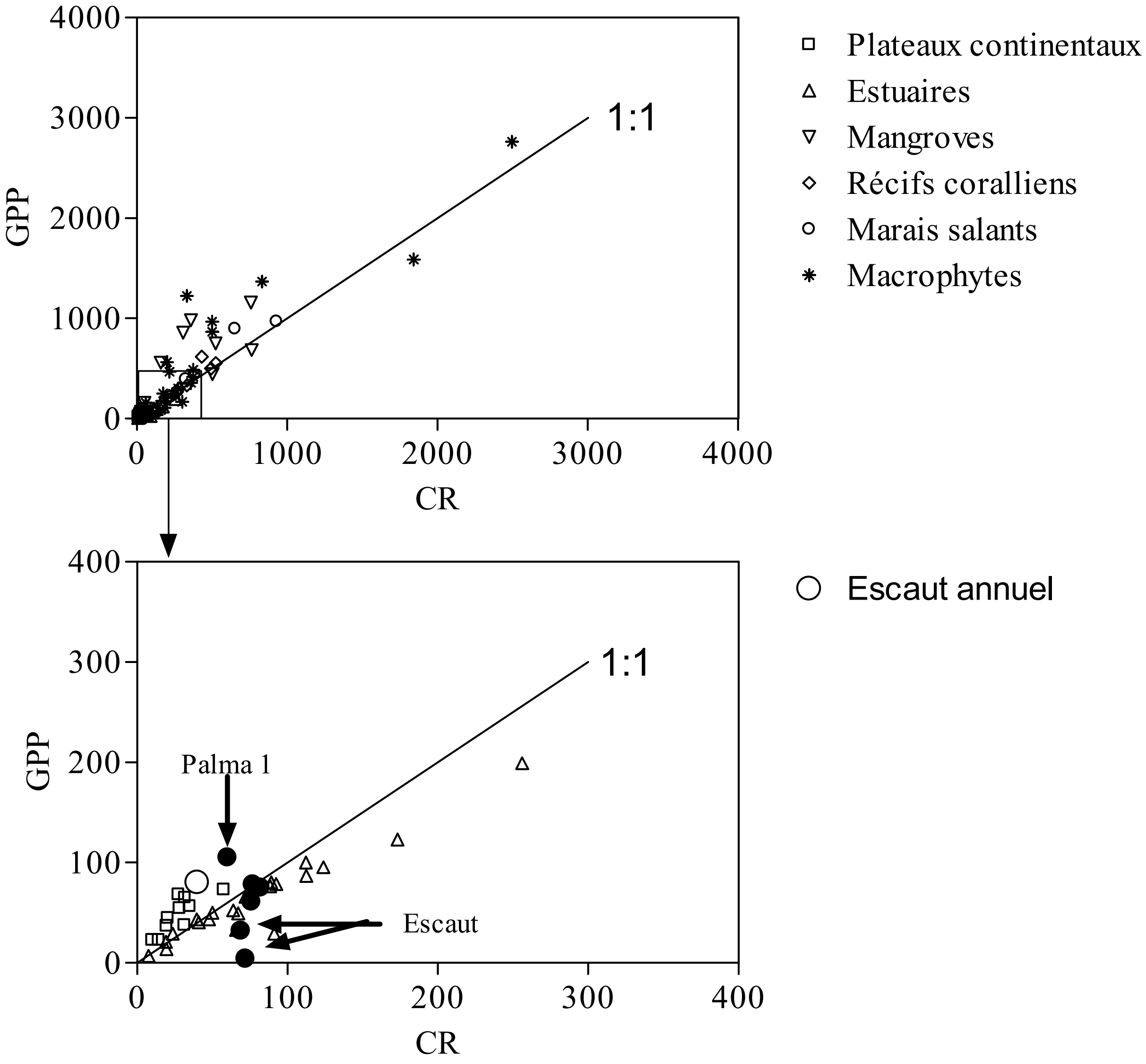


Figure 5 Comparaison des données de la production primaire brute (GPP) et de la respiration communautaire (CR; exprimées en mmol O_2 m^{-2} d^{-1}) acquises pendant les six campagnes avec les données compilées par Gattuso *et al.* (1998).

Les méthodes d'estimation du statut trophique en zone côtière

Une part importante de ce travail était de tester et de comparer différentes méthodes d'estimation du statut trophique des écosystèmes côtiers. Pour rappel, ces méthodes sont :

- Incubations (O_2) et extrapolation à l'échelle de l'écosystème
- Méthode LOICZ basée sur l'estimation des flux non conservatifs de DIP et de carbone inorganique dissous (DIC)
- Méthodes en système ouvert (*open-system*) telles que la méthode RSD ou les budgets de DIC et d'O_2 basés sur des cycles journaliers.

Nous venons (section précédente) de présenter et de comparer les résultats obtenus à partir de la méthode des incubations dans les trois sites d'étude. Nous allons ici dresser un inventaire des avantages et inconvénients liés à chacune de ces méthodes.

Les incubations oxygène

Les difficultés et erreurs majeures associées à l'utilisation de la technique des incubations à plusieurs stations dans un écosystème sont :

1) l'investissement en temps important que ce soit au niveau des incubations (12 ou 24 h) ou des analyses post-incubatoires
2) la prise en compte de toutes les communautés qui composent l'écosystème étudié (plancton, microphytobenthos, macrophytes, éventuellement bactéries nitrifiantes etc…)
3) le cumul des erreurs associées à l'estimation du métabolisme de chaque communauté du système étudié
4) l'extrapolation de ces données à l'échelle de l'écosystème qui nécessite la connaissance de la bathymétrie et de la pénétration de la lumière.

L'avantage majeur de cette technique réside dans le fait que les processus sont mesurés directement et non par l'intermédiaire d'un proxy comme c'est le cas, par exemple, pour la méthode LOICZ. Toutefois, comme nous l'avons vu précédemment (chapitre 3.3), une différence importante est généralement observée entre les résultats obtenus par la méthode des incubations et les méthodes en milieu ouvert. Ces différences sont attribuées en partie au fait que les incubations réduisent de façon significative la turbulence et ainsi inhibent les processus tels que la production phytoplanctonique et(ou) la minéralisation bactérienne . De plus, certains auteurs (Kemp et Boynton 1980) estiment qu'il demeure très difficile de prendre en compte toutes les communautés d'un système à partir des incubations, sous-estimant ainsi de façon significative les taux métaboliques intégrés.

Enfin, la méthode des incubations implique généralement une mesure de NCP pendant une période voire la totalité de la journée éclairée ainsi qu'une mesure de CR dans des bouteilles noires incubées elles aussi pendant la journée éclairée. En considérant que CR est un paramètre constant sur 24 h, il est ainsi possible d'estimer GPP à partir de ces deux paramètres. NCP sur 24 h est alors calculée comme la somme de CR et GPP en unité journalière. Lors des deux campagnes dans la baie de Palma, nous avons mesuré la NCP sur 12 h (NCP_d) et sur 24 h (NCP_{24h}), ainsi que CR dans les bouteilles opaques incubées pendant 24 h. La procédure développée ci-dessus (à partir de NCP_d et CR) donne des résultats de NCP (NCP_{calc}) similaires à ceux mesurés sur 24 h (NCP_{24h} ; Fig. 6). Toutefois, nous observons une pente légèrement supérieure à 1. Cette pente différente de 1 pourrait trouver son origine au cumul des erreurs liées à l'estimation de GPP et CR. La différence entre NCP_{24h} et NCP_{12h} permet d'estimer les taux de CR, ceux-ci sont en moyenne deux fois supérieurs aux taux mesurés dans les bouteilles opaques durant la journée, le rapport étant très variable entre les stations ainsi qu'en fonction de la profondeur d'incubation. Ainsi, la question soulevée est : la procédure d'"incubation au noir" pendant la journée est-elle valable ? Par manque d'indices, il est impossible de donner une explication pour le moment à la différence observée. Néanmoins, nous nous proposons de donner ici quelques hypothèses :

- incuber les cellules en obscurité forcée peut induire un stress pour les cellules inhibant les processus métaboliques
- dans les milieux où les substrats organiques sont limitants pour la croissance bactérienne, incuber les échantillons en obscurité forcée après une nuit "naturelle" peut induire un appauvrissement significatif en matériel organique disponible et ainsi inhiber la respiration.

Dans la plupart des publications, GPP étant déduite de NCP_d et CR, une sous-estimation de CR induit inévitablement une sous-estimation de GPP. Ceci pourrait être une des raisons des différences observées entre les méthodes en milieu ouvert et les méthodes d'incubation et mériterait une attention particulière à l'avenir (voir chapitre 5).

Nous avons indiqué précédemment que la conversion entre O_2 et C pouvait poser problème. Le quotient photosynthétique (PQ) est le rapport molaire entre la production d'O_2 et consommation de CO_2 par la photosynthèse. Williams et Robertson (1991) ont estimé que celui-ci varie entre 1 et 1.36 pour le phytoplancton principalement en fonction du substrat disponible (ammonium ou nitrate). Il faut noter que ce facteur varie également en fonction du type de producteur primaire considéré, les valeurs concernant les macrophytes étant plus proches de 1 (voir chapitre 3.1). De plus, dans les systèmes où la nitrification est intense (cas de l'Escaut par exemple), ce processus doit être mesuré afin de corriger les variations en O_2 observées et non attribuées à la respiration. Dans la grande majorité des cas, un RQ de 1 est utilisé bien que la validité de cette hypothèse soit souvent fausse (Hopkinson & Smith sous presse), principalement au niveau du compartiment benthique. La méthode basée sur l'O_2 peut significativement sous-estimer la CR benthique du fait de la présence de processus anaérobiques. En effet, il se peut qu'une large part des métabolites réduits (Mn^{2+}, Fe^{2+}, H_2S etc…) ne soit pas réoxydée en atteignant la surface du sédiment, ce qui induirait une sous-estimation de la minéralisation totale par la méthode de l'O_2 (Thamdrup & Canfield 2000). De ce fait, de grandes variations au niveau du RQ ont été observées en fonction du site étudié, et l'utilisation d'une valeur unique semble très risquée, particulièrement dans les estuaires.

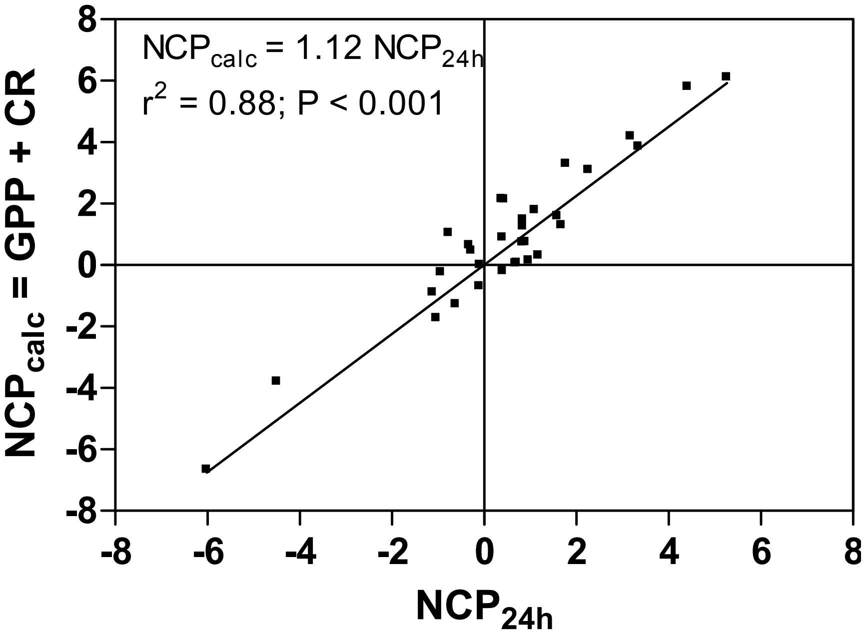


Figure 6 Comparaison entre les estimations de production nette communautaire (NCP) à partir de la production primaire brute (GPP) et de la respiration communautaire (CR; NCP_{calc}) et les mesures directes sur 24 h (NCP_{24h}). Les valeurs sont en mmol O_2 m^{-3} d^{-1}.

La méthode LOICZ

En règle générale, les méthodes que nous avons testées ont fourni des résultats similaires dans chacun des trois sites, à l'exception de la méthode LOICZ basée sur le DIP dans l'estuaire de l'Escaut. Il semble donc que cette méthode ne soit pas applicable aux estuaires turbides ou les processus d'adsorption et/ou de désorption, qui ont été estimés, peuvent être importants et introduire un biais dans les calculs. Un autre inconvénient majeur de cette méthode est qu'elle nécessite un gradient de salinité conséquent entre le système et l'environnement extérieur et ainsi interdit son utilisation dans les baies dépourvues d'apport en eau douce (telles que la baie de Palma). Dans ces systèmes, un modèle hydrodynamique permettant l'estimation des flux d'eau et de matière entrants et sortants doit impérativement être réalisé. De plus, nous avons vu dans le fjord du Randers et dans l'estuaire de l'Escaut que les apports latéraux peuvent avoir un impact non négligeable sur le fonctionnement de ces systèmes. En effet, à Randers lors de la seconde campagne (chapitre 3.3), une forte pluie semble avoir provoqué un apport de DIP par ruissellement qui a considérablement dynamisé la production phytoplanctonique. Dans l'Escaut, les maxima de respiration ont été rencontrés lors des deux mois les plus pluvieux de l'année. Etant donné que le flux d'eau douce en provenance de la rivière n'a pas varié de façon importante durant ces périodes et que de fortes concentrations en POC ont été mesurées, il semblerait qu'il s'agisse ici également d'un apport par ruissellement latéral. Toutefois, ces apports diffus sont très difficiles à estimer et ne sont, dans la plupart des cas, pas pris en compte. Les mêmes inconvénients sont évidemment valables pour la méthode LOICZ appliquée au DIC. De plus, cette dernière nécessite une estimation très précise des flux de CO_2 à l'interface air-mer et ainsi du coefficient d'échange. Nous reparlerons de ce problème dans la section suivante.

Il convient de noter que la méthode LOICZ permet d'estimer la NEP d'un système mais ne permet pas de distinguer GPP de CR, contrairement aux autres méthodes testées dans cette étude. Enfin, les résultats obtenus à partir de la méthode LOICZ basée sur le DIP doivent être convertis en unité C. Généralement, le rapport $(C:P)_{part}$ de Redfield (106:1) est utilisé. Toutefois, les macroalgues ont un rapport proche de 550:1 (Atkinson & Smith 1983), l'utilisation d'un facteur de conversion "générique" peut poser problème dans les systèmes où l'impact de ces espèces est important.

Les avantages majeurs de la méthode LOICZ sont qu'elle permet une estimation du statut trophique sur de larges échelles spatio-temporelles et qu'elle nécessite un investissement beaucoup moins important que les méthodes d'incubations classiques.

En conclusion, cette étude nous a permis de valider la méthode LOICZ appliquée au DIP dans un estuaire peu turbide (Randers) et démontré que celle-ci n'est pas applicable dans des estuaires tels que l'Escaut. De plus, nous avons montré que cette méthode nécessite une parfaite connaissance du site étudié et des sources potentielles d'eau et de matière.

Les autres méthodes en milieu ouvert

Les autres méthodes *open-system*, telles que la méthode response surface difference (RSD) ou les budgets de DIC et d'O_2 utilisés dans cette étude, présentent bien évidemment l'avantage de pouvoir couvrir des échelles spatiales et temporelles supérieures à celles couvertes par les méthodes d'incubations classiques pour un investissement en temps et en matériel beaucoup moins important. Toutefois, leur utilisation implique que les variations d'O_2 et/ou DIC observées sont uniquement dues à des processus biologiques et non à des processus d'advection, soit de prendre en compte ces processus hydrologiques (advection, stratification etc..) dans l'établissement des budgets, comme c'est le cas pour la méthode RSD. Nous avons vu que ces méthodes ont fourni des résultats de NEP proches de ceux estimés par les méthodes d'incubation (budget DIC et O_2 dans la baie de Palma et méthode RSD dans le fjord de Randers) avec toutefois de grands écarts concernant les estimations de GPP et CR. Les causes éventuelles de ces différences ont été abordées précédemment. De plus, ces méthodes ne peuvent être utilisées dans les systèmes où une partie de la production est attribuée aux organismes chemoautotrophes tels que les bactéries nitrifiantes. En effet, il est impossible de différencier, à partir de ces techniques, la consommation d'O_2 par ce processus de la consommation d'O_2 par la respiration, ce qui limite de façon significative leur champ d'application. Il est étonnant que ce problème n'ait pas été soulevé par Caffrey (2004). Cet auteur a étudié le métabolisme de 42 sites estuariens aux Etats-Unis et estimé une NEP moyenne de -111 mmol C m^{-2} d^{-1}. Dans ces systèmes très eutrophisés, la non prise en compte de la nitrification pourrait être à l'origine des très faibles valeurs de NEP estimées dans cette étude.

Nous avons également vu que le transfert d'O_2 et de CO_2 à travers l'interface air-mer représente une part importante de la dynamique de ces constituants dans les systèmes étudiés ainsi que de l'erreur associée à l'estimation des paramètres métaboliques. L'étude menée dans le fjord de Randers et les estuaires de la Tamise et de l'Escaut (chapitre 3.2) a montré que la paramétrisation de la vitesse de transfert du CO_2 en fonction de la vitesse du vent variait de façon significative en fonction des caractéristiques du système considéré. Il paraît donc très délicat d'utiliser une seule et unique relation voir un coefficient d'échange constant tel que l'a fait Caffrey (2004). Dans l'estuaire de l'Escaut, une relation liant le coefficient d'échange dans ce système macrotidal aux vitesses de vent et de courant a été estimée (Borges *et al.* 2004). Malheureusement, il a été impossible de valider cette relation à partir de la méthode LOICZ appliquée au DIC dans cet estuaire (chapitre 3.2). Malgré nos efforts pour limiter les erreurs dues à l'estimation du flux de gaz à l'interface air-mer, il semble que ce processus soit encore très critique lors de l'utilisation de méthodes en système ouvert.

Comme pour la méthode d'incubation O_2, des facteurs de conversion sont nécessaires pour exprimer les résultats en C. Le problème est encore plus complexe que pour les incubations car les variations d'O_2 représentent la totalité de l'écosystème. Comme nous l'avons vu, les quotients photosynthétique et respiratoire (PQ et RQ) varient de façon significative, non seulement en fonction du site étudié, mais également en fonction de la communauté considérée (plancton, benthos, macroalgues…). Il paraît donc très difficile voir impossible d'appliquer un facteur unique.

Finalement, la méthode RSD développée pour des systèmes partiellement stratifiés tels que l'Hudson a été appliquée à un système stratifié (le fjord de Randers). Nous avons vu (chapitre 3.3) que les régressions linéaires entre la variation observée d'O_2, la profondeur, la salinité et le temps donnait des résultats associés à une large erreur. Il faut souligner que cette méthode impliquant l'utilisation de transects le long d'un estuaire à différentes périodes de la journée se limite logiquement à des systèmes de relativement faible superficie.

Pour résumer, ces méthodes en système ouvert sont facilement applicables mais requièrent de réelles précautions principalement liées à l'estimation des échanges de gaz avec l'atmosphère ainsi que qu'à la connaissance des processus physiques ou biologiques susceptibles d'intervenir dans la dynamique de ces gaz.

Les avantages et inconvénients de chaque méthode sont synthétisés dans le Tableau 5.

Tableau 5 Synthèse des avantages et inconvénients des méthodes testées dans cette étude

Méthode	Processus estimés	Avantages	Inconvénients/Difficultés
Incubations O_2	GPP, CR, nitrification, NEP	- Mesure direct des processus - Prise en compte de la nitrification possible	- Coût important en temps - Diminution turbulence (*bottle effect*) - Prise en compte de toutes les communautés - Assume respiration constante sur 24h - Nécessité de facteurs de conversion (O_2 vs. C) - Sous-estimation possible CR benthique - Difficultés d'extrapolation
RSD	GPP, CR, NEP	- Méthode intégrative - Facilement applicable - Etude à long terme possible	- Possible problème en système stratifié - Assume respiration constante sur 24h - Problème sites avec nitrification - Paramétrisation du coefficient d'échange - Nécessité de facteurs de conversion (O_2 vs. C)
LOICZ	NEP $n_{fix-ndenit}$	- Méthode intégrative - Paramètres facilement mesurables (DIP, DIC, DIN) - Etude à long terme possible	- Différence de salinité nécessaire entre le système étudié et l'extérieur - Si appliquée au DIP: problème processus d'adsorption/désorption - Si appliquée au DIC: paramétrisation du coefficient d'échange - Connaissance de toutes les sources d'eau et de matière - Nécessité de facteurs de conversion (P vs. C et P vs. N) - Pas d'estimation de GPP et CR

Chapitre 5

Conclusions et perspectives

Par le biais d'une compilation de paramètres métaboliques en zone côtière à partir de méthodes d'incubations et basés sur la méthode Land-Ocean Interaction in the Coastal Zone (LOICZ; Gordon et al. 1996), ce travail a permis de mettre en évidence d'importantes lacunes au niveau de notre compréhension du cycle du carbone en zone côtière. En particulier, nous avons constaté que le paramètre le moins bien documenté dans la littérature est la respiration planctonique. Il devient crucial d'obtenir une connaissance approfondie de ce processus au niveau de la zone côtière afin d'être en mesure d'estimer les flux de matière entre celle-ci et l'océan ouvert.

Une amélioration de ces connaissances passe également par (1) par une multiplication des mesures de métabolisme, particulièrement dans des régions jusqu'à maintenant relativement négligées telles que le bassin Est de la mer Méditerranée, la Baltique nord et le bassin Nord de la mer du Nord et/ou (2) l'utilisation de méthodes intégratives permettant l'estimation du statut métabolique de la zone côtière à de plus larges échelles spatio-temporelles.

Nous avons testé plusieurs de ces méthodes: la méthode LOICZ, ainsi que d'autres méthodes en système ouvert telle que la méthode response surface difference (RSD) développée par Swaney *et al.* (1999) et l'utilisation de cycles journaliers de carbone inorganique dissous (DIC) et d'oxygène (O_2), dans trois sites côtiers européens bien contrastés. La principale conclusion de ce travail est qu'il n'existe malheureusement pas de "recette miracle". En effet, bien que les différentes méthodes fournissent des résultats similaires dans la plupart des cas, chacune d'entre elles possède clairement des inconvénients qui limitent leur champ d'application.

La méthode LOICZ semble intéressante car il s'agit d'une technique simple se basant sur des paramètres fréquemment mesurés en zone côtière depuis de nombreuses années. Toutefois, nous avons montré que cette méthode appliquée au phosphore inorganique dissous (DIP) ne pouvait être utilisée dans des estuaires turbides car une part significative des flux non-conservatifs de DIP ne sont pas liés à la production et minéralisation de matière organique mais à des interactions entre le DIP et les particules en suspension et(ou) le sédiment (processus d'adsorption/desorption). Ceci ajouté au fait qu'un gradient de salinité est nécessaire pour estimer les flux d'échange entre le système et l'extérieur limite son utilisation au niveau de système peu turbides recevant des apports en eau douce suffisants. Il faut souligner également qu'à l'heure actuelle, il est très difficile d'estimer dans quelle mesure les résultats obtenus par la méthode LOICZ sont fiables. En effet, les estimations sont généralement basées sur les paramètres moyennés sur de longues périodes de temps et des surfaces importantes. Il existe actuellement des programmes permettant de développer des modèles LOICZ. Il serait très intéressant d'intégrer à ces programmes des méthodes permettant d'estimer les erreurs associées telles que la méthode Monte-Carlo.

Les autres méthodes en système ouvert (RSD, cycles de DIC et O_2) sont également de plus en plus utilisées. Une différence significative concernant les estimations de la production primaire brute (GPP) et la respiration communautaire (CR) a été mise en évidence. Ce n'est pas la première fois qu'une telle observation est faite et cette incohérence mériterait une attention plus importante à l'avenir. De plus, ces méthodes sont difficilement applicables dans des systèmes où d'autres processus peuvent avoir un impact sur la variation du constituant considéré (ex: O_2 consommé par la nitrification, CO_2 produit par la précipitation de carbonate de calcium).

Le problème majeur associé à l'utilisation de ces méthodes en milieu ouvert reste toutefois l'estimation du coefficient d'échange du gaz considéré (CO_2 ou O_2) à l'interface air-mer. Le présent travail a clairement montré que la relation existant entre celui-ci et la vitesse du vent différait en fonction du site étudié (Borges et al. 2004), sans toutefois pouvoir valider la relation établie pour l'estuaire de l'Escaut. Les écarts de production nette observés entre les mesures par incubations et la méthode LOICZ appliquée au DIC peuvent avoir de nombreuses explications (cf. chapitre 3.4). Toutefois, il serait intéressant de comparer la relation établie dans l'Escaut avec des estimations du coefficient d'échange basées sur des méthodes de traceurs tels que les chlorofluorocarbones (Clark et al. 1992), ^{222}Rn (Elsinger and Moore 1983), 3He et SF6 (Clark et al. 1994; Carini et al. 1996).

Dans l'introduction, nous avons mentionné que la calcification semblait avoir un rôle très important au niveau du cycle du carbone en zone côtière. Pour le moment, les estimations de production de carbonate de calcium (Milliman 1993; Milliman and Droxler 1996) concernent principalement les récifs coralliens, peu d'études s'étant focalisées sur les systèmes tempérés. Il serait donc très intéressant d'étudier la contribution de la calcification, pélagique et benthique, au niveau du cycle du carbone dans la zone côtière européenne. Ceci sera une des problématiques du programme européen "Carbo-Ocean" qui sera initié fin 2004-début 2005.

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