Université de Liège

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Dynamics of carbon dioxide and methane in the mangroves of Vietnam, and the rivers and the lagoons of Ivory Coast

Dynamique du dioxyde de carbone et du méthane dans les mangroves du Vietnam, les rivières et les lagunes de la Côte d'Ivoire

Dissertation présentée par

Yéfanlan José-Mathieu Koné

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Travaux co-dirigés par
Dr A.V. Borges et Pr F. Ronday

Jury :
Pr J.-M. Bouquegneau, Professeur à l'Université de Liège (Président du Jury)
Dr A.V. Borges, Chercheur Qualifié au FNRS (Promoteur)
Pr F. Ronday, Administrateur de l'Université de Liège (Co-Promoteur)
Pr A. Ouattara, Professeur à l'Université d'Abobo-Adjamé
Dr B. Delille, Chercheur à l'Université de Liège
Dr G. Abril, Chargé de recherche au CNRS
Dr S. Bouillon, Professeur associé à la Katholieke Universiteit Leuven

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Abstract

Tropical near-shore coastal ecosystems receive 60% of the world freshwater and an equivalent fraction of organic matter. Thus, these regions are expected to have a major role in the overall budgets of CO_2 and CH_4, two major greenhouse gases, in the coastal and global oceans. As a contribution to the understanding of the role of the coastal ocean and continental aquatic environments in the global cycle of these gases, we report the seasonal variability of partial pressure of CO_2 (pCO_2), CH_4 concentration, related air-water fluxes of CO_2 and CH_4 and ancillary data in several contrasted tropical coastal ecosystems in terms of geomorphology, lithology of the drainage basin, freshwater and seawater inputs, and riparian population and related anthropogenic pressure (land use change, aquaculture, waste waters release, eutrophication, and invasive species proliferation).

We investigated waters surrounding two forested mangrove sites (Tam Giang and Kiên Vàng) located in Ca Mau Province (South-West Vietnam), in five lagoons (Grand-Lahou, Ebrié, Potou, Aby and Tendo) and three rivers (Comoé, Bia and Tanoé) flowing into these lagoons in Ivory Coast.

Data from the two forested mangrove sites in South-West Vietnam were obtained during the dry and rainy seasons, providing for the first time information on the seasonality of dissolved inorganic carbon (DIC) and air-water CO_2 fluxes in the water surrounding mangrove ecosystems. Our data suggest an increase of heterotrophic activity in sediments and/or the water column during the rainy season that could be due to an increase of carbon inputs from soil flushing, probably from the land surrounding the mangrove forests. The air-water CO_2 fluxes we computed are consistent with the few data available so far in waters surrounding mangrove forests, and confirming that this emission of CO_2 is significant for the carbon budget of mangrove forests, and also for the regional CO_2 budget at tropical and sub-tropical latitudes.

Data in lagoons and rivers of Ivory Coast were obtained during four cruises covering the main climatic seasons (high dry season, high rainy season, low dry season and low rainy season). The three rivers were oversaturated in CO_2 and CH_4 with respect to atmospheric equilibrium, and the seasonal variability of pCO_2 and CH_4 concentrations was due to dilution during the flooding period. The invasive floating hyacinth *Eichhornia crassipes* that cover

these rivers can significantly contribute to the CO_2 emission to the atmosphere from the aquatic compartment due to root respiration and organic matter degradation derived from these plants. However, floating macrophytes are atmospheric CO_2 sinks.

The surface waters of the Potou, Ebrié and Grand-Lahou lagoons were oversaturated in CO_2 and CH_4 with respect to the atmosphere during all seasons. In contrast, the Aby and Tendo lagoons exhibit enhanced over-saturation in CH_4 but under-saturation in CO_2 because of their permanent haline stratification (unlike the other lagoons) that seemed to lead to higher phytoplankton production and export of organic carbon below the pycnocline. However, the permanent stratification also leads to anoxic bottom waters favorable to a large CH_4 production. Thus, the largest CH_4 over-saturations and diffusive air-water CH_4 fluxes were observed in the Tendo and Aby lagoons while they can act as a sink for atmospheric CO_2. We highlight the importance of physical settings (permanent versus seasonal stratification) in controlling the organic C flows, modulating the atmospheric CO_2 source-sink status, and the intensity of CH_4 emissions to the atmosphere in these near-shore coastal ecosystems.

Résumé

Les écosystèmes côtiers tropicaux reçoivent 60% de l’eau douce mondiale et une fraction équivalente de la matière organique. Ainsi, ces régions sont supposées avoir un rôle important dans les budgets globaux de CO_2 et de CH_4, deux gaz à effets de serre majeurs, dans les océans côtier et ouvert. Pour contribuer à la compréhension du rôle de l’océan côtier et des environnements aquatiques continentaux dans les cycles globaux de ces gaz, nous rapportons la variabilité saisonnière de la pression partielle de CO_2 (pCO_2), de la concentration en CH_4, des flux air-eau de CO_2 et de CH_4 ainsi que de certains paramètres complémentaires dans plusieurs écosystèmes côtiers tropicaux contrastés en termes de géomorphologie, de lithologie du bassin versant, d'entrées d'eau douce et d'eau de mer, de populations avoisinantes et de la pression anthropique résultante (changement dans l'utilisation des sols, aquaculture, rejets d'eaux usées, eutrophisation et prolifération d'espèces invasives).

Nous avons étudiés les eaux entourant deux sites de forêts de mangroves (Tam Giang et Kiên Vàng) situés dans la Province de Ca Mau (sud-ouest du Vietnam), cinq lagunes (Grand-Lahou, Ebrié, Potou, Aby et Tendo) et trois rivières (Comoé, Bia et Tanoé) se jetant dans ces lagunes de Côte d’Ivoire.

Les données des deux sites de forêts de mangroves du sud-ouest du Vietnam ont été obtenues pendant les saisons sèche et pluvieuse, fournissant pour la première fois une information sur la variabilité saisonnière du carbone inorganique dissous (DIC) et des flux air-eau de CO_2 dans des eaux entourant des écosystèmes de mangroves. Nos données montrent une augmentation de l’activité hétérotrophe dans les sédiments et/ou dans la colonne d’eau pendant la saison pluvieuse qui pourrait être due à une augmentation des apports de carbone liés au lessivage des sols, probablement de la terre entourant les forêts de mangroves. Les flux air-eau de CO_2 que nous avons calculés sont en accord avec les quelques rares données disponibles dans les eaux entourant des forêts de mangroves, et confirment que les émissions du CO_2 sont significatives par rapport au budget du carbone des forêts de mangroves, mais aussi par rapport au budget régional des émissions de CO_2 aux latitudes tropicales et subtropicales.

Les données dans les lagunes et des rivières de Côte d’Ivoire ont été obtenues pendant quatre campagnes couvrant les principales saisons climatiques (grande saison sèche, grande saison pluvieuse, petite saison sèche, petite saison pluvieuse). Les trois rivières étaient sursaturées en CO_2 et en CH_4 par rapport à l’équilibre atmosphérique, et la variabilité saisonnière de la pCO_2 et des concentrations du CH_4 était liée à la dilution durant la période de crue. Cependant, les espèces invasives de jacinthes flottantes *Eichhornia crassipes* qui recouvrent ces rivières peuvent être des contributrices significatives aux émissions de CO_2 depuis le compartiment aquatique vers l’atmosphère à cause de la respiration des racines et de la degradation de la matière organique provenant de ces plantes. Toutefois, les macrophytes flottants sont des puits du CO_2 atmosphérique.

Les eaux de surface des lagunes Potou, Ebrié et Grand-Lahou étaient sursaturées en CO_2 et CH_4 par rapport à l'atmosphère à toutes les saisons. Par contre, les lagunes Aby et Tendo présentaient des sursaturations accrues en CH_4, mais des sous-saturations en CO_2 du fait de leur stratification haline permanente qui semblait conduire à une forte production phytoplanctonique et à une exportation du carbone organique en dessous de la pycnocline. Ainsi, les plus fortes sursaturations et des flux diffusifs air-eau de CH_4 ont été observés dans les lagunes Aby et Tendo qui sont cependant des puits de CO_2 pour l'atmosphère. Ces résultats soulignent l’importance des caractéristiques physiques des lagunes (stratification) dans le contrôle de la dynamique du carbone organique, la modulation du statut source-puits de CO_2 atmosphérique et l’intensité des émissions de CH_4 vers l’atmosphère dans ces écosystèmes côtiers.

Contents

1 Introduction

1.1 Global cycle of CO_2

1.1.1 CO_2 and the earth system

Atmospheric carbon dioxide (CO_2) concentration is one of the key variables of the Earth system flowing between the atmosphere, oceans, soils and biota and determines climate at the Earth's surface. Atmospheric CO_2 plays several roles in this system, for example, it is the carbon source for nearly all photosynthetic organisms, and the source of carbonic acid (H_2CO_3) to weather rocks. It is also an important greenhouse gas, with a central role in modulating the climate of the planet (e.g., Goudriaan, 1995; Nemani et al., 2003; Feely et al., 2004; Harley et al., 2006; IPCC, 2007; Canadell et al., 2007; Cole et al., 2007).

Figure 1.1 shows the major carbon reservoirs and the rates at which carbon is transferred among these reservoirs, known as the carbon cycle. Two features are immediately evident: i) the water column of the oceans holds much more carbon than the atmosphere, although much lower than in marine sediments; ii) the exchange between the atmosphere and the biosphere and between the atmosphere and the surface oceans is much higher than the other fluxes. Looking at the relative sizes of the reservoirs of carbon, it might at first sight surprising that the burning of fossil fuels could be a problem because there appears to be plenty of capacity for the uptake of CO_2 from the atmosphere into other reservoirs, especially the oceans.

One of the more commonly known exchanges in the carbon cycle is its absorption, in the form of CO_2 by trees and herbaceous plants on land during photosynthesis (the production of organic carbon from inorganic carbon), and subsequent release back into the atmosphere by respiration. As shown on **Figure 1.1**, every year the atmosphere exchanges ~122 PgC ($1 \text{ Pg} = 1\text{Gt} = 10^{15}$ g) with the terrestrial ecosystems through photosynthesis and respiration. The uptake of carbon through photosynthesis is gross primary production (GPP). At least half of this production is respired by the plants themselves (autotrophic respiration), leaving a net primary production (NPP) of ~60 PgC. Recent estimates of global terrestrial NPP vary between 56.4 and 62.6 PgC yr^{-1} (Houghton, 2005). NPP is largely consumed by grazers such as insects and various kinds of animals or decomposed by fungi and bacteria. Live biomass is estimated to be about 550 PgC mainly in the form of wood (Houghton, 2005).

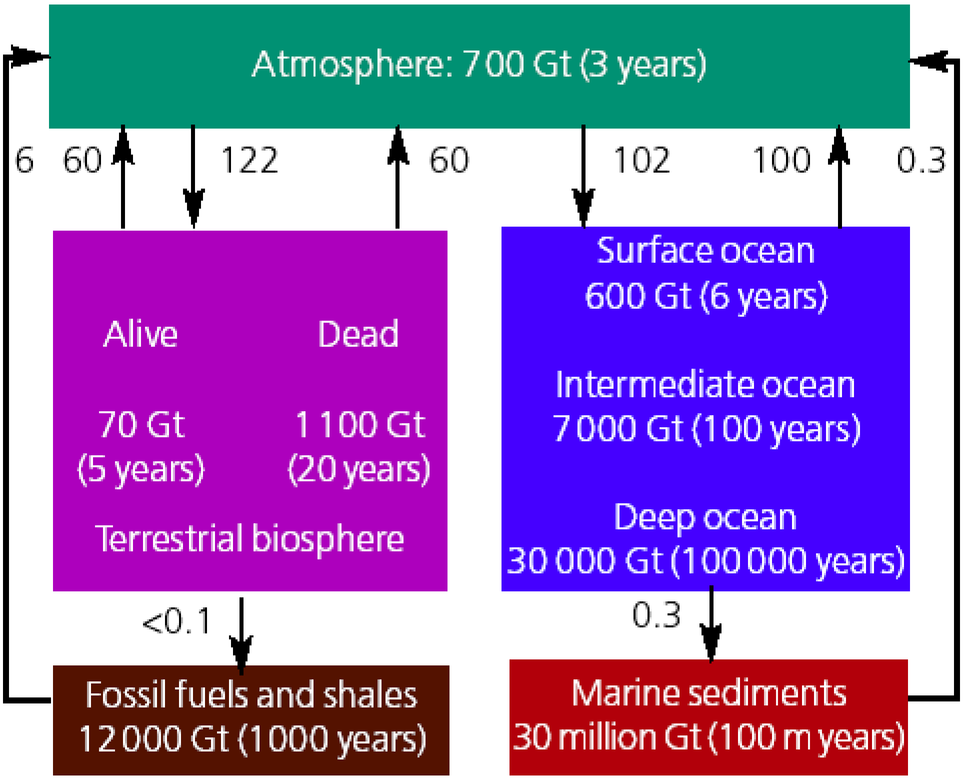

Figure 1.1: Diagram of the global carbon cycle showing sizes of carbon reservoirs (units are gigatonnes (Gt); (1Gt = 10^{15} grams) and exchanges rates (fluxes) between reservoirs (units are Gt yr^{-1}) in the terrestrial (green) and the oceanic (dark blue) parts of the Earth system. Also shown are residence times (in years) of carbon in each reservoir: however, some mixing between the deep oceans and marine sediments does occur on shorter timescales. Carbon exchanges readily between the atmosphere, the surface oceans and terrestrial biosphere. However, the residence time of carbon in the atmosphere, oceans and biosphere combined, relative to exchange with the solid earth, is about 100 000 years (Royal Society, 2005). Note that this budget does not take account the CO_2 fluxes in coastal ecosystems, continental aquatics ecosystems and the continental weathering.

After death it turns to litter and eventually to soil organic matter. Deforestation reduces the uptake of atmospheric CO_2 by terrestrial biosphere and on the long term, this will be an additional source of CO_2 to the atmosphere at the rate of about 1 to 2 PgC yr^{-1} (Goudriaan, 1995). However, satellite observations and model estimates indicate that the global NPP of land ecosystems has increased by 6% (3.4 PgC between 1982 to 1999) (Nemani et al., 2003). The largest increase was in tropical ecosystems particularly in the

Amazon region. Despite this fact, tropical regions are not, on average, a significant net sink for carbon due to the fact that at such latitudes, NPP and soil respiration are tightly coupled compared with ecosystems at other latitudes. Thus, in the future, the combined effects of higher CO_2 concentrations, warmer temperatures and changing hydrological regime will significant affect regional ecology processes and hence carbon dynamics (Nemani et al., 2003).

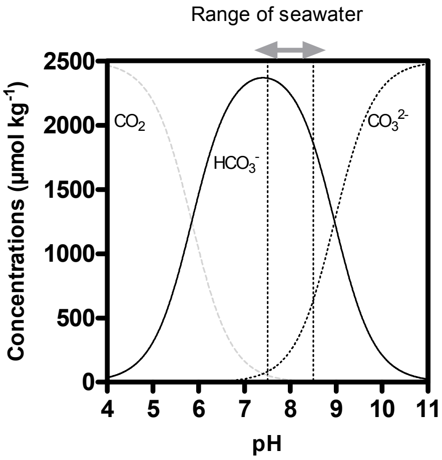

Figure 1.2: Variation of the concentrations (µmol kg^{-1}) of the three inorganic forms of CO_2 dissolved in seawater as function of pH. The arrows at the top indicate the narrow range of pH (7.5-8.5) that is likely to be found in the oceans now and in the future.

Carbon dioxide also dissolves in the oceans and can be released back to the atmosphere, making the oceans a considerable point of exchange in the carbon cycle. Dissolved CO_2 in seawater exists in three main forms collectively known as dissolved inorganic carbon (DIC): i) aqueous CO_2 (about 1% of DIC); in the present thesis this term also includes carbonic acid (H_2CO_3); ii) bicarbonate ion (HCO_3^-, about 90% of DIC); and iii) carbonates ion (CO_3^{2-}, about 9% of DIC). Thus under current ocean conditions (pH between 7.5 and 8.5), bicarbonate is the most abundant form of DIC in seawater followed by carbonate and aqueous CO_2 (**Figure 1.2**). One of the overall effects of CO_2 dissolving in seawater is to increase the concentrations of hydrogen ions (H^+). This is the result of an initial reaction between water (H_2O) and CO_2 to form H_2CO_3. This weak acid readily releases H^+ and is in equilibrium with CO_3^{2-} and HCO_3^- and as shown on **Figure 1.2**, the concentration of the three forms of DIC is a function of the pH of seawater. Thus DIC operates as a natural buffer to the addition of H^+ and it is called the seawater carbonate buffer. However, the capacity of the buffer to restrict pH ranges diminishes as increased amounts of CO_2 are absorbed by oceans. This is because when CO_2 dissolves, the thermodynamic equilibrium that take place reduces the amount of CO_3^{2-} ions, which are required for the seawater buffer. Based on recent measurements in the North Sea, Thomas et al. (2007) demonstrate a significant decline in the buffering capacity in the inorganic carbonate system in the surface waters due to the uptake of anthropogenic CO_2. The projections of future pH change also show that if the release of CO_2 from human activities is allowed to continue on present trends this will lead to a decrease in pH of up to 0.5 units by the year 2100 in the surface oceans (Caldeira and Wickett, 2005).

Lower surface water temperatures tend to increase CO_2 uptake, whilst surface warming drives its release (e.g., Hales et al., 2003). This process is known as the solubility pump and it is quite efficient in atmospheric CO_2 uptake at high latitudes. Warming of the oceans leads to increased vertical stratification, which would reduce CO_2 uptake, in effect, reducing the oceanic volume available to CO_2 absorption from the atmosphere. Stratification will reduce the return flow of both carbon and nutrients from the depth to the surface. The removal of nutrients from the upper oceans with a slower return flow could have negative impact on life in the surface oceans. In fact, organisms within the surface ocean exchange CO_2 in much the same way as the biological processes on land. Although the biological uptake (also called the biological pump) of CO_2 per unit area of the surface ocean is lower than that in the most terrestrial systems, the overall biological absorption is almost as large as that in terrestrial environment due to the fact that oceans occupy 70% of the Earth's surface (Field et al., 1998). Without the biological pump, the upper oceans would be oversaturated with respect to CO_2 and the atmospheric levels of CO_2. This biological pump can be separated into an organic pump and calcium carbonate pump. The gross flux of organic pump is estimated to be 20-51 PgC yr^{-1} (Wong and Matear, 1995). The calcium carbonate ($CaCO_3$) pump plays also an important role in the marine carbon cycle. In the upper ocean, several autotrophs and heterotrophs form calcium carbonate skeletons by precipitating carbonate ions. The biogenic $CaCO_3$ particles can sediment to depth ($CaCO_3$ pump) where they can dissolve or be preserved in sediments. The calcium $CaCO_3$ pump creates a surface depletion of DIC and alkalinity (TA) as described by the following equation:

$$Ca^{2+} + 2HCO_3^{-} \longleftrightarrow CaCO_3 + H_2O + CO_2 \quad (1)$$

Although the $CaCO_3$ pump exports carbon the increase of CO_2 in surface waters creates a source for atmospheric CO_2.

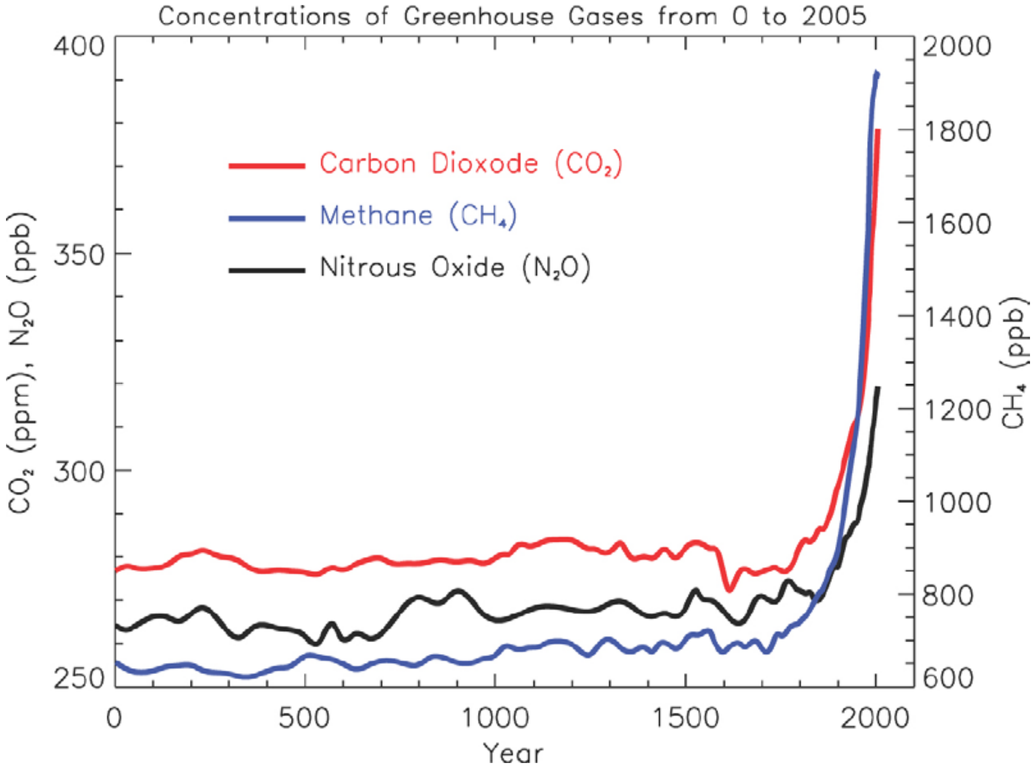

Figure 1.3: Atmospheric concentrations of important long-lived greenhouse gases over the last 2000 years. Increases since about 1750 are attributed to human activities during the industrial era. Concentration units are parts per million (ppm) or parts per billion (ppb), indicating the number of molecules of the greenhouse gas per million or billion air molecules, respectively, in an atmospheric sample (IPCC, 2007).

The oceans are a substantial carbon reservoir (**Figure 1.1**) and on short timescales (~ 100 yr), the largest CO_2 fluxes are with the atmosphere. The pre-industrial oceanic carbon reservoir has been estimated at about 38 000 PgC, compared with the about 700 PgC in the atmosphere and somewhat less than 2000 PgC in the terrestrial biosphere (Brovkin et al., 2002). These reservoirs exchange quantities of carbon each year that are large relative to the amount of carbon stored within the reservoirs themselves. **Figure 1.1** shows that the oceans are acting as an important carbon sink, absorbing 2 PgC yr^{-1} more CO_2 than they are releasing into the atmosphere. This is small in comparison to the amount of carbon that is cycled between the different reservoirs but is a significant proportion of the 6 GtC yr^{-1} into the atmosphere from human activities (**Figure 1.1**). However, it is important to note that, in this budget neither the fluxes of CO_2 in the coastal ocean nor in the freshwater ecosystems are taken account. As it will be discussed in the next sections, coastal environments are very heterogeneous and they are characterised by high spatial and temporal variability of surface partial pressure of CO_2 (pCO_2). Some are sources of CO_2 to atmosphere while the others are acting as sinks of atmospheric CO_2. Because of this variability, it is difficult to integrate the corresponding fluxes in the global budget. Freshwater ecosystems (streams, lakes, reservoirs, wetland and rivers) are sources of CO_2 to the atmosphere but, they are generally neglected in the global budget. Continental weathering acts as a sink of atmospheric CO_2 and could represent a flux of about 0.7 PgC yr^{-1} of carbon exported from the continent to the oceans (Ludwig et al., 1998). Thus, the inclusion of CO_2 fluxes from continental ecosystems and the coastal ecosystems could reduce the gap estimates of the terrestrial carbon sink based on the carbon-stock change models globally (Siemens, 2003) or regionally (Borges et al., 2006).

The carbon stored in some reservoirs, such as rocks and organic rich shale, exchanges with the other reservoirs on geological timescales. As a result, these reservoirs will not affect the carbon content of the atmosphere or the oceans on shorter timescales (<1000 years) unless exchange rates are artificially increased by human activities such as limestone mining, oil, gas and coal extraction and consumption. It is well established today that human activities have increased atmospheric concentrations of CO_2 to levels unprecedented for at least 420 000 years and possibly for the past tens of millions of years (IPCC, 2007). Antarctica ice core data indicate that atmospheric CO_2 concentrations during the past 650 000 years are highly correlated with changes in temperatures, varying between minima of ~200 parts per million (ppm) during cold glacial periods and maxima of 280 to 300 ppm during interglacials. By comparison, atmospheric concentrations of CO_2 averaged 380 ppm in 2005 (IPCC, 2007). Prior to industrial revolution, land use change was likely a human source of greenhouse gas (GHG) emissions. The land clearing and rice cultivation by expanding human settlements in Europe and Asia (during the late Holocene) already began to alter the atmospheric composition of greenhouse gases, thus making the onset of the “Anthropocene era” of earth climate history (Ruddiman, 2003). **Figure 1.3** shows the atmospheric concentrations of the most important natural occurring greenhouse gases (besides water vapour) over the last 2000 years (IPCC, 2007). Increases of greenhouse gases since about 1750 are attributed to human activities during the industrial era. Currently CO_2 accounts for ~63% of anthropogenic greenhouse forcing (IPCC, 2007). Due to their high global warming potentials (GWP) relative to CO_2 (**Table 1.1**), CH_4 and N_2O currently contribute ~18% and ~6%, respectively, to anthropogenic greenhouse forcing (IPCC, 2007).

Table 1.1: Global warming potentials (GWP) of CO_2, CH_4 and N_2O (CO_2-equivalent*); estimates for 20, 100, and 500 year timeframes (Upstill-Goddard et al., 2007).

	20 years	100 years	500 years
CO2	1	1	1
CH_4	62	23	7
N_2O	275	296	156

*CO_2-equivalent emission is the amount of CO_2 that would cause the same time-integrated radiative forcing over a given time horizon, as an emitted amount of a long-live greenhouse gas (GHG) or a mixture of greenhouse gases (GHGs). The equivalent CO_2 emission is obtained by multiplying the emission of a GHG by its GWP for the given time horizon. For a mix of GHGs, it is obtained by summing the equivalent CO_2 emissions of each gas. Equivalent CO_2 emission is a standard and useful metric for comparing emissions of different GHGs but does not imply the same climate change responses (IPCC, 2007).

Roughly half of the CO_2 released by human activities between 1800 and 1994 is now stored in the ocean (Sabine et al., 2004), and about 30% of modern CO_2 emissions are taken by oceans today (Feely et al., 2004). However, warming reduces terrestrial and ocean uptake of atmospheric CO_2, increasing the fraction of anthropogenic emissions remaining in the atmosphere (IPCC, 2007). In fact, whereas both land and ocean sinks continue to accumulate carbon on average at 5.0 ± 0.6 PgC yr^{-1} since 2000; large sinks have been weakening (Canadell et al., 2007). For instance, in the Southern Ocean, the poleward displacement and intensification of westerly winds caused by human activities (related to both greenhouse gas emissions and ozone loss) has enhanced the ventilation of carbon-rich waters normally isolated from the atmosphere at least since 1980, and contributed nearly half of the decrease in the ocean CO_2 uptake (Le Quéré et al., 2007). On land, a number of major droughts in mid latitude regions in 2002-2005 have contributed to the weakening of the growth rate of terrestrial carbon sink in these regions (Canadell et al., 2007). Continued uptake of atmospheric CO_2 is expected to substantial decrease oceanic pH over the next few centuries, changing the saturation horizons of aragonite, calcite and other minerals essential to calcifying organisms (Kleypas et al., 1999; Feely et al., 2004; Orr et al. 2005).

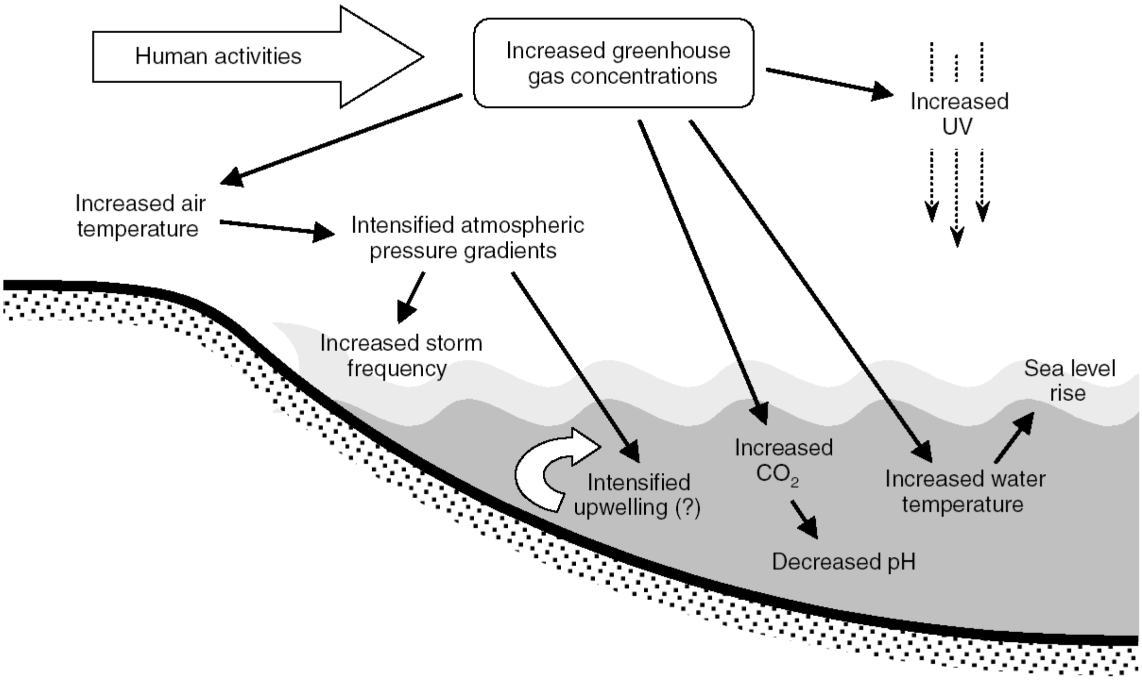

Figure 1.4: Important abiotic changes associated to climate change (Harley et al., 2006). Human activities such as fossil fuel burning and deforestation lead to higher concentrations of greenhouse gases in the atmosphere, which in turn leads to suite of physical and chemical changes in coastal oceans. The question mark indicates that the relationship between climate change and upwelling is uncertain.

While many organisms have adapted to thermal fluctuations in the last few millions years, the expected change in pH are higher than any other pH changes inferred from the fossil record over the past 200-300 millions years (Caldeira and Wickett, 2003). Together, elevated atmospheric CO_2 and the resultant increase in the global mean temperature will result in a cascade of the physical and chemical changes in marine systems (**Figure 1.4**). Because warming trends will be stronger over continental interiors than over oceans, the atmospheric pressure gradient, and thus wind fields, along the ocean margins will intensify (Harley et al., 2006). Atmospheric circulation changes might also change storms frequency (Bromirski et al., 2003), and will also influence precipitation patterns that will affect coastal salinity, turbidity and inputs of terrestrial-derived nutrients and pollutants (IPCC, 2007). Climate change could also alter large scale ocean circulation. Increasing CO_2 levels in the atmosphere have been postulated to deplete the ozone layer (Austin et al., 1992), potentially leading to enhanced levels of ultraviolet radiation at the Earth's surface.

1.1.2 Air-water CO_2 exchanges:

The sequestration of atmospheric CO_2 by the surface water depends on differences in the partial pressure of CO_2 between the surface water ($pCO_{2\ water}$) and the atmosphere ($pCO_{2\ air}$), ΔpCO_2. When ΔpCO_2 is positive, i.e. $pCO_{2\ water}$ is greater than $pCO_{2\ air}$, CO_2 gas escapes from the surface water to the atmosphere; the aquatic ecosystem is referred as a source of CO_2. If ΔpCO_2 is negative then the aquatic ecosystem is a sink for atmospheric CO_2. The magnitude of the air-sea flux of CO_2 (F in mmol m^{-2} d^{-1}) between the surface water and atmosphere is described by the following equation:

$$F = \varepsilon . \alpha . k . \Delta pCO_2 \quad (2)$$

The flux is a function of the chemical enhancement factor of gas exchange (ε; that is usually negligible, except under very low turbulent conditions), solubility coefficient (α in mol atm^{-1} m^{-3}), gas transfer velocity (k in cm h^{-1}) and ΔpCO_2 (in ppm).

Methodology for measuring pCO_2 in both air and water has progressed to the stage where it is now possible to make continuous, accurate measurements of the ΔpCO_2 by a variety of means in almost any type of aquatic system. Thus, the largest uncertainty in the computation of F comes from k (since α is straightforwardly computed from salinity and water temperature) that depends on water turbulence mainly generated by wind stress and on a number of processes including surfactant damping, boundary layer stability, precipitation, air bubbles, wave breaking and evaporation/condensation. Therefore, developing accurate estimates of the gas transfer velocity in aquatic systems is an important and controversial research (e.g., Raymond and Cole, 2001; Borges et al., 2004). For consistency, k is often reported as k_{600} or k_{660} which is k for CO_2 at 20 °C (Schmidt number, (Sc)) of 600 or 660 in freshwater and seawater, respectively. The Schmidt number is defined as the ratio of transfer coefficients for momentum and mass, which are respectively kinematic viscosity of water (ν_w in m^2 s^{-1}) and the molecular diffusivity coefficient (D in m^2 s^{-1}) of the gas in water. This latter is specific to a given gas, and depends on temperature and salinity and is related to the Schmidt number by the following equation:

$Sc = \nu_w/D$ (3)

Thus, the main resistance to the CO_2 transfer across the air-water interface is due to molecular diffusion through a laminar layer of water adjacent to the air-water interface. The thickness of this layer (~10 to ~100 µm) controls *k* and depends largely on the wind speeds in open oceans, while in rivers and streams, the source of turbulence is mainly due to bottom stress of the flow and *k* is a function of the stream depth and flow velocity. In estuaries, turbulence in water can originate from both wind and tidal currents, and therefore depends on the depth, mean tidal velocity, and wind regime of a given estuary. For instance, Borges et al. (2004) showed that the contribution of turbulence generated by tidal current is negligible in the microtidal estuary (such as Randers Fjord) while is significant at low to moderate wind speeds in macrotidal estuaries (such as Scheldt and Thames).

The way turbulence is taken account results in three main models of gas transfer at water surfaces (Brtko and Kabel, 1978). These models differ in the way the molecular diffusivity coefficient is accounted, hence also the Schmidt number.

In the film model, it is postulated that adjacent to the free liquid surface there exists a stagnant film below which the liquid is well mixed. It assumed that air-water exchange of gas is mainly controlled by molecular diffusion in the boundary layer (film). The film represents then the major resistance to the air-water exchange. The gas transfer velocity is therefore proportional to molecular diffusion:

$k \propto D \propto Sc^{-1}$

The boundary layer model was first developed for smooth and rigid surfaces and then adapted for rough surfaces. In this model the mass transfer process is characterized by molecular diffusion into fluid elements transported from the bulk liquid to near the free liquid surface by turbulent eddies. The diffusion of mass into the fluid elements occurs for a prescribed time which is assumed to be uniform for all turbulent eddies. According this model *k* is given by:

$k \propto D^{2/3} \propto Sc^{-2/3}$

The surface renewal model considers that there should be a random age distribution of fluid elements rather than a uniform contact time. The fractional rate of replacement of the fluid elements belonging to any age group is assumed to be equal to the surface renewal rate. The air-water exchange is then limited by the rate of replacement of the micro-layer and *k* is given by:

$k \propto D^{0.5} \propto Sc^{-0.5}$

However, on the whole, wind speed is recognised as the main factor on *k*, since the effects of other factors such as waves, air bubbles, surface films, heat exchange at the interface are more or less directly related to wind conditions. Therefore, a variety of different parameterizations of *k* as a function of wind speed were proposed to calculate the CO_2 transfer velocity based on fields (deliberate tracers SF_6 and ^3He, bomb produced ^{14}C, ^{222}Rn deficiency method, floating bell method, eddy covariance, gradient flux technique) or laboratory approaches (wind-tunnel experiments). Simple linear relationships were suggested by Smethie et al (1985) and Tans et al. (1990), whereas Liss and Merlivat (1986) described *k* by three separated linear functions that each refer to different states of the sea surface. Functions including a quadratic term were proposed by Wanninkhof (1992), Jacobs et al. (1999), Nightingale et al. (2000) and Ho et al. (2006) whereas cubic functions have been considered by Schneider et al. (1999) and Wanninkhof and McGillis (1999). The most frequently *k*-wind relationships used in the open ocean are those from Liss and Merlivat (1986), Wanninkhof (1992), Wanninkhof and McGillis (1999) and Nightingale et al. (2000).

In estuaries, four approaches can be used to obtain *k*: natural tracers, purposeful tracer additions, floating domes and micro-meteorological methods (eddy covariance and gradient flux technique). However, *k* values obtained through these approaches are fairly different particularly at high wind speeds. Raymond and Cole (2001) argued that only the natural tracer approach provides the correct estimates of *k* in estuaries. However, Borges et al. (2004) based on floating method in three European estuaries, showed that the formulation of *k* as a function of wind speed is site specific in estuarine environments. Thus, there is no consensus hitherto to choice the best *k* formulation in estuarine environments and future works will help to resolve gas transfer velocity in these ecosystems. In the present work, only the formulations of *k* as function of wind speed from Carini et al. (1996) and Raymond and Cole (2001) have been used. These two *k* formulations as a function of wind speed are based on natural and deliberate tracers and values computed can be considered conservative (Zappa et al., 2003; Borges et al., 2004; Zappa et al. 2007).

Air-water exchange processes of CO_2 are much slower compared to other processes such as biological activity or even temperature change. Furthermore, due to seawater buffer effect, only a larger amount of CO_2 needs to be transferred to restore the equilibrium between the atmosphere and water surface than in freshwater. This buffering effect of seawater is called the Revelle factor (β). It is the ratio of the fractional change of pCO_2 in the water to the fractional change of the DIC in the water. This is an important quantity because it allows predicting the capacity of surface water to take up the anthropogenic atmospheric CO_2.

$$\beta = (\Delta pCO_2/pCO_2)/(\ \Delta DIC/DIC)\ (4)$$

β is about 14 for cold waters and 8 for warm waters (the global ocean average value is about 10). Thus, a 10% change in pCO_2 only results in a 1% DIC and air-water CO_2 exchange have a small effect on the DIC dynamics in water column.

Based on the air-water CO_2 fluxes, the world oceans can be divided into 3 major areas: i) CO_2 source areas in the equatorial oceans (mainly the equatorial Pacific) and in the coastal upwelling zones caused by the supply of CO_2 rich deep water, e.g. along the east boundary currents (California current, Humboldt current, Benguela current, …); ii) CO_2 sink areas in both hemispheres where enhanced solubility of CO_2 in the surface waters makes these areas capable of absorbing CO_2 from the atmosphere, e.g. the Sargasso sea in North Atlantic where high evaporation over precipitation produces very alkaline waters, or the Labrador sea and Weddell sea where cold surface water has high CO_2 solubility; iii) seasonal CO_2 source/sink areas where a complex interplay occurs between CO_2 uptake created by high productivity in summer and the high CO_2 solubility in winter and CO_2 release by winter remineralisation of detritus and summer heating of the water (Wong and Matear, 1995).

1.1.3 CO_2 chemistry in natural waters

The following section is based on DOE (1994), Millero (2007) and Dickson et al. (2007).

CO_2 in the atmosphere is a chemically uncreative gas but, when dissolved in water it reacts through thermodynamic equilibrium with bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydrogen (H^+) ions. The CO_2 chemistry in water is intimately linked to pH (**Figure 1.2**) according to the following equations:

$CO_2\ (g) \longleftrightarrow CO_2\ (aq)$ (5)

$CO_2\ (aq) + H_2O\ (1) \longleftrightarrow H_2CO_3\ (aq)$ (6)

$H_2CO_3\ (aq) \longleftrightarrow H^+(aq) + HCO_3^-\ (aq)$ (7)

$HCO_3^-\ (aq) \longleftrightarrow H^+\ (aq) + CO_3^{2-}$ (8)

The notations (g) and (aq) in equation (5) refer to the state of CO_2, respectively in gaseous and dissolved in seawater. It is not possible to analytically distinguish between the species CO_2 (aq) and H_2CO_3 (aq) and the latter is present in small quantities ([CO_2 (aq)]/([H_2CO_3 (aq)] ~ 650). Thus, these species are combined as the sum of the concentration of a hypothetical species, CO_2^* (aq).

$CO_2^*\ (aq) = CO_2\ (aq) + H_2CO_3\ (aq) \approx CO_2\ (aq)$ (9)

Redefining (5), (6) and (7), one gets:

$CO_2\ (g) \longleftrightarrow CO_2^*\ (aq)$ (10)

$CO_2^*\ (aq) + H_2O\ (1) \longleftrightarrow H^+\ (aq) + HCO_3^-\ (aq)$ (11)

The equilibrium constant of equations (8) and (11) are given by:

$K_1 = [H^+]\ [HCO_3^-]/\ [\ CO_2^*]$ (12)

$K_2 = [H^+] [CO_3^{2-}]/[HCO_3^-]$ (13)

While the pCO_2 is related to $[CO_2^*]$ by Henry's law:

$K_0 = [CO_2^*]/pCO_2$ (14)

K_0 is the solubility coefficient of CO_2 (µmol kg^{-1} μatm^{-1}) and K_1 and K_2 are the first and second dissociation constants of carbonic acid, respectively. These equilibrium constants above are dependant on temperature, pressure and salinity of the solution (e.g., seawater). Note that strictly, equations (12) to (13) should be expressed in terms of activities rather than concentrations. However, it is not possible analytically to determine activities of HCO_3^-, CO_3^{2-} or CO_2 since the concentration of a single ion cannot vary independently since electroneutrality is required. Hence, ocean chemists use apparent thermodynamic constants to examine the carbonate system. Furthermore, as the activity coefficients are approximately constant for the small amounts of reacting species in a background medium, these expressions are valid and correspond to "ionic medium" equilibrium constants based on a seawater medium.

The term pH describes the acidity of the medium and is defined as:

$pH = -\log(a_{H+})$ (15)

Where aH^+ is the activity of H^+

It is measured using a combined electrode or by spectrophotometry (in the present work a combined electrode method was used). However, as notice above, it is not possible to determine individual activities of ions. To overcome this situation, four operational definitions of pH in water were proposed. The first practical definition of pH (also called NBS scale) was given by the U. S. National Bureau of Standards. The pH_{NBS} of a solution determined from measurements the electrode potential (mV) is given by the following equation

:

$pH (X) = pH (S) + [E(X)-E(S)]/(2.303*RT/F)$ (16)

Where pH (X) and pH (S) are respectively the pH of water sample and the standard (buffer) at a given temperature, E (S) and E (X) are respectively the electrode potential (mV) of the standard and the sample water, R is the gas constant (8.3145107 J K^{-1} mol^{-1}), T is the absolute temperature (K), and F is the Faraday constant (96485.30929 °C mol^{-1}).

In solutions of high ionic strength, this scale does not give reliable values due to differences in liquid junction potentials of combined electrodes in the dilute buffers and the ionic media. Thus, it not recommended for seawater pH measurements, but it is appropriate for pH measurements in freshwater and brackish waters, such as estuaries, lagoons and mangrove ecosystems (Frankignoulle and Borges, 2001b). The three other pH scales have been developed for seawater based on the use of buffers made from artificial seawater, that largely overcome the problem of junction potential, since buffers and samples have similar ionic strengths. The difference between these three pH scales relies on the fact that the protons in seawater interact with sulphate and fluoride ions. The definition of these three pH scales is given in **Table 1.2**:

Table 1.2: Definition of pH scales in seawater

Free scale	$pH_F = -\log[H^+]_F$
Total scale	$pH_T= -\log([H^+]_F + [HSO_4^-])$
Seawater scale	$pH_{SWS}= -\log([H^+]_F + [HSO_4^-] + [HF])$

Note that in practice, the pH of seawater samples is computed using the Nernst equation given by equation (16). According to Dickson (1993), the Free scale is inappropriate because it omits the interaction with sulphate and fluoride ions, thus inducing an important bias in the pH measurements. The difference of pH measured on the Total hydrogen ion concentration scale and Seawater scale is very low (0.001), since $[HSO_4^-]$ is much higher than [HF] in seawater. Therefore, the Total hydrogen ion concentration is the most appropriate and commonly used pH scale for seawater samples.

One of the fundamental approach in inorganic carbon chemistry is the determination of the speciation, i.e. the concentrations of H^+, CO_2^*, HCO_3^- and CO_3^{2-}. Assuming that the values of K_1 and K_2 are known (determined from empirical formulations as a function of salinity and temperature), equations 12 and 13 constitute a system of two equations with four unknowns. Two additional equations that do not introduce additional unknowns are then needed to solve the speciation. There are four parameters that can be measured: pH, TA, DIC, and pCO_2. A combination of two of these parameters is used together K_1 and K_2 to obtain the speciation of the carbon dioxide system in water.

DIC is the sum of the three dissolved inorganic carbon species:

$$DIC = [CO_2^*] + [HCO_3^-] + [CO_3^{2-}] \quad (17)$$

The relative contribution to DIC of each species for standard seawater is approximately 90, 9 and 1% from respectively HCO_3^-, CO_3^{2-} and CO_2^*. Thus, CO_2* that is involved in air-seawater exchange and photosynthesis and respiration is a minor part of DIC. Also, CO_3^{2-} involved in calcification and $CaCO_3$ dissolution is also in much lower concentrations than HCO_3^{2-}. In freshwater ecosystems (e.g., rivers, lakes), the contribution of CO_2* to DIC pool is also low where HCO_3^- account for more than 80% of DIC.

The currently accepted definition of TA was proposed by Dickson (1981): the number of moles of hydrogen ion equivalent to the excess of proton acceptors (bases formed from weak acids with dissociation constant $K \leq 10^{-4.5}$ at 25°C and zero ionic strength) over proton donors (acids with $K > 10^{-4.5}$) in 1 kilogram of sample. TA is given by the following equation:

$$TA = [HCO_3^-] + 2[CO_3^{-2}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] + 2[S^{2-}] - [H^+] - [HSO_4^-] - [HF] - [H_3PO_4] \quad (18)$$

TA relates readily to the titration of water with a strong acid, usually HCl, in which the equivalence point is determined by following the decrease of pH. TA is therefore sometimes referred as titration alkalinity. In common seawater conditions, most species can be neglected in comparison with the bicarbonate and carbonate concentrations, except for borate so the above equation can be rewritten as follows:

$TA = [HCO_3^-] + 2[CO_3^{-2}] +[B(OH)_4^-] + [OH^-] - [H^+]$ (19)

The other components are minor species. However, in anoxic environments (such as estuaries), polluted rivers, or in phosphate and silicates rich deep seawater samples, the contribution of minor species can be significant. The borate ion does not introduce an additional unknown in the inorganic carbon calculations because its concentration can be readily computed from salinity, temperature and pH according the following equations:

$B(OH)_3 + H_2O \longleftrightarrow B(OH)_4^- + H^+$ (20)

$K_B = [B(OH)_4^-].[H^+]/[B(OH)_3]$ (21)

$B_T = [B(OH)_3] + [B(OH)_4^-]$ (22)

$[B(OH)_4^-] = K_B.B_T/([H+]+B_T)$ (23)

BT is computed as a function of salinity.

Carbonate alkalinity (CA) is given by the following equation:

$CA = [HCO_3^-] + 2[CO_3^{-2}]$ (24)

Equation 19 can be rewritten as:

$TA = CA + [B(OH)_4^-] + [OH^-] - [H^+]$ (25)

In the open ocean TA is conservative with salinity (e.g., Millero et al., 1998) but in coastal environments TA can be affected by several aerobic/anaerobic reactions that produce or consume protons (**Table 1.3**). During photosynthesis, TA increases due to the consumption of nitrates whereas the assimilation of ammonium has an opposite effect. The consumption of CO_2 during photosynthesis decreases DIC, pCO_2 and increases pH, whereas the aerobic respiration will obviously have the opposite effect of photosynthesis on DIC, pCO_2 and pH. Ammonification increases TA (proton consumption), whereas nitrification decreases TA (proton production).

Denitrification, Maganese, Iron and sulphate reductions, and methanogenesis that are anaerobic organic carbon degradation processes release CO_2 and therefore increase DIC, pCO_2 and decrease pH. All these processes (except the methanogenesis) increase TA by the consumption of protons. Anoxic processes occur mainly in the sediments, and due to the much larger abundance in seawater of SO_4^{2-}, sulphate reduction is the main anaerobic diagenetic organic matter degradation pathway. In presence of O_2, H_2S is oxidized producing protons.

Hence, a net flux of TA from the sediment to the water column should not occur unless reduced sulphur is permanently trapped, namely as pyrite, which only significantly occurs in iron rich sediments such as those of mangrove ecosystems. Furthermore, the acidification related to the production of protons from the oxidation of H_2S in sub-oxic and oxic layers of the sediments can lead to the dissolution of calcium carbonate ($CaCO_3$) and a net TA production (Barrón et al., 2006).

Table 1.3: stoichiometry of reactions that can affect TA, DIC, pCO_2 and pH in aquatic environments (adapted from Abril and Frankignoulle, 2001). R represents organic mater.

Photosynthesis:

$$106\,CO_2 + 138\,H_2O + 16\,NO_3^- \longleftrightarrow (CH_2O)_{106}(NH)_{16} + \mathbf{16\,OH^-} + 138\,O_2$$

$$106\,CO_2 + 138\,H_2O + 16\,NH_4^+ \longleftrightarrow (CH_2O)_{16} + \mathbf{16\,H^+} + 138\,O_2$$

Nitrification:

$$NH_4^+ + 2\,O_2 \longrightarrow NO_3^- + \mathbf{2\,H^+} + H_2O$$

Ammonification:

$$R\text{-}NH_2 + H^+ + H_2O \longrightarrow R\text{-}OH + NH_4^+$$

Precipitation /dissolution of $CaCO_3$:

$$Ca^{2+} + \mathbf{2HCO_3^-} \longleftrightarrow CaCO_3 + CO_2 + H_2O$$

Denitrification:

$$5\,CH_2O + 4\,NO_3^- + \mathbf{4\,H^+} \longrightarrow 5\,CO_2 + 7\,\mathrm{H2O} + 2\,N_2$$

Manganese reduction:

$$CH_2O + 2\,MnO_2 + \mathbf{4\,H^+} \longrightarrow CO_2 + 3\,H_2O + 2\,Mn^{2+}$$

Iron reduction:

$$CH_2O + 2\,Fe_2O_3 + \mathbf{8\,H^+} \longrightarrow CO_2 + 5\,H_2O + 4\,Fe^{2+}$$

Sulphate reduction:

$$2\,CH_2O + SO_4^{2-} + \mathbf{2\,H^+} \longrightarrow 2\,CO_2 + 2\,H_2O + H_2S$$

Methanogenesis:

$$2\,CH_2O \longrightarrow CO_2 + CH_4$$

Calcification also affects TA and DIC dynamics. Calcification is the biologically mediated precipitation of $CaCO_3$ by either planktonic (coccolithophores, foraminifera, pteropods, …) or benthic (bivalves, corals, calcareous algae, …) organisms. Carbonate minerals are present in various forms such as calcite, aragonite and mixed calcium/magnesium carbonates. Calcite and aragonite are both calcium carbonate forms and they differ in their crystallographic structure. The precipitation of $CaCO_3$ is given by equation (1). For each mole of $CaCO_3$ precipitated, one mole of CO_2 is released. However, the released CO_2 will interact with HCO_3^- and CO_3^{2-} by thermodynamic equilibria, hence the ratio (ψ) of CO_2 production to $CaCO_3$ precipitation depends in general on the thermodynamic equilibria and in particular on temperature. In freshwater $\psi = 1$ and for standard seawater conditions $\psi = 0.6$. Calcification decreases DIC but the resulting production of CO_2 can lead to oversaturation of CO_2 with respect to the atmospheric content as shown in coral reefs (e.g. Gattuso et al., 1993, 1996; Frankignoulle et al., 1996). In the open ocean, the most important pelagic calcifying organisms are coccolithophorids. Purdie and Finch (1994) and Crawford and Purdie (1997) have shown that coccolithophorid calcification was a source of CO_2 to the water mass and a potential source to the atmosphere, when the release of CO_2 exceeds its consumption (e.g. Head et al., 1998). The effect of calcification on carbonate speciation reduced the air-sea pCO_2 gradient by ~15 ppm in a huge coccolithophorid bloom in the North Atlantic (Robertson et al., 1994). Bates et al. (1996) reported TA depletion in the upper water column of the Sargasso Sea was associated to higher pCO_2 values and were probably the biogeochemical signature of calcification. In the Bering Sea, TA decreases of more than 80 μmol kg^{-1} have been reported in association with coccolithophore blooms (Murata and Takizawa, 2002). In the Bay of Biscay, decreases of TA of ~30 μmol kg^{-1} lead to an increase of surface water pCO_2 values of about 50 ppm, yet did not induce an over-saturation of CO_2 and the area still acted as a sink for atmospheric CO_2 (Borges, unpublished; Suykens et al., 2008).

The degree of saturation of seawater with respect to aragonite or calcite (Ω_{arg} or Ω_{cal}) is the ion product of the concentrations of calcium and carbonate ions divided by the stoichiometric solubility product (Ks), at the *in situ* temperature, salinity, and pressure:

$$\Omega_{arg} = [Ca^{2+}]\,[CO_3^{2-}]/Ks_{arg.} \quad (26)$$

$$\Omega_{cal} = [Ca^{2+}]\,[CO_3^{2-}]/Ks_{cal.} \quad (27)$$

Where the calcium concentration is estimated from salinity and the carbonate ion concentration is calculated from the DIC and TA data. Because the ratio calcium to salinity in seawater does not vary by more than 1.5%, variations in the ratio of $[CO_3^{2-}]$ to the stoichiometric solubility product primarily govern the degree of saturation of seawater with respect to aragonite and calcite.

Ω_{arg} (Ω_{cal})> 1 corresponds to aragonite (calcite) oversaturation, when $CaCO_3$ precipitation is thermodynamically favoured and Ω_{arg} (Ω_{cal})<1 correspond to aragonite (calcite) under-saturation when $CaCO_3$ dissolution is thermodynamically favoured.

Until recently, it had been commonly though that the dissolution of pelagic $CaCO_3$ particles primarily occurs below the calcite saturation depth (Ω_{cal} =1). However, recent analyses of the global carbonate budget and carbonate data for the global oceans have indicated that perhaps as much as 60 to 80% of the $CaCO_3$ that is exported out of the surface ocean dissolves in the upper 1000 m (Feely et al., 2004). Milliman et al. (1999) explored the biologically mediated dissolution above the saturation horizon and suggested various pathways by which dissolution could take place. Even if grazing pressure is supposed to contribute greatly to dissolution, the influence of microbial activity, whether it is associated or not within microenvironments, cannot be excluded.

Aragonite and magnesian calcite are at least 50% more soluble in seawater than calcite (Kawahata et al., 2000), suggesting that organisms that form these types of $CaCO_3$ may be particularly affected by ocean acidification (increasing pCO_2 and decreasing pH in surface waters leading to a decrease of CO_3^{2-} and Ω).

The present day accumulation of $CaCO_3$ in marine sediments is about 0.10 to 0.14 Pg of $CaCO_3$ per year along the continental margins or in deep sea, and 0.13 to 0.17 Pg of $CaCO_3$ per year in continental shelf sediments (Catubig et al., 1998; Iglesias-Rodriguez et al., 2002). The global new production of $CaCO_3$ ranges from 0.8 to 1.4 Pg of $CaCO_3$ per year based on models or observations of seasonal changes in alkalinity in the euphotic zone (Lee, 2001; Iglesias-Rodriguez et al., 2002). Balch et al. (2007) recently estimated global pelagic calcification to 1.6±0.3 Pg of $CaCO_3$ yr^{-1}, based on remote sensing data. Thus, of the total amount of $CaCO_3$ that is produced annually, no more than ~30% is buried in shallow and deep sediments. The rest is dissolved in the water column, at the sediment-seawater interface or in the upper sediments (Feely et al., 2004).

1.1.4 CO_2 dynamics in coastal zone and freshwater ecosystems

1.1.4.1 Carbon fluxes in rivers

Rivers, in particular, large rivers, play an essential role in the transport and transformation of carbon from the land and the atmosphere to the ocean (Sabine et al., 2003; Richey et al. 2002; Chen, 2004). Using an empirical model, Ludwig et al. (1998) estimated that a total of 0.721 PgC yr^{-1} is exported from the continents to the ocean. Of this total continental erosion flux, about 0.096 PgC yr^{-1} is as particulate inorganic carbon (PIC). Of the reaming 0.625 PgC, 33% is dissolved organic carbon (DOC), 30% as the particulate organic carbon (POC) and 37% as HCO_3^- from carbonate rock weathering. The total organic carbon flux (0.394 PgC yr^{-1}) to the ocean estimated by Ludwig et al. (1998) is similar to earlier estimates summarized by Smith and Hollibaugh (1993), although more recent literature has suggested fluxes between 0.43 and 0.50 Pg C yr^{-1} (Schlunz and Schneider, 2000; Mackenzie et al., 2004). In a recent review, Richey (2004) argued that the POC flux alone can be as high as 0.50 PgC yr^{-1} if the higher sediment yield from tropical and subtropical mountainous rivers is included. The total riverine HCO_3^- flux of Ludwig et al. (1998) (0.329 Pg C yr^{-1}) is somewhat lower than that reported by Mackenzie and co-workers (0.41 Pg C yr^{-1}; Mackenzie et al, 1998; Mackenzie et al., 2004). The flux of PIC has also been evaluated at higher rates of 0.180 Pg yr^{-1} (Mackenzie et al., 2004).

Nearly all carbon in the form of DOC and POC in rivers is directly or indirectly of atmospheric origin. Organic carbon flux (~1.5 PgC yr^{-1}) from land to the rivers carries the biomass produced by photosynthesis (~60 PgC yr^{-1}) in excess of losses due to respiration and forest fires (Schlesinger, 1997). During the transport towards the oceans, a large part of the organic carbon may be decomposed and released back to rivers and the atmosphere as CO_2 through microbial respiration (Richey et al., 2002). Most of the terrestrial DOC and POC reaching the ocean are believed to be decomposed in the ocean margins with less than a total of 0.150 PgC yr^{-1} of POC being buried in marine sediments (Mckee, 2003). Most of inorganic carbon is transported as HCO_3^- and is derived from atmospheric CO_2 involved in mineral weathering and from the dissolution of carbonate minerals in sedimentary rocks. Consequently export rates from catchments will be strongly related to bedrock geology. **Table 1.4** gives the concentrations and fluxes of HCO_3^- in the 25 largest rivers in the world. The following major features can be identified: i) HCO_3^- concentrations are highest in the mid latitude rivers and lowest in the tropical and subtropical rivers. For example, the Amazon has a low [HCO_3^-] of only 0.369 mmol kg^{-1} in contrast with the high average concentrations of 2.591, 1.780, 1.535 and 2.074 mmol kg^{-1} respectively in the Huange, Changjiang, Pearl and Mississippi rivers; ii) Bicarbonate specific fluxes are highest in the mid latitude although the maximum shifts somewhat towards the subtropical rivers. The three mid latitude large rivers, the Changjiang, the Mississippi and the Columbia, have lower specific fluxes relative to the pattern of their concentrations, while the Huange has a very low specific HCO_3^- flux because of low carbonate mineral content on the catchment and a dry climate; iii) As far as the total inorganic carbon flux is concerned, the three largest rivers that carry HCO_3^- to the oceans are the Amazon, the Mississippi, and the Changjiang. These distribution patterns of HCO_3^- concentration and flux are consistent with the global distribution pattern of continental carbonate rocks. For the 25 rivers, rivers in low (< 30°), mid (30-60°) and high (> 60°) latitudes have an average HCO_3^- concentration of 0.584, 1.649 and 1.154 mmol kg^{-1} respectively and they account for 43, 47 and 10% respectively of the total DIC flux to the ocean. Thus mid latitude rivers deliver a disproportionally high DIC flux with a relatively small (26%) amount of freshwater discharge (Cai et al., 2008). Mineral weathering is known to be a major regulator of atmospheric CO_2 concentrations over geological time scales (Berner et al., 1983). Recent studies of the Mississippi river HCO_3^- fluxes suggest that weathering rates may change over much shorter time scales (e.g. over decades), and may respond to changes in land use (Cai, 2003; Raymond and Cole, 2003). This additional information highlights the pressing need for a better understanding of DIC export associated with weathering processes and temporal and spatial variations.

1.1.4.2 Processes controlling pCO_2 in river waters

The pCO_2 in river waters is controlled by both internal carbon dynamics and external biogeochemical processes in upstream terrestrial ecosystems. These processes include: 1) production and transport of soil CO_2; 2) in situ respiration and degradation of organic matter within the water column; 3) photosynthesis by aquatic plants; 4) CO_2 evasion from water to air, in which the former two processes produce CO_2 and make the water pCO_2 increase, while the latter two cause water pCO_2 levels to decrease.

The surface pCO_2 dynamics in river systems are closely related to the soils characteristics of the basin they drain (Hope et al., 2004). The pCO_2 in soil atmosphere, mainly resulting from respiration and decomposition of organic matter, is generally much higher than ambient atmospheric CO_2 (Finlay, 2003). The variation in soil CO_2 content is positively correlated with seasonal changes of temperature and precipitation in the basin (Jassal et al., 2004). When soils are wetted by precipitation, together with proper temperature and high retention times of waters in soils, active bacterial activities produce significant CO_2 making soil become highly enriched in CO_2 (Hope et al., 2004).

Dissolution of soil CO_2 and subsequent transport to the stream via base flow and inter flow is likely the main reason for pCO_2 super-saturation in river waters. The seasonal variation in soil CO_2 content results in seasonal variation in pCO_2 of river waters. In addition, the intensity of rainfall, hydrological flow path and river discharge are other factors impacting pCO_2 in river waters. Heavy rain that directly flows into the stream through surface runoff without penetrating into the soil will dilute the pCO_2 in river waters. Beside the dilution effect, the fast flow velocity, which increases water turbulence, greatly enhances CO_2 outgassing from river water to the atmosphere and it is another reason for lower pCO_2 levels during the flood periods. Biogenic CO_2 uptake and release, i.e., photosynthesis of aquatic plants and respiration and degradation of organic matter in the river itself also impact the pCO_2 in river systems. In general, *in situ* photosynthesis takes up aqueous CO_2, making the water pCO_2 decrease, while respiration and degradation of organic matter release CO_2, resulting in a rise in water pCO_2.

Table 1.4: Basic information and flux data for the 25 world's largest rivers (Cai et al., 2008)

Basin latitude (°)	River	Basin area (10^3 km^2)	Discharge (km^3 yr^{-1})	Runoff (mm yr^{-1})	Carbonate (%)	HCO_3^- (mmol kg^{-1})	Specific DIC flux (10^3 mol km^{-2} yr^{-1})	DIC flux (10^9 mol yr^{-1})
Low (< 30°)								
2	Amazon	5854	6642	1135	3.9	0.369	419	2450
4	Congo	3699	1308	354	10.1	0.224	79	293
7.5	Orinoco	1039	1129	1087	1.3	0.423	460	477
25	Brahmaputra	583	628	1077	33.8	1.114	1200	700
23	Parana	2661	568	213	1.2	0.764	163	434
20	Mekong	774	525	678	21.4	0.949	644	498
26	Ganges	956	404	423	33.8	1.966	831	794
23	Pearl river	477	343	719	n.d.	1.535	1104	527
23	Xijiang	409	270	660	82.4	1.938	1279	523
2.5	Ubangi	356	228	640	n.d.	0.317	203	72
10	Niger	2240	193	86	6.3	0.550	47	106
29	Indus	1143	104	91	26.0	1.681	153	175
21	Godavari	312	97	311	0.0	2.156	670	209
Mid (30-60°)								
30	Changjiang	1794	944	526	44.0	1.780	937	1680
36	Mississippi	3203	610	190	18.1	2.074	395	1265
60	Yenisei	2582	599	232	6.9	0.905	210	542
60	Ob	2570	412	160	2.7	1.251	201	515
47	St Lawrence	1267	363	287	24.9	1.339	384	486
42	Columbia	724	252	348	n.d.	1.246	434	314
48	Danube	788	202	256	14.5	3.115	798	629
36	Huange	894	47	53	7.6	2.591	136	122
High (> 60°)								
63	Lena	2418	531	220	11.2	0.870	191	462
64	Mackenzie	1713	290	169	20.6	1.800	305	522
64	Yukon	852	212	249	0.0	1.363	339	289
67	Kolyma	666	118	117	0.0	0.467	83	55

The active degree of biological activities in rivers is mainly controlled by seasonally and spatially changed temperature, turbulence and flow velocity of water. The pCO_2 will change seasonally or at different stretches because of changing biological activities. If biological activities are significant, biological CO_2 uptake and release would cause great shifts in water pCO_2. Varying relative dominance of *in situ* respiration and degradation of organic matter versus photosynthesis in different seasons and in different stretches makes pCO_2 rise or fall. In tropical rivers, the respiration and decomposition from floating and emerged macrophytes can constitute an important source of CO_2 to the water column. For instance, in the Amazon river root respiration from and decomposition of floating and emerged macrophytes contribute to 25% or more of CO_2 evasion to atmosphere from the water column (Richey et al., 2002; Engle et al., 2008).

Streams and rivers are usually net sources of CO_2 to the atmosphere. For instance, CO_2 evasion from global river systems extrapolated from mostly temperate rivers reaches about 0.3 PgC yr^{-1}, nearly equivalent to riverine total organic carbon or DIC export (Cole and Caraco, 2001). Similarly, Richey et al. (2002) estimated that the loss of CO_2 from rivers in lowland humid tropical forests is 0.9 PgC yr^{-1}. Such a large CO_2 source urges us to reconsider the global carbon budget, and direct measurements of land-atmosphere CO_2 gas exchange that ignore water-borne fluxes might significantly overestimate terrestrial carbon accumulation (Hope et al., 2001; Siemens, 2003; Borges et al., 2006). Therefore, CO_2 degassing to the atmosphere from river systems should be considered a significant component of regional net carbon budgets in future studies.

1.1.4.3 The role of freshwater ecosystems in the global carbon cycle

Figure 1.4 shows the role of inland aquatic systems in the global carbon balance. Overall, freshwater ecosystems (particularly rivers, lakes, and reservoirs) receive 1.90 PgC yr^{-1} from the terrestrial landscape of which 0.23 PgC yr^{-1} is buried in aquatic sediments, at least 0.75 (possibly much more) is returned to the atmosphere as gas exchange while the remaining 0.92 Pg C yr^{-1} is delivered to the oceans, roughly equally as inorganic and organic carbon (Cole et al., 2007). Thus, roughly twice as much carbon enters inland aquatic systems from land as is exported from land to the sea. In addition to transporting carbon to the oceans, freshwater systems represent an active component of the global carbon cycle that deserves attention. The C flows estimates in **Figure 1.4** do not include the floodplains of large rivers that are atmospheric CO_2 sinks, but significant organic carbon inputs into the rivers. Thus, although their area is small, freshwater aquatic systems affect the global carbon budget.

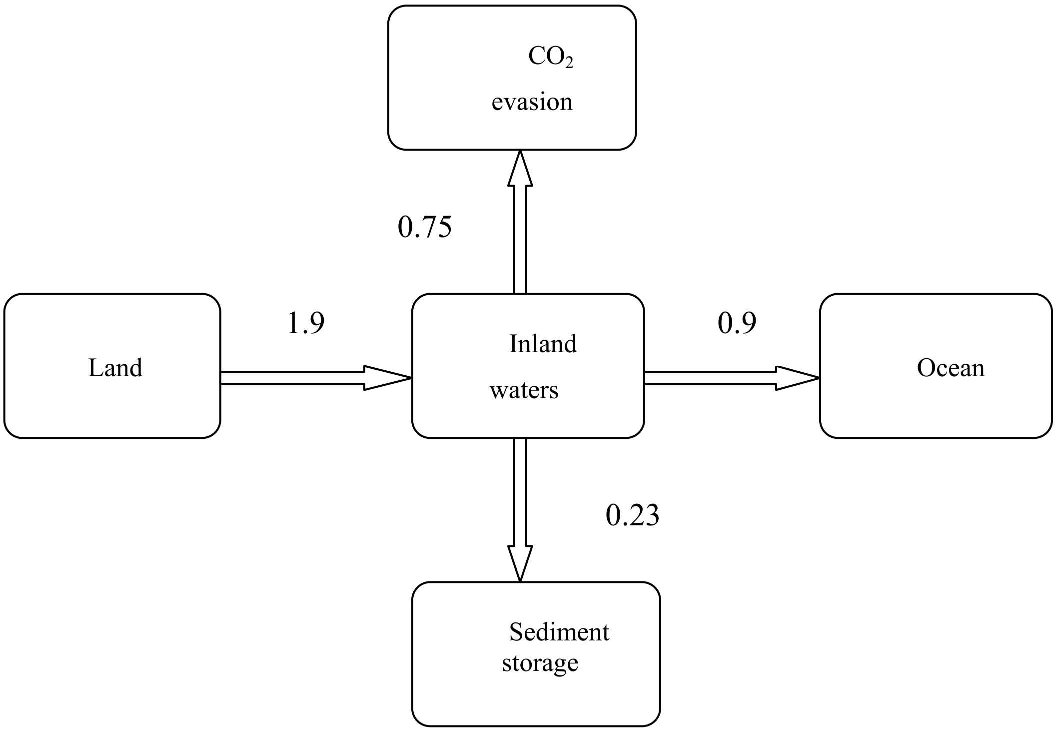

Figure 1.4: Diagram showing the global carbon cycle (PgC yr^{-1}) in the inland waters (Cole et al., 2007).

1.1.4.4 Coastal Zone

The coastal zone is a transition area between land and the open ocean, and receives considerable amounts of freshwater, nutrients, dissolved and particulate organic matter from land and also exchanges matter and energy with the open ocean. The coastal zone consists of continental shelves and numerous near-shore ecosystems such as coral reefs, deltas, salt marshes, estuaries, bays, banks, mangroves and lagoons. The outer boundary of the coastal zone is usually defined by the marked change in the bathymetry corresponding to the shelf break. It is located between the continental shelf and the continental slope, at an average isobath of 130 m, although regionally variable. For instance, the mean depth at the shelf break is 200 m in the European section of the Atlantic Ocean whereas is about 100 m off the African and North American Coast. The overall surface of the coastal zone (26 10^6 km^2) is about 7% of the oceanic surface area (360 10^6 km^2), but hosts approximately 10% to 30% of the world's marine primary production. 80% of suspended matter inputs from the land to sea are deposited in the coastal zone, and 85% of organic carbon and 45% of inorganic carbon are buried in the sediments of the coastal zone (Gattuso et al., 1998; Wollast, 1998). Additionally, the coastal zone provides 90% of the world fish catch and its overall economic value has been estimated as 43% of the value of the world's ecosystem services and natural capital (Costanza et al 1997; Gattuso et al., 1998). The coastal environments are also heavily impacted by human activities, as nearly 40% of the global population lives within 100 km of the coastline (Andersson and Mackenzie, 2004).

During the last 200 years, the coastal ocean has been exposed to large perturbations, mostly related to human activities on land. Prolonged and intensive use of inorganic fertilizer in agriculture, changes in land use patterns, deforestation, and discharge of industrial and municipal waste have all contributed to the eutrophication of river water and of the coastal ocean on a global scale. This phenomenon has led to severe degradation of water quality and alteration of marine food web and community structure. Over the past 50 years, the fluxes of natural and synthetic material from the terrestrial environment to the coastal margin have increased by a factor of 1.5 to 2.0 because of human perturbations (Rabouille et al., 2001).

The coastal zone can be divided into two adjacent zones: proximal and distal. In the proximal coastal zone, large inputs from the rivers of particulate and dissolved organic and inorganic material are delivered into a relatively small reservoir. In addition, there is a strong degree of coupling between the processes of sediment recycling and nutrient utilization in the photic layer. For example, suspended sediments in turbid plumes typically create light limiting conditions which inhibit primary production. As turbidity decreases, due to particle settling and dilution, light availability increases and pelagic food webs can be greatly stimulated by river-derived nutrients. The mean water depth in the proximal region is about 20 m and the sedimentation rates are estimated to be in the range of 0.1-1.0 cm yr^{-1} (Heip et al., 1995). In the distal zone, material inputs are mainly from the open ocean and the adjacent proximal zone. The coupling between the processes of benthic recycling and production is weaker compared to the proximal zone because of the greater depth of the water column. The distal zone includes the open continental shelves down to the mean depth of the shelf break. The sedimentation rate in the distal region is estimated to be between 0.01 and 0.1 cm yr^{-1}, an order of magnitude lower than that of the proximal zone (Wollast, 1998).

1.1.4.5 Global coastal carbon fluxes

The carbon cycle in the coastal involves a series of processes, including C inputs from land, upwelling and mixing at continental margins, photosynthesis, respiration and export resulting in CO_2 exchange with the atmosphere. Open continental shelves are sinks of atmospheric CO_2, although the earlier estimation of 1.0 PgC yr^{-1} given by Tsunogai et al. (1999) has been re-evaluated and more recent estimations converge towards 0.3-0.4 PgC yr^{-1} (Thomas et al. 2004; Borges, 2005; Borges et al., 2005; Cai et al. 2006; Chen and Borges, 2008). This corresponds to an additional sink of ~30% of the CO_2 uptake by oceans based on the most recent pCO_2 climatology of Takahashi et al. (2008). Near-shore environments such as bays, estuaries, salt marsh ecosystems, lagoons, mangroves ecosystems, coral reef and some upwelling systems act as sources of CO_2 to the atmosphere (Borges, 2005; Borges et al. 2005; Chen and Borges, 2008). Estuaries, for instance, act as a source due to their heterotrophic ecosystem metabolic status (Odum and Hoskin, 1958; Odum and Wilson, 1962; Heip et al., 1995; Kemp et al., 1997; Gattuso et al., 1998; Gazeau et al., 2004; Hopkinson and Smith, 2005). The input of dissolved CO_2 from the upstream river contributes to about 10% of the emission of CO_2 from macrotidal estuaries; the remaining fraction of the emission of CO_2 is then due to heterotrophy or lateral inputs of CO_2 (Borges et al., 2006). The net heterotrophy of the estuaries is sustained by terrestrial/riverine organic carbon inputs (freshwater phytoplankton and soil carbon), and in populated area by waste waters.

Coral reefs are considered to be slightly net autotrophic, but still act as a source of CO_2, due to high calcification rates. Globally, coral reefs are responsible for a net flux of carbon to the atmosphere of about 0.73 mol C m^{-2} yr^{-1} (Borges, 2005). Upwelled waters are colder and contain more DIC than surface waters, due to extensive remineralisation of settling organic matter. When they reach the surface over the continental shelf, temperature increases, the solubility of CO_2 decreases, resulting in increased pCO_2 and, generally, a flux of CO_2 to the atmosphere. This CO_2 venting has been observed, for example, in the upwelling systems off the Oman and California coasts (Borges, 2005). However, a recent study at Cape Perpetua, an area of substantial upwelling along Oregon coast indicated, that this region as opposed to other upwelling regions, acted as an important sink of CO_2 (Hales et al., 2003). These authors suggest that production in the region was only limited by available nitrate, resulting in consumption of nitrate and CO_2 in stoichiometric proportions. In addition, the upwelling waters had very high total alkalinity and pre-formed nitrate relative to DIC and were subject to only moderate warming and changes in CO_2 solubility, because of the relatively high latitude and mild temperatures of this region. However, it is important to note that Hales et al. (2003) only obtained data during one season (summer). Borges and Frankignoulle (2001) also showed that the upwelling system off the Galician coast behaves as a sink for atmospheric CO_2. Off the Galician coast, large upwelling filaments are characterized by stronger under-saturation with respect to atmospheric CO_2 than offshore water affecting significantly the overall budget of air-water CO_2 fluxes in non-coastal (offshore) waters.

Mangroves surrounding waters act as CO_2 sources to the atmosphere also due to the heterotrophic nature of water column and inter-tidal sediments. Heterotrophy is sustained by inputs of organic carbon that has several sources, either autochtonous (mangrove detritus, and microphytobenthos) or allochtonous (phytoplankton, seagrass derived material, and terrestrial non-mangrove forests). However, the relative contribution of these sources varies considerably from one site to another (Bouillon and Boschker, 2006). The emission of CO_2 from mangrove surrounding waters is also sustained by the input of CO_2-rich pore waters during ebbing (Ovalle et al., 1990; Borges et al., 2003; Bouillon et al., 2007c). Tidal pumping of pore water makes creek waters act as conduits for the emission of CO_2 produced by diagenetic organic carbon degradation, leading to an under-estimate of traditional measurements of benthic metabolism (Bouillon et al., 2008). The aquatic compartment of salt-marshes is also a source of CO_2 to atmosphere due to its net heterotrophic status sustained by allochtonous and autochtonous organic carbon inputs (Cai et al., 2003; Wang and Cai, 2004) with a strong contribution of dissolved inorganic carbon inputs from the inter-tidal and sub-tidal benthic compartments (Ferrón et al., 2007). However, mangrove and salt marshes ecosystems as a whole (including the aquatic compartment, the benthic compartment and above-ground biomass) act as sinks for atmospheric CO_2 due to the important above-ground primary production. A recent data compilation in mangrove ecosystems yields an above-ground net primary production (including litter fall, wood production and fine root production) of 114 mol C m^{-2} yr^{-1} (Bouillon et al., 2008). In comparison, the emission of CO_2 to the atmosphere from the aquatic compartment is 27.2 mol C m^{-2} yr^{-1}. Similarly, in the

Duplin river salt marsh ecosystem, net primary production from above-ground vegetation is about 149.2 mol C m^{-2} yr^{-1} (Hopkinson, 1988) a sink of atmospheric CO_2 higher than the report emission of CO_2 to the atmosphere from aquatic compartment of 21.4 mol C m^{-2} yr^{-1} (Wang and Cai, 2004).

The net ecosystem production (NEP) is the difference between total organic carbon production (GPP) and total organic carbon consumption by autotrophs and heterotrophs in the pelagic and benthic compartments (community respiration, R) (Odum, 1956). Environments where GPP>R (NEP>0) at annual scale are net autotrophic and export or store organic carbon, while environments where GPP<R (NEP<0) at annual scale are net heterotrophic and their metabolism must be sustained by external organic carbon inputs. At sub-annual scale, there is a decoupling at ecosystem scale of organic carbon production and organic carbon consumption, leading to an alternation of periods of net autotrophy, net heterotrophy and periods of balanced ecosystem metabolism (e.g. Gazeau et al., 2005; Borges et al., 2008). Gattuso et al. (1998) reviewed GPP, R, calcification, carbon burial and exchange with adjacent systems, including the atmosphere, in the major coastal ecosystems (estuaries, macrophyte communities, mangroves, coral reefs, and the remaining continental shelf). All ecosystems examined, except estuaries, were found to be net autotrophic. Note that for mangrove ecosystems the whole ecosystem is net autotrophic (above ground, sediment and aquatic compartments), yet the sediment and aquatic compartments are net heterotrophic. The conclusions of Gattuso et al. (1998) on metabolic functioning in coastal environments have been updated and confirmed by latter reviews (Gazeau et al., 2004; Hopkinson and Smith 2005; Duarte et al., 2005; Bouillon et al., 2008).

The determination of NEP is of interest for the understanding of the CO_2 cycle within a given ecosystem, however, in coastal environments, the link between the exchange of CO_2 with the atmosphere and the metabolic status of surface waters is not direct. Indeed, the net CO_2 flux between the atmosphere and the water column in these environments is also modulated by other biogeochemical processes ($CaCO_3$ production/dissolution); exchange of water with adjacent aquatic systems and the CO_2 content of the exchange water mass; residence time of the water mass within the system; decoupling of organic carbon production and degradation across the water column related to the physical settings of the systems (Borges, 2005; Borges et al., 2006).

1.2 CH_4 global cycle

The role of atmospheric methane (CH_4) in the Earth's radiative and chemical balance is well recognized. Atmospheric CH_4 levels have been increasing approximately 1% per year over the last 200 years, resulting in a contribution to the radiative forcing of the atmosphere which is estimated to 20-30% of the one caused by the increase in atmospheric CO_2 (Sansone et al., 1998). However, during the 1980s and 1990s, the rate of CH_4 atmospheric growth rate slowed steadily and stabilized since the mid-1990's due to changes in CH_4 sinks and sources CH_4. Although the exact cause of this short-term decline in the CH_4 atmospheric growth rate is still unresolved, Dlugokencky et al. (1998; 2003) suggested that a steady state was reached with CH_4 net emissions and the hydroxyl radical (OH) levels were constant during the 1990's. In contrast, Bousquet et al. (2006) showed that the decrease in atmospheric methane growth during the 1990's was caused by a decline in anthropogenic emissions. Large fluctuations in the growth rate of atmospheric methane are also observed from one year to the next (**Figure 1.5**), but their causes remain uncertain. Bousquet et al. (2006) used an inversion model of atmospheric transport and chemistry to quantify the processes that controlled variations in methane emissions between 1984 and 2003. Their results indicate that wetland emissions dominated the inter-annual variability of methane sources, whereas fire emissions played a smaller role, except during the 1997-1998 El Niño event. These emissions are in turn sensitive to meteorological parameters: during dry periods, methane flux from wetlands is depressed (Lelieveld, 2006). Thus, during the most recent part of the analysis period from 1999 onward, extended droughts have reduced natural methane emissions. This has concealed the fact that anthropogenic emissions have resumed their increase, an increase perhaps associated with the accelerating use of fossil fuel by booming Asian economies (Lelieveld, 2006). Moreover, the dryness aggravates vegetation fires, which release large amounts of carbon monoxide, and this pollutant gas also consumes hydroxyl. With less hydroxyl around, less methane is broken down, and the decrease in methane concentration is not as large as might be expected (Lelieveld, 2006).

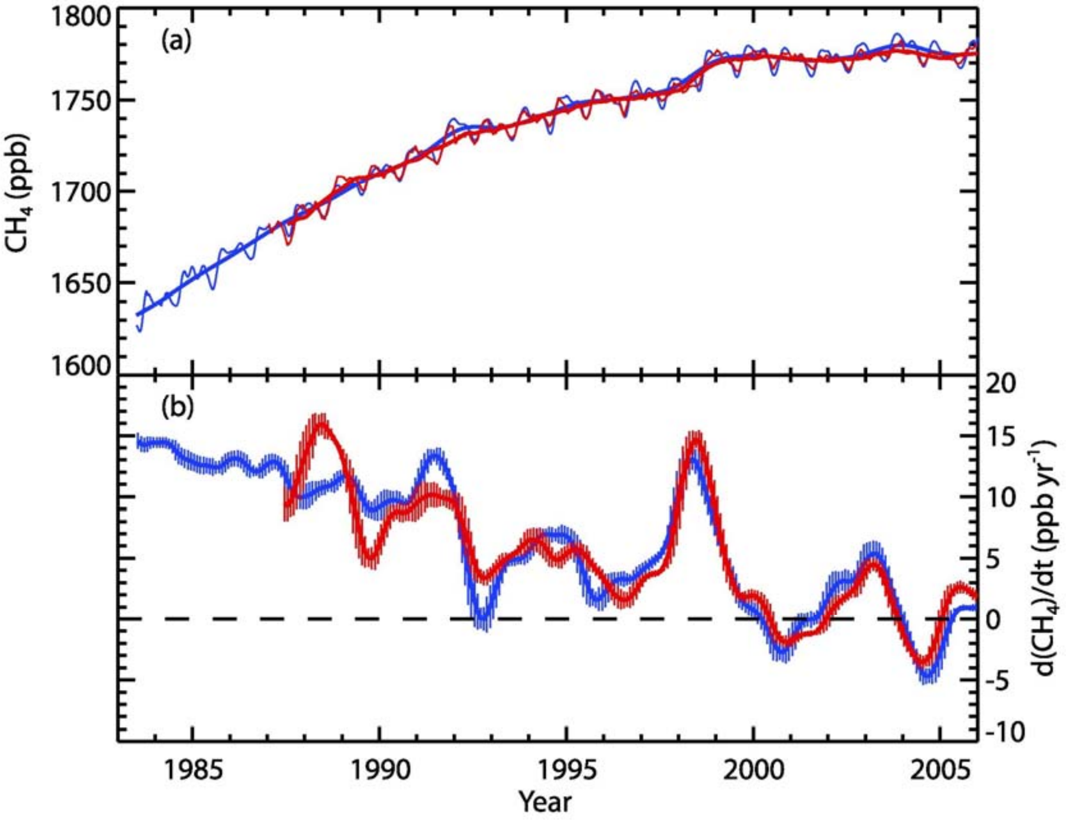

Figure 1.5: Recent atmospheric CH_4 concentrations and annual growth trends. (a) Time series of global CH_4 abundance mole fraction (in ppb) derived from surface sites operated by NOAA/GMD (blue lines) and AGAGE (red lines). The thinner lines show the CH_4 global averages and the thicker lines are the de-seasonalized global average trends from both networks. (b) Annual growth rate (ppb yr^{-1}) in global atmospheric CH_4 abundance from 1984 through the end of 2005 (NOAA/GMD, blue), and from 1988 to the end of 2005 (AGAGE, red) (IPCC, 2007).

1.2.1 Sources of atmospheric CH_4

Atmospheric CH_4 originates from both non-biogenic and biogenic sources. Non-biogenic CH_4 includes emissions from fossil fuel mining and burning (natural gas, petroleum and coal), biomass burning, waste treatment and geological sources (fossil CH_4 from natural gas seepage in sedimentary basins and geothermal/volcanic CH_4). However, CH_4 emissions from biogenic sources account for more than 70% of the global total. These sources include wetlands, rice agriculture, livestock, landfills, forests, oceans and termites. Emissions of CH_4 from most of these sources involve ecosystem processes that result from complex sequences of events beginning with primary fermentation of organic macromolecules to acetic acid (CH_3COOH), other carboxylic acids, alcohols, CO_2 and hydrogen (H_2), followed the secondary fermentation of the alcohols and carboxylic acids to acetate, H_2 and CO_2, which are finally converted to CH_4 by the so-called methanogenic Archaea (Conrad, 1996):

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad (28)$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad (29)$$

Alternatively, CH_4 sources can be divided into anthropogenic and natural (**Table 1.5**). The anthropogenic CH_4 sources include rice agriculture, livestock, landfills and waste treatment, biomass burning, and fossil fuel combustion. Natural CH_4 is emitted from sources such as wetlands, oceans, forests, fires, termites and geological sources.

The net rate of CH_4 emissions is generally estimated from three approaches: i) extrapolation from direct flux measurements and observations, ii) process-based modeling (bottom-up approach) and iii) inverse modeling that relies on spatial distributed, temporally continuous observations of concentration, and in some cases isotopic composition in the atmosphere (top-down approach). The top-down method also includes aircraft and satellite observations (e.g. Xiao et al., 2004; Frankenberg et al., 2006). When the bottom-up approach is used to extrapolate the emissions to larger scales, uncertainty results from the inherent large temporal and spatial variations of CH_4 fluxes and limited range of observational conditions. The top-down approach helps to overcome the weaknesses in bottom-up methods. However, obstacles to extensive application of the top-down approach include inadequate observations, and insufficient capabilities of the models to account for error amplification in the inversion process and to simulate complex topography and meteorology (e.g., Chen and Prinn, 2005; 2006). Measurements of isotopes of CH_4 provide additional constraints on CH_4 budgets and specific sources, but such data are even more limited (e.g. Bergamaschi et al., 2000; Mikaloff Fletcher et al., 2004).

Total global pre-industrial emissions of CH_4 are estimated to be 200 to 250 $TgCH_4\ yr^{-1}$ (e.g., Houveling et al., 2000; Ferretti et al., 2005). Of this, natural CH_4 sources emitted between 190 and 220 $TgCH_4\ yr^{-1}$, and anthropogenic sources accounted for the rest (Houveling et al., 2000; Ruddiman and Thomson, 2001). In contrast, anthropogenic emissions dominate present-day CH_4 budgets, accounting for more than 60% of the total global budget (**Table 1.5**).

Emissions from natural wetlands contribute significantly to the atmospheric CH_4 budget (**Table 1.5**). However, quantification of this source is difficult, because individual wetlands often show great spatial and temporal variations in CH_4 emission. This variability in time and space is related to environmental factors that affect CH_4 production, oxidation or transport. These factors include the type and amount of organic matter, the dominant organic matter decomposition pathway, temperature, hydrological conditions and vegetation. Recent estimates combined bottom-up and top-down fluxes (Chen and Prinn, 2006) show that southern and tropical regions account for more than 70% of total global wetland emissions. However, several bottom-up studies indicate fewer emissions from tropical rice agriculture (e.g., Li et al., 2002; Yan et al., 2003; Khalil and Shearer, 2006). Frankenberg et al. (2006) and Keppler et al. (2006) suggest that tropical trees emit CH_4 via an unidentified process. The first estimate of this source was 10 to 30% (62-236 $TgCH_4\ yr^{-1}$) of the global total, but Kirschbaum et al. (2006) revise this estimate downwards to 10 to 60 $TgCH_4\ yr^{-1}$.

Table 1.5: Sources, sinks and atmospheric budgets of CH_4 in $TgCH_4\ yr^{-1}$ (IPCC, 2007)

References	Hein et al. (1997)	Houweling et al. (2000)	Wuebbles and Hayhoe (2002)	Wang et al. (2004)	Mikaloff Fletcher et al. (2004)	Chen and Prinn, (2006)	IPCC, 2001	IPCC, 2007
Base year	1983-1989	2000	2000	1994	1999	1996-2001	1998	2000-2004
Natural Sources		**222**	**145**	**200**	**260**	**168**		
Wetlands	231	163	100	176	231	145		
Termites		20	20	20	29	23		
Ocean		15	4					
Hydrates			5	4				
Geological sources		4	14					
Wild animals		15						
Wildfires		5	2					
Anthropogenic sources	**361**		**358**	**307**	**350**	**428**		
Energy				77				
Coal, mining	32		46		30	48		
Gas, oil, industry	68		60		52	36		
Landfills and wastes	43		61	49	35			
Ruminants	92		81	83	91	189		
Rice agriculture	83		60	57	54	112		
Biomass burning	43		50	41	88	43		
C3 vegetation								
C4 vegetation								
Total sources	**592**		**503**	**507**	**610**	**596**	**598**	**582**
Imbalance	+33						+22	+1
Sinks								
Soils			30	34	30		30	30
Trospopheric OH			445	428	507		506	511
Stratospheric loss			40	30	40		40	40
Total sinks			**515**	**492**	**577**		**576**	**581**

Geological sources of CH_4 are currently neglected (range: 4-14 TgCH_4 yr^{-1}; **Table 1.5**) in the budget. However, several studies suggest that significant amounts of CH_4, produced within the Earth's crust (mainly by bacterial and thermogenic processes), are released into the atmosphere through faults and fractured rocks, mud volcanoes on land and seafloor, submarine gas seepage, microseepage over dry lands and geothermal seeps (e.g., Etiope and Klusman, 2002; Etiope, 2004). Emissions from these sources are estimated to be as large as 40 to 60 TgCH_4 yr^{-1}.

1.2.2 CH_4 sinks

In contrast to the numerous sources of CH_4 (**Table 1.5**), there are only one major and two minor sinks for atmospheric CH_4. Reaction with the hydroxyl radical is responsible for the removal of approximately 500 TgCH_4 yr^{-1} (almost 90% of the total sink), making the concentration of OH the most important determinant of the rate at which CH_4 is removed from the atmosphere (Wuebbles and Hayhoe, 2002). The remainder of CH_4 is removed through dry soil oxidation, ~30 Tg CH_4 yr^{-1}, and the transport to the stratosphere, estimated at ~40 TgCH_4 yr^{-1}. OH is formed from photo dissociation of tropospheric ozone and water vapour, and is the primary oxidant for tropospheric pollutants, including carbon monoxide (CO), nitrogen oxides (NO_X), and organic compounds. Changes in OH concentrations will therefore impact the abundances of many trace species, affecting local air pollution. At the present time, OH concentration appears to be relatively steady or perhaps increasing, with the effects of increasing CH_4 and CO balanced by increases in troposphoric ozone (O_3) concentrations and emissions of NO_X and non-methane hydrocarbons (NMHCs) (Wuebbles and Hayhoe, 2002). Soils are the largest biotic sink for atmospheric CH_4, and geographical distribution of methane consumption shows that subtropical and dry tropical ecosystems account for over half of the global uptake (Curry, 2007). Dutaur and Verchot (2007) found similar results and showed that ecosystem type, geographic zone, and soil texture strongly control CH_4 uptake. Several model studies indicate that CH_4 oxidation in soil is relatively insensitive to temperature increase (e.g., Ridgwell et al., 1999; Zhuang et al., 2004). A doubling of atmospheric CO_2 would likely change the sink strength only marginally (in the range of -1 to +3 TgCH_4 yr^{-1}; Ridgwell et al., 1999). However, any change in climate that alters the amount and pattern of precipitation may significantly affect the CH_4 oxidation capacity of soils (IPCC, 2007). A process-based model simulation indicate that CH_4 oxidation strongly depends on soil gas diffusivity, which is a function of soil bulk density and soil moisture content (Bogner et al., 2000; Del Grosso et al., 2000). Finally, it should be noted that most of the biogenic CH_4 emissions listed in **Table 1.5** will probably increase with global warming, since CH_4 release from ecosystems has been reported to be positively related to increasing temperatures (Cicerone and Oremland, 1988).

1.2.3 CH_4 dynamics in estuaries and freshwater ecosystems

1.2.3.1 Methane emission in inland waters

In the literature, dissolved CH_4 in aquatic systems is generally either expressed as concentration (in nmol L^{-1}, nmol kg^{-1} and µg L^{-1}) or saturation (%), which is the ratio of the measured gas concentration to the expected equilibrium concentration. The equilibrium concentration in turn depends on the water temperature, salinity, barometric pressure and the atmospheric CH_4 mixing ratio. Thus a saturation of 100% indicates that the water phase is in equilibrium with overlying atmosphere. Saturation values < 100% indicate under-saturation (i.e. flux of CH_4 from the atmosphere to water), whereas saturations values >100% stand for super-saturation (i.e. CH_4 release from water to the atmosphere).

CH_4, like CO_2, is typically supersaturated in streams and rivers and is almost entirely derived from biotic processes. However, CH_4 surface concentrations in rivers (**Table 1.6**) are highly variable and values range from just below the atmospheric equilibrium value ~3 nmol L^{-1} to ~4 10^5 nmol L^{-1}. Rivers are ecosystems where oxic conditions generally prevail and where CH_4 production is expected to be limited. Thus, CH_4 found in rivers is produced in majority in surrounding areas like floodplains or soils or groundwaters. From the riparian zone, CH_4 is transported to surface waters, where the concentration is considerably lower because of loss through evasion to the atmosphere and from oxidation by methanotrophic bacteria. The oxidation of CH_4 by methanotrophic bacteria can account for substantial loss of CH_4 from surface waters. For instance, in the Walker Branch, CH_4 oxidation potentially consumes 2-21% of CH_4 inputs, rates equivalent to 3 to 37% of evasion (Jones and Mulholland, 1998b). However, despite this reduction in CH_4, rivers are highly supersaturated with respect to the atmosphere (except one sample in the upper Adyar river, India) and Rajkumar et al. (2008) recently reported values that reach 15440000% in the lower Adjar river due to an intense methanogenesis fuelled by the high input rate of organic carbonic, which is largely composed of fresh domestic organic wastes. The concentration of CH_4 in surface water is governed by smaller scale inputs in groundwater, in stream production and oxidation, and diffusion to the atmosphere, as well as larger scale processes controlling the extent of anaerobic metabolism within a catchment. Characteristics of the catchments such as soil organic matter storage, hydrologic residence time, and subsurface flow paths regulate the extent of area where CH_4 is produced and the rate at which it is generated. For example, the streams draining catchments underlain by dolomite have on average, less than half the concentration of CH_4 of streams draining catchments underlain by shale, with means of 120 nmol L^{-1} and 273 nmol L^{-1}, respectively (Jones and Mulholland, 1998c). The more than twofold difference in CH_4 concentration presumably results from differences in catchment geomorphology, valley floor width, soil development, and hydrologic residence times and flow paths, features regulated in part by geology (Jones and Mulholland, 1998c). River size may be an important factor governing CH_4 concentrations in a single drainage basin, but is not the only important factor across different systems. Middelburg et al. (2002) have reported CH_4 concentrations in nine rivers (freshwater end-members) along the European Atlantic coast. Riverine end-member CH_4 concentrations in small drainage basin such as those of the Ems (50 nmol L^{-1}) and Sado (40 nmol L^{-1}) are indeed relatively low, but those of the Thames (273 nmol L^{-1}) and Scheldt (170 to 485 nmol L^{-1}) are intermediate to high. Rivers having a large drainage basin such as the Elbe (111 nmol L^{-1}) and Douro (63-128 nmol L^{-1}) have low to intermediate concentrations, whereas the Loire (10-671 nmol L^{-1}) and Rhine (37-1026 nmol L^{-1}) revealed variable and high concentrations (**Table 1.6**). Thus, the heterogeneity in CH_4 production and hydrologic flow paths between soils and rivers undoubtedly results in high spatial variation in CH_4 input into surface waters. From the river surface, CH_4 is lost to the atmosphere via diffusion. The rate of evasion is principally regulated by gas concentration, temperature, and turbulence. For instance, De Angelis and Lilley (1987) reported values ranging from 1 to 36 mg CH_4 m^{-2} d^{-1} in several rivers in western Oregon, while values varying from 0 to 1160 mg CH_4 m^{-2} d^{-1} have been reported in Amazon rivers (Bartlett et al., 1990).

Table 1.6: CH_4 concentration (nmol L^{-1}) and saturation (%) in some rivers and upper estuaries

Rivers	Concentration (nmol L^{-1})	Saturation (%)	References
Mississippi River	107-366	3600-15200	Swinnerton and Lamontagne, 1974
York River	38	2100	Lamontagne et al., 1973
Potomac River	1700	57500	Lamontagne et al., 1973
Sepik River	80-130	3200-5200	Wilkniss et al., 1978
Alsea	22-729	700-30000	De Angelis and Lilley, 1987
Yaquina	276-1730	9500-59800	De Angelis and Lilley, 1987
Siletz	500-1100	17500-38500	De Angelis and Lilley, 1987
McKenzie	5-1018	200-34300	De Angelis and Lilley, 1987
Willamette	155-298	5200-11100	De Angelis and Lilley, 1987
Ogeechee	156-1406	6240-56240	Pulliam, 1993
Hudson	98-940	2700-42400	De Angelis and Scranton, 1993
Amazon	60-12000	1750-420000	Richey et al., 1988
Upper Scheldt estuary	400-600	16000-24000	Scranton and McShane, 1991
Kaneohe	33	1820	Sansone et al., 1999
Elbe	60-120	1750-3500	Wernecke et al., 1994
Merrimack	740	29600	Sansone et al., 1999
Parker	580-930	23200-37200	Sansone et al., 1999
Rivers in Florida	40-690	1600-27600	Bugna et al., 1996
Creeks near Tomales Bay	140-950	5600-38000	Sansone et al., 1998
Upper Elbe estuary	111	4440	Rehder et al., 1998
Scheldt	179-485	7160-19400	Middelburg et al., 2002
Rhine	37-1437	1480-57480	Middelburg et al., 2002
Loire	10-671	400-26840	Middelburg et al., 2002
Douro	63-128	2520-5120	Middelburg et al., 2002
Sado	40	1600	Middelburg et al., 2002
Thames	273	10920	Middelburg et al., 2002
Ems	51	2040	Middelburg et al., 2002
Elbe	111	4440	Middelburg et al., 2002
Rivers in the Great Bay area	580-2440	23200-97600	Sansone et al., 1999
Walker Branch, eastern Tennessee	42-98	1680-3920	Jones and Mulholland, 1998b
Sinnamary river	630-2523	25200-100920	Guérin et al., 2006
Stream in Brocky Burn	300-1900	12000-76000	Hope et al., 2001
Picassic	880-2240	35200-89600	Sansone et al., 1999
River Frome	160-1430	6400-57200	Sanders et al., 2007
Garonne	5-627	200-25080	Abril et al., 2007
Dordogne	49-764	1960-30560	Abril et al., 2007
Yangtze	112-190	4480-7600	Zhang et al., 2004
Adyar	2-386000	80-15440000	Rajkumar et al., 2008

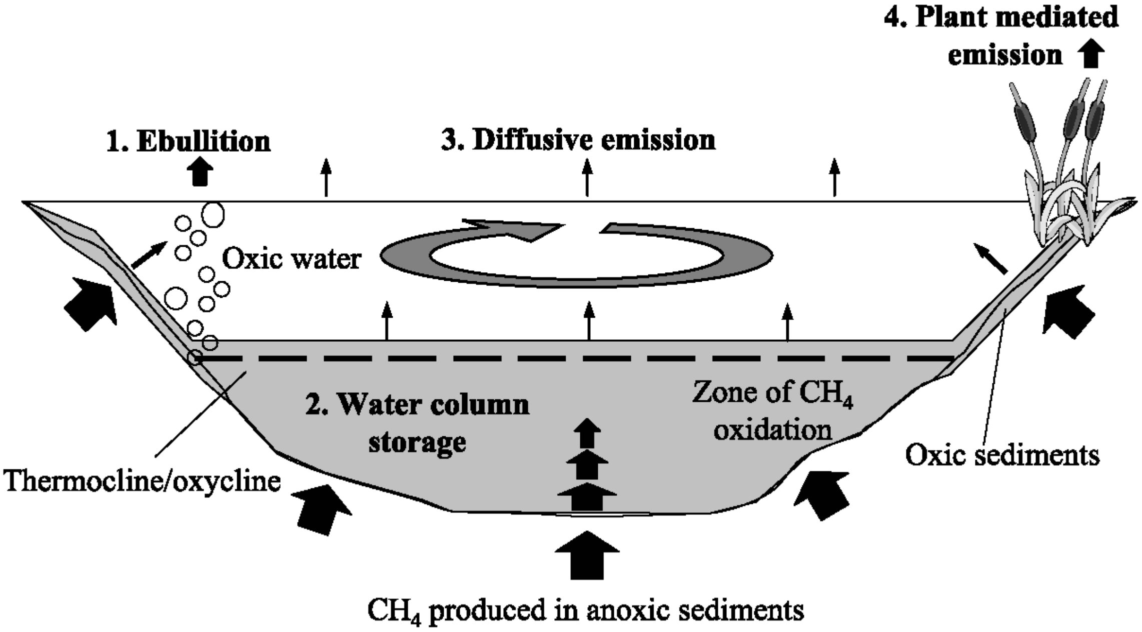

Figure 1.6: Emission pathways and methane dynamics in a stratified lake (Bastviken et al., 2004).

Lakes are important inland aquatic sources of CH_4 to the atmosphere. St. Louis et al. (2000) estimated that CH_4 emissions from man-made reservoirs alone could represent 12% of global CH_4 emissions, and 90% of these CH_4 emissions is suggested to be from reservoir in the tropics. However, estimating emissions from lakes and reservoirs is difficult, since there are at least four emission pathways which may be regulated differently: ebullition flux, diffusive flux, storage flux, and flux through aquatic vegetation (Bastviken et al., 2004; Abril and Guérin, 2008). CH_4 can be exported from the sediment either by ebullition or by diffusion (**Figure 1.6**). Ebullition results in direct flux of methane from the sediment to the atmosphere, with limited impact of methane oxidation in the water column. Hence, the ebullition flux should be related primarily to the net methane production rate in the sediments (i.e., the gross CH_4 production rate minus CH_4 oxidation) and the hydrostatic pressure which has to be overcome for the bubbles to leave the sediment. As a result of the diffusive export from anoxic sediment, CH_4 eventually enters the water column. As soon as CH_4 reaches oxic sediment or water, a large proportion is likely oxidized by methane oxidizing bacteria (Bastviken et al., 2002). For instance, Guérin and Abril (2007) showed that nearly 90% of the CH_4 reaching the hypolimnion of the Petit Saut dam (French Guiana) was oxidized either in the epilimnion or in the downstream river. Most of the CH_4 that escapes oxidation and reaches the upper mixed layer of the water column will be emitted by diffusive flux. This flux component depends on the difference in CH_4 concentration between the water and atmosphere, and on the physical rate of exchange between the air and water, usually expressed as *k* (see section 1.1.2.). For stratified lakes, there can be a build up of CH_4 in the anoxic layer, resulting in CH_4 storage in the water column. This storage will be emitted rapidly by diffusion during periods of lake overturns, for example, during spring and fall in dimitic temperate lakes (Riera et al., 1999). The "storage flux" component is likely a function of CH_4 production rates, the volume of the anoxic water layer, and the losses by CH_4 oxidation and diffusion to upper layers. The fourth potential flux component includes plant-mediated emission in littoral zones with emergent vegetation. This component depends on CH_4 production and oxidation in the sediments, and vegetation characteristics and has been extensively studied in wetlands (e.g., Van der Nat and Middelburg, 1998; Van der Nat et al., 1998; Ding et al., 2003). Global CH_4 emissions of lakes range from 8 to 48 $TgCH_4\ yr^{-1}$ (6-19% of total natural methane emissions and greater than oceanic emission (**Table 1.5**; Bastviken et al., 2004) indicating that lakes and other inland waters should be included as a significant source in global methane budgets.

Beside these four emission pathways, a large fraction of methane produced in reservoirs is transported in rivers downstream of dams. This fraction is estimated to range from 9 to 33% of the emissions across the reservoir surfaces (Guérin et al., 2006). At Petit Saut Reservoir in French Guiana, it was shown that large amounts of CH_4 pass through the turbines and degas downstream of the dam, partly at an aerating weir and partly more downstream in the river (Abril et al., 2005). At this site, over ten years, about 70% of CH_4 emissions occurred downstream of the dam.

1.2.3.2 Methane emissions from estuaries

CH_4 surface saturations and concentrations for various estuaries are listed in **Table 1.7** CH_4 in the surface waters ranges from slight under-saturation (70%; 2 nmol L^{-1}) to extreme super-saturation (548000%; 13700 nmol L^{-1}) indicating a high site-to-site variability, and seasonal and spatial variability within one given site. Indeed, CH_4 distribution in coastal environments is influenced by several factors: sediment and water column production and oxidation, diffusive and advective transport in sediments, mixing with low CH_4 concentration seawater, freshwater inputs, and atmospheric evasion. The relative importance of these processes may vary seasonally (i.e., benthic production and mixing) as well as on a time scale of hours or days (i.e., storm events, winds, and tidal exchange). Exchange across the sediment-water interface in coastal aquatic environments is controlled by physical mixing processes, bubble transport, biological activity, and transport through emergent aquatic macrophytes. In the Tomales Bay (California), Sansone et al. (1998) showed that during winter, CH_4 surface concentration was dominated by the freshwater input while, during the summer, benthic flux was a significant CH_4 sources into the bay. Shifts from oxic to anoxic conditions significantly enhance CH_4 formation in the sediments and water column (Huttunen et al., 2003; Bastviken et al., 2004). Moreover, seasonal variations of water temperature, wind speeds and availability of organic matter have been identified to regulate, directly or indirectly, estuarine CH_4 emission to the atmosphere (Abril and Iversen, 2002).

The distribution of CH_4 in some estuaries is largely governed by riverine inputs and conservative mixing (e.g. De Angelis and Lilley, 1987), while non conservative behaviour due to CH_4 outgassing, oxidation and estuarine sources have been identified in some other estuaries (e.g., Sansone et al., 1999; Abril and Borges, 2004). Thus, CH_4 concentration in estuaries may decrease or increase along the salinity gradient. The decrease of CH_4 with increasing salinity is due to a high river end-member concentration and subsequent consumption of CH_4 by oxidation and/or loss to the atmosphere. CH_4 oxidation can turnover the dissolved CH_4 pool rapidly: 1.4 to 9 days in the upper Hudson estuary (De Angelis and Scranton, 1993), <2 hours to 1 day in the Ogeechee river depending on temperature (Pulliam, 1993), 0.5 to 1.8 days in the Randers Fjord (Abril and Iversen, 2002), <2 hours in the upper Scheldt estuary (Van der Nat et al., 1997). CH_4 oxidation is particularly enhanced in the estuarine turbidity maximum (ETM), where surface particulate matter exceeds 100 mg L^{-1}. For instance, in Gironde estuary, as soon as the ETM appeared and surface particulate matter exceeded 100 mg L^{-1}, CH_4 concentrations decreased from 600 to 30 nmol L^{-1} in one month. In addition, during this period CH_4 concentrations were occasionally below atmospheric equilibrium (Abril et al., 2007). In contrast, in a low turbidity system like the Rhine estuary, CH_4 concentrations occasionally exceed 1000 nmol L^{-1}. Clearly, CH_4 oxidation is an important sink of CH_4 in estuaries, but strongly depends on the temperature and the salinity with very low oxidation rates at salinities above 6 (De Angelis and Scranton, 1993). The sources of CH_4 at intermediate to high salinities are attributed to lateral CH_4 inputs from tidal flats and marshes. CH_4 production is particularly intense in tidal flats and marshes because of large inputs of organic matter at anoxic depths by plants rooted in the sediments (Kelley et al., 1995). However, CH_4 emission from estuarine tidal flats and marshes highly decrease from freshwater sites to seawater sites due to sulphate that increases with salinity. Indeed sulphate inhibition of methanogenesis is widely known as mechanism for reduced CH_4 production by anoxic sediments (e.g., Bartlett et al, 1987; Middelburg et al., 1996b; Upstill-Goddard et al., 2000; Shalini et al., 2006). CH_4 emissions from estuaries (excluding tidal marshes) have been integrated at the global scale by several authors. Estimates are 0.8-1.3 $TgCH_4$ yr^{-1} (Bange et al., 1994); 0.9-1.7 $TgCH_4$ yr^{-1} (Upstill-Goddard et al., 2000), 1.8-3.0 $TgCH_4$ yr^{-1} (Midderburg et al., 2002) and 0.2-4.1 $TgCH_4$ yr^{-1} (Abril and Borges, 2004). Thus, although estuaries represent only about 0.4% of the global ocean area, they account for about 7.4% of the oceanic emission (Bange et al., 1994). According these authors, the continental shelf (~15.2% of the global ocean area) accounts for ~68% of the oceanic CH_4 emission. However, these estimates for the coastal environment are rather uncertain due to high spatial and temporal variability and the limited data available. Data from tropical and subtropical estuaries are scarce, however few data that are available suggest that CH_4 emissions from polluted tropical estuaries are up to 20 times greater than unpolluted ones and exceed those from temperate estuaries (e.g. Granberg et al., 1997; Purvaja and Ramesh, 2000). A study of CH_4 emissions in the Adyar river and estuary of the south-east India showed that emissions for the whole Adyar system alone are ~2.5 10^{-4} $TgCH_4$ yr^{-1} (Rajkumar et al., 2008). CH_4 ebullition is not taken into account by gas exchange models based solely on dissolved gas concentrations. However, CH_4 ebullition has been shown to greatly exceed diffusive CH_4 fluxes from mangroves (Barnes et al., 2006) and tropical lagoons (Shalini et al., 2006) at low wind speeds, and from a subtropical lake at high wind speeds (Ostrovsky, 2003). Rajkumar et al. (2008) indicated that ebullition might account for much as 97% of the total CH_4 emission from the Adyar estuary. In this estuary ebullition flux is estimated to be about ~2.0 10^{-3} Tg CH_4 yr^{-1}. Thus, ebullition flux in this estuary is one order of magnitude higher than the diffusive CH_4 flux. Clearly, tropical estuaries and lagoons that receive large organic carbon flux could be large emitters of tropospheric CH_4.

1.2.4 CH_4 emissions from the open ocean

CH_4 emissions in the open ocean range from 4 to 15 $TgCH_4$ yr^{-1} (**Table 1.5**). However, the observation of methane super-saturation in the surface layer of the open ocean, away from sedimentary sources, raises some questions which remain unanswered. The reported concentrations of CH_4 in the surface ocean waters cannot be explained by normal methanogenesis mechanism, which requires strictly anoxic and highly reducing conditions, or by physical transport processes (Bange et al., 1994). Therefore an additional *in situ* mode of CH_4 production is required. Various mechanisms have been discussed, e.g., formation in anoxic microniches (i.e., in decaying organic particles, faecal pellets, or zooplankton gut) or production in association with phytoplankton (e.g., Burke et al., 1983; Conrad and Seiler, 1988; Karl and Tilbrook, 1994). Recently, Karl et al. (2008) showed that methane is produced aerobically as a by-product of methylphosphonate (MPn) decomposition in phosphate-stressed waters. Methylphosphonate, the simplest of C-P bonded compounds, may be both a precursor for the biosynthesis of more complex phosphonate molecules and a partial degradation product thereof. In *Escherichia coli*, *Pseudomonas* and many other bacteria, MPn can be used as a sole source of P during aerobic growth. During MPn utilization, methane is quantitatively released, whereas P is incorporated into new cell mass (Daugton et al., 1979).

Methylphosphoante decomposition, and thus methane production, may be enhanced by the activity of nitrogen-fixing microorganisms. Thus, aerobic marine methane production will be sensitive to the changes in water-column stratification and nutrient limitation that are likely to result from greenhouse gas induced ocean warming (Karl et al., 2008). Continued greenhouse gas induced global warming could lead to enhanced stratification of the surface ocean and expansion of phosphate limited, nitrogen fixation favorable marine habitats (Karl, 2007). Such climate driven modifications could reinforce aerobic CH_4 production, resulting in accelerated greenhouse warming and the ecological consequences thereof (Karl et al., 2008).

Table 1.7: CH_4 concentrations (nmol L^{-1}) and saturations (%) in some estuaries and bays.

	Concentration (nmol L^{-1})	Saturation (%)	References
Lake Nitinat	48	1900	Lamontagne et al., 1973
Chesapeake Bay	28-43	1100-1700	Swinnerton et al., 1969
Saanich Inlet	33	1300	Lilley et al., 1982
Alsea Bay	6-695	300-29000	De Angelis and Lilley, 1987
Yaquina Bay	8-323	300-11600	De Angelis and Lilley, 1987
Salmon Bay	123-323	5200-12400	De Angelis and Lilley, 1987
Pettaquamscutt River estuary	200-275	8000-11000	Scranton et al., 1993
Hudson estuary	50-940	2500-7200	De Angelis and Scranton, 1993
Amvrakikos Bay	4-24	146-974	Bange et al., 1994
Randers Fjord	28-290	1120-11600	Abril and Iversen, 2002
Bodden Waters	3-388	105-15500	Bange et al., 1998
Eckernförde Bay	20-183	793-7803	Bussmann and Suess, 1998
Elbe estuary	3-745	130-29800	Middelburg et al., 2002
Ems estuary	230-328	9200-13100	Middelburg et al., 2002
Thames estuary	4-168	150-6700	Middelburg et al., 2002
Rhine estuary	4-1243	140-49700	Middelburg et al., 2002
Scheldt estuary	10-80,2	380-3210	Middelburg et al., 2002
Loire estuary	9-578	340-23100	Middelburg et al., 2002
Gironde estuary	2-34	70-1370	Middelburg et al., 2002
Douro estuary	16-143	620-5720	Middelburg et al., 2002
Sado estuary	24-3950	940-158000	Middelburg et al., 2002
Humber estuary	4-666	238-21048	Upstill-Goddard et al., 2000
Tyne estuary	14-654	450-20000	Upstill-Goddard et al., 2000
Walvis Bay	5-750	200-30000	Scranton and Farrington, 1977
Tomales bay	8-100	320-4000	Sansone et al., 1998
Pulicat lake	94-500	3760-20000	Shalini et al., 2006
Adyar estuary	5-13700	200-548000	Rajkumar et al., 2008

1.3 Mangrove ecosystems

1.3.1 Origin and distribution of mangroves

Mangroves are forests of trees that grow at the interface between land and sea in inter-tidal environments in tropical and subtropical latitudes. These trees, and the associated microbes, fungi, plants, and animals, constitute the mangrove forest community or mangal. The mangal and its associated abiotic components (e.g. salinity, temperature, winds, tidal amplitudes, river discharge, and soil characteristics) constitute the mangrove ecosystem. The term “mangrove” often refers to both the plants and the forest community. To avoid confusion, Macnae (1968) proposed that “mangal” should refer to the forest community while “mangroves” should refer to the individual plant species. Duke (1992) defined a mangrove as “… a tree, shrub, palm or ground fern, generally exceeding one half meter in height, and which normally grows above mean sea level in the intertidal zone of marine environments, or estuarine margins.” This definition is acceptable except that ground ferns should probably be considered mangrove associates rather than true mangroves. The term “mangrove” is also used as an adjective, as in “mangrove tree” or “mangrove fauna.” Mangrove forests are sometimes called “tidal forests”, “coastal woodlands”, or “oceanic rain forests”.

Tomlinson (1986) recognized three groups of mangroves: major mangrove species, minor mangrove species and mangrove associates. The major species are the strict or true mangroves, recognized by most or all of the following features: 1) they occur exclusively in mangal, 2) they play a major role in the structure of the community and have the ability to form pure stands, 3) they have morphological specializations, especially aerial roots and specialized mechanisms of gas exchange, 4) they have physiological mechanisms for salt exclusion and/or excretion, 5) they have viviparous reproduction, and 6) they are taxonomically isolated from terrestrial relatives. The minor mangrove species are less conspicuous elements of the vegetation and rarely form pure stands. According to Tomlinson (1986), the major mangroves include 34 species in 9 genera and 5 families. The minor species contribute 20 additional species in 11 genera and 11 families for a total of 54 mangrove species belonging to 26 genera and 16 families. Duke (1992), on the other hand, identified 69 mangrove species belong to 26 genera in 20 families. By reconciling common features from

Tomlinson (1986) and Duke (1992), 65 mangrove species in 22 genera and 16 families can be found.

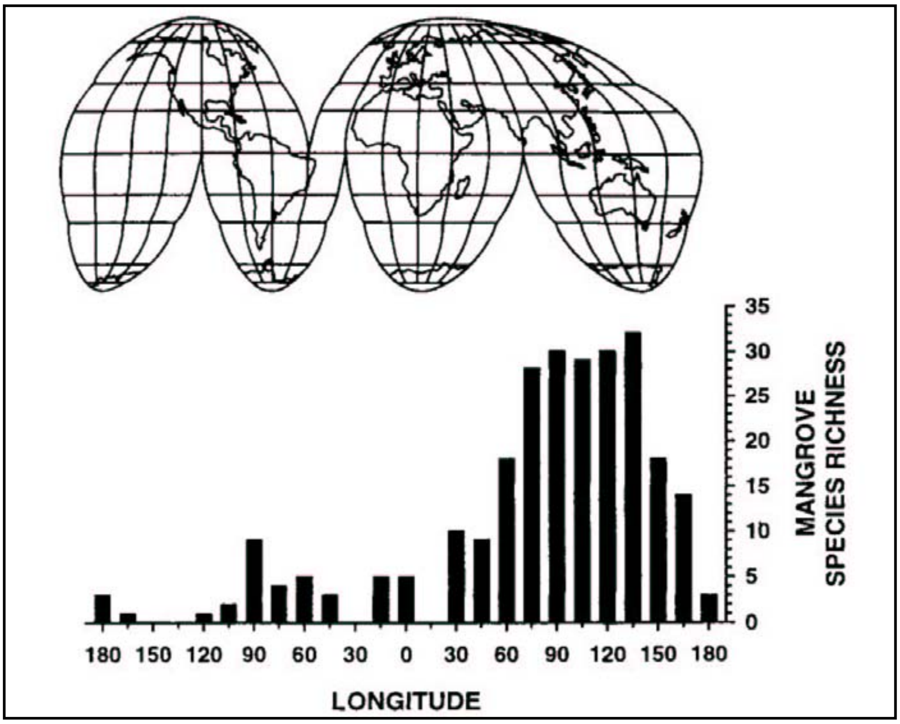

Figure 1.7: Species richness of mangroves as a function of longitude (in 15° increments) (Ellison et al., 1999).

Mangrove species richness declines dramatically from a maximum in the Indo-West Pacific (IWP) to a minimum in the Caribbean and Western Atlantic (**Figure 1.7**).

Explaining this "anomalous" biogeographic pattern has been a focus of discussion for most of this century. Two hypotheses have been put forward to explain the mangrove biodiversity anomaly. The "centre-of-origin hypothesis" asserts that all mangrove taxa originated in the IWP and subsequently dispersed to other parts of the world. The "vicariance hypothesis" asserts that mangrove taxa evolved around the Tethys Sea during the Late Cretaceous, and regional species diversity resulted from in situ diversification after continental drift.

Ellison et al. (1999) evaluated these two hypotheses using 1) a review of the mangrove fossil record, 2) a comparison of modern and fossil distributions of mangroves and mangrove-associated gastropods, 3) an analysis of nestedness patterns of individual plants and gastropods communities, 4) an analysis of species-area relationships of mangroves and gastropods, and 5) an analysis of nestedness patterns of individual plants and individual gastropod species. The evidence from all 5 analyses supported the vicariance hypothesis, suggesting a Tethyan origin of mangroves. This argues that the much higher diversity of mangroves in IWP relates to conditions there that favoured diversification. For example, the continual presence of extensive wet habitat may have allowed more species to make the transition from terrestrial to brackish-water habitats. The Atlantic, Caribbean and/or East Pacific all saw periods of drying which could prevent such adaptation. Ricklefs and Latham (1993) suggest that limited dispersal, combined with the closure of the Tethys connection to the Atlantic Ocean in the mid-Tertiary, restricted most mangrove taxa to the Indo-Pacific.

The influences of precipitation and temperature on mangrove distributions were analyzed by Blasco (1984). He reported four classification groupings: i) warm humid areas where 90% of the world's mangroves are found, notably from South Mexico to Colombia, in the Caribbean, North Brazil, and from S.E. Asia to N. Queensland (Australia); ii) sub-humid areas where mangroves are occasionally found, such as East Africa, India, S. Queensland (Australia), Mexico and Venezuela; iii) semi-arid areas where mangroves are rarely found, usually close to major river mouths, such as the Indus Delta (Pakistan), Gujarat (India), the Western and Northern Territory provinces of Australia, and Ecuador; and iv) arid areas where mangrove are practically unknown, except where there are winter rains, for example along the Ethiopian and Egyptian coastlines of the Red Sea, the Persian Gulf and the Gulf of California.

In equatorial and tropical summer rainfall regions, mangroves are tall, dense and floristically diverse. In subtropical arid regions mangroves are low, scattered and sporadic. Areas of higher coastal rainfall and high riverine inputs of freshwater tend to support more diverse communities than areas of low coastal rainfall and limited runoff. This is shown in Australia, where at 22.5°S (Tropic of Capricorn) there are four species on the dry west coast and twenty species on the wet east coast (Tomlinson, 1986; Duke, 1992). On the eastern coastline, the tallest (up to 35 m tall) and more dense forests of mangroves inhabit areas where mean annual rainfall is >1500 mm and distributed throughout the year. In areas where rainfall is <1500 mm, mangroves are much shorter, around 1-6 m. In these drier areas, there are also larger vegetation free zones bordering the landward fringes. In general, the suitability of habitat for particular mangrove species depends on climatic conditions and the coastal geography. **Figure 1.8** illustrates the word distribution of mangroves in six biogeographic regions: 1) western Americas and the eastern Pacific, 2) eastern Americas and the Caribbean, 3) western Africa, 4) eastern Africa and Madagascar, 5) Indo-Malaysia and Asia, and 6)

Australia and the western Pacific. However, mangrove species are divided primarily, into two global hemispheres, the Atlantic East Pacific (AEP), and the IWP. The region with fewest species is western Africa (region 3), in the AEP. It has seven species, whilst Indo-Malaysia (region 5) in the IWP, has more than forty-nine. In the IWP, the east African region is the most depauperate with only ten species. Note that there is an overlap of only one species between hemispheres, namely *Acrostichum aureum*, a mangrove fern.

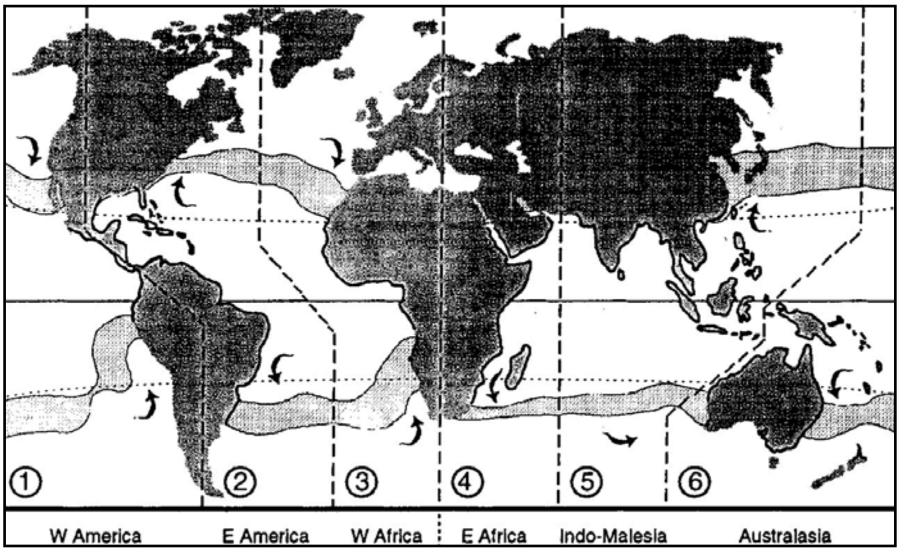

Figure 1.8: World distribution of mangroves (solid coastlines) showing extent within six biogeographic regions (Duke et al., 1998). The poleward extent of mangroves is usually associated with the winter position of the 20°C isotherm (range of summer and winter positions shown) and this is influenced by ocean currents (shown by arrows).

Zonation can be a structural feature of mangrove forests in some parts of the world (Woodroffe, 1992). However, unlike open coast habitats where zonation patterns are distinct, mangrove distributions are extremely variable and extensive surveys may be necessary to fully document patterns, particularly if diversity is high. The "zones" may be obscured by broad overlap in species distributions (Bunt and Bunt, 1999) or they may simply be absent in some mangals. Bunt (1999) has developed methods specifically for evaluating and describing mangrove zonation. Where zonation does occur, contributing factors may include plant succession, geomorphology, physiological adaptation, propagule size, seed predation and interspecific interactions (Ellison and Farnsworth, 1993). The relative importance of these factors, however, depends on the individual habitat and there is disagreement about the general importance of some of them. For example, Robertson et al. (1991) argue that succession plays a minor role in mangrove zonation and that simple erosion and sedimentation control uniqueness of these communities may make it difficult even to define succession stages. One potential cause of mangrove zonation is the differential ability of propagules to establish at different tidal heights. This is directly related to propagule size. It has been suggested that small propagules drift further inland and establish better in shallow water than do large propagules (thus producing a species zonation dependent on propagule size). The importance of this process to the creation of mangrove zones has been clearly for *Avicennia bicolour* and *Rhizophora racemosa* on the Pacific coast of Costa Rica (Jiménez and Sauter, 1991). However, the more general importance of this process has been contested (Smith, 1992). Interspecific differences in tolerance for physiological stress are perhaps the best demonstrated cause of mangrove zonation. However, while physiological responses to physicochemical conditions undoubtedly influence mangrove distributions in some habitats, conclusions must be made cautiously since field measurements do not always support laboratory conclusion (Schwamborn and Saint-Paul, 1996). Despite this limitation, it is clear that mangrove species respond differently to different tidal regimes. For example, in the Indian Sunderbans, a mangrove forest that experiences total diurnal inundation is dominated by *Avicennia marina* and *Avicennia alba* while *Excoecaria agallocha*, *Ceriops decandra* and *Acanthus ilicifolius* dominate sites that are not completely inundated (Saha and Choudhury, 1995).

Bhosale and Mulik (1991) described four methods of mangrove reproduction: viviparity, cryptoviviparity, normal germination on soil, and vegetative propagation. Vivipary, the precocious and continuous growth of offspring while still attached to the maternal plant, is a unique adaptation to shallow marine habitats (Thomas and Paul, 1996). True viviparous species remain attached to the maternal plant for a full year while cryptoviviparous offspring are only attached for 1-2 months (Bhosale and Mulik, 1991). Smith and Snedaker (1995) suggest that viviparous reproductive patterns allow seedlings to develop some salinity tolerance before being released from the present tree. The timing of mangrove reproduction depends on local environment conditions and may differ broadly over the range of a species. For example, Duke (1990) found that flowering in *Avicennia marina* occurred 6 months earlier in Papua New Guinea than in Southern Australia and New Zealand. The period from flowering to fruiting was 2-3 months in the northern tropical site but stretched to 10 months in the southern temperate locations. Flowering appeared to be controlled by daylength while air temperature set the period for fruit maturation.

Mangroves are highly adapted to the coastal environment, with exposed breathing roots, extensive support roots and buttresses, salt-excreting leaves, and viviparous water-dispersed propagules. These adaptations vary among taxa and with the physico-chemical nature of the habitat (Duke, 1992). Perhaps the most remarkable adaptations of the mangroves however are the stilt roots (or prop roots) of *Rhizophora*, the pneumatophores of *Avicennia* (**Figure 1.9**), the root knees of *Bruguiera*, *Ceriops* and *Xylocarpus* and the buttress roots of *Xylocarpus* and *Heritiera*. The roots of many mangroves do not penetrate far into the anaerobic substrata. Instead, the trees produce profuse lateral roots for support. Their effectiveness is well illustrated by the tallest mangrove trees, found in Ecuador, which attain heights of more than 60 m (Emilio, 1997). The specialized roots are important sites of gas exchange for mangroves living in anaerobic substrata. These exposed surfaces may have numerous lenticels (loose, air-breathing aggregations of cells; Tomlinson, 1986). *Avicennia* possesses lenticel-equipped pneumatophores (upward directed roots) through which oxygen passively diffuses. The lenticels may be closed, partially opened or fully opened, depending on environmental conditions. The spongy pneumatophores are generally short (< 30 cm), but grow much larger and become more numerous in *Avicennia marina* living in anaerobic and oil-polluted conditions. This phenotypic response apparently increases surface area for gas exchange. Compared to the underground roots, the aerial roots have an exaggerated zone of elongation behind the apical meristem (Tomlinson, 1986). They also have significant secondary thickening (similar to the stems). When the aerial roots reach the ground, they shift to having a short elongation zone and little to no secondary growth. They also become spongy to adapt to sub-soil existence. In *Rhizophora*, the roots become thinner and form “capillary rootlets” with a simple diarch stele and narrow cortex. Like aquatic plants, true mangrove lack roots hairs. Hence, the endodermis is an effective absorbing layer (Tomlinson, 1986).

1.3.2 Ecological roles of mangrove ecosystems

Mangrove ecosystems produce large amounts of litter in the form of falling leaves, branches and other debris. Decomposition of the litter contributes to the production of dissolved organic matter and the recycling of nutrients both in the mangal and in adjacent habitats. The organic detritus and nutrients could potentially enrich the coastal sea and, ultimately, support fishery resources. The contribution of the mangroves could be particularly important in clear tropical waters where nutrient concentrations are normally low.

The nutrient cycling begins when leaves fall from the mangroves and are subjected to a combination of leaching and microbial degradation (Chale, 1993). Leaching alone removes a number of substances and can produce high levels of DOC (Benner et al., 1990a). Potassium is the most thoroughly leached element with up to 95% of the total potassium being removed in a very short time (Steinke et al., 1993). Carbohydrates also leach quickly during early decomposition. Tannins, in contrast, leach very slowly and the high tannin contents may slow establishment of bacterial populations in the initial period of decomposition. As the tannins are eventually leached, the bacterial populations rapidly increase (Rajendran and Kathiresan, 1999).

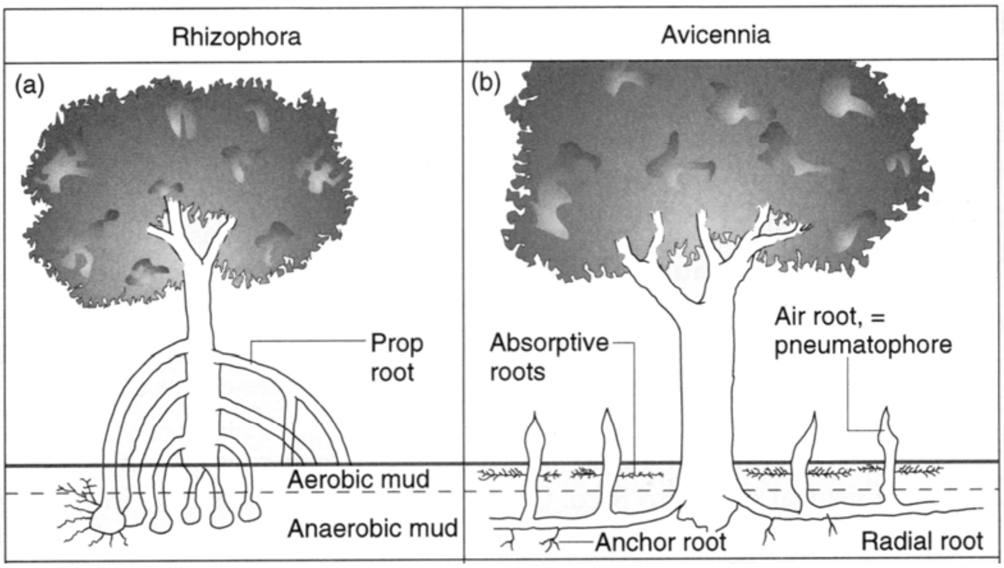

Figure 1.9: Root systems of *Rhizophora* (a) and *Avicennia* (b). The function of the above-ground aerating component related to gas exchange, keeping the below-ground roots well oxygenated. The absorbing and anchoring component of the root system provide a dual function. It provides physical support for the main trunk and serves as an anchor in an unstable environment, and it is involved in water and nutrient absorption. The cable component constitutes the lateral root system that unifies the aerating and absorbing/anchoring part of the system (Tomlinson, 1986).

Bacteria and fungi contribute to decomposition of the mangrove material and the transformation and cycling of nutrients. Fungi are the primary litter invaders, reaching their peak in the early phases of decomposition (Rajendran, 1997). Bacterial colonies appear shortly after the litter has been colonized by fungi. The N_2-fixing azotobacters are one of the important groups in the decomposing litter and their activities may increase the nitrogen content of the leaves 2-3 times (Wafar et al., 1997).

Chale (1993) measured a similar rapid increase in leaves after six weeks of decomposition and suggested that the litter 1) provides a surface for microbial nitrogen synthesis and 2) acts as a nitrogen reservoir. The C:N ratio of decomposing of *Avicennia marina* leaves drops dramatically from approximately 1432 to 28, due primarily to a large increase in their nitrogen content (Mann and Steinke, 1992). In another study, Tam et al. (1990) saw the C:N ratio in decomposing leaves increase for one week, then decrease, and finally stabilize at approximately 74. They hypothesized that the initial increase resulted from the conversion of particulate and soluble nitrogen in the litter to proteins in bacteria and fungi.

A number of factors can affect the rate of litter decomposition, and therefore, the rates of nutrient cycling. For example, litter decomposition rates vary among mangrove species. *Avicennia* leaves, because they are thinner and have fewer tannins, decompose faster than those of other species. *Avicennia* leaves also sink and begin to decompose immediately whereas the leaves of other species (e.g. *Rhizophora* and *Sonneratia*) may float for several days (Wafar et al., 1997). Decomposition is influenced by tidal height, rainfall and temperature. In subtropical mangrove forests, mangrove debris decomposes substantially faster in the rainy season. Mackey and Smail (1996) studied decomposition of *Avicennia marina*. They found significantly faster decomposition in lower intertidal zones with greater inundation. They also found an exponential relationship between leaf decomposition rate and latitude with leaves decomposing most quickly at low latitudes. They attributed the pattern to temperature differences, and concluded that seasonality can have important effects on organic cycling and nutrient export from mangrove systems.

Breakdown and decomposition of mangrove litter is accelerated by the feeding activities of invertebrates. The animals may process large volumes of the litter, contributing significantly to nutrient dynamics. In field experiments, Twilley et al. (1997) found that mangrove crabs process the mangrove material very quickly. They removed a full day's accumulation of mangrove leaf litter in only 1 hour. Because the mangrove material is quite refractory, it may need to decompose for some time before it is useful to other invertebrates. Wafar et al. (1997) estimated that litter needs to decompose for about two months before it can be used in most detritivores' diets. *In situ* observations verify that mangrove leaves attract shrimp, crabs, and fish (particularly juveniles), but only after several weeks of decomposition (Rajendran, 1997). Because of this, only limited number of invertebrates use directly mangrove derived carbon. The other use freshly deposited phytodetritus, benthic microalgae, and N_2-fixing microepiphytes (Bouillon et al., 2002).

Mangals contribute to complex food webs and important energy transfers. However, it is not clear how, or whether, these processes affect the larger ecosystem. While, the living vegetation is a valuable food resource for insects, crustaceans, and some vertebrates, most of the mangrove production is transferred to other trophic levels through litterfall and detrital pathways. Mangrove forests produce organic carbon well in excess of the ecosystem requirements. Duarte and Cebrián (1996), estimate that the excess photosynthetic carbon approaches 40% of net primary production. While some of this organic matter simply accumulates in the sediments, large amounts could potentially be transported offshore (Lee, 1995). The amount of material exported, however, depends strongly on local conditions and varies enormously among mangroves (Twilley et al., 1992). Material exported from the mangroves could potentially support offshore communities, but the connections between mangroves and the adjacent habitats are complex, dynamic, and have been difficult to demonstrate unequivocally (Alongi, 1998). For instance, Jennerjahn and Ittekkot (1997) found that organic matter in continental sediments in eastern Brazil was very different from that in mangrove environments and concluded the mangrove matter is largely retained and decomposed within the mangal itself. Studies with stable isotopes also suggest that mangroves do not make major contribution to coastal food webs (e.g., Loneragan et al., 1997; Bouillon et al., 2002). In fact, the data suggest that carbon may instead be flowing from oceanic systems into mangrove habitat. Oceanic carbon contributed up to 86% of the particulate organic carbon in water samples from a Brazilian mangal (Rezende et al., 1990).

It appears that mangroves, in general, make only a localized contribution to the food web (Mohammed and Johnstone, 1995). Sediment meiofauna, for example, feed directly on mangrove detritus. The composition of the meiofaunal community changes during the process of litter decay, suggesting that community is responding to chemical changes in the leaves. The meiofaunal community, though large in some habitats, may largely be a trophic dead end that contributes little to the larger food web (Schrijvers et al., 1998).

The mangroves may have stronger trophic linkages with epibenthic invertebrates and fish living in the mangal and in nearby habitats (e.g. seagrass beds). For example, mangroves detritus contribute to the nutrition of juvenile prawn *Penaeus merguiensis* living in tidal creeks. The juveniles feed directly on mangrove detritus, on other small detritivorous invertebrates, and on benthic microalgae growing in the mangal (Newell et al., 1995). Invertebrates may also feed on the variety of cyanobacteria and microalgae that live on submerged portions of the mangroves and on leaf litter (Farnsworth and Ellison, 1995). Shrimp in mangrove estuaries may also feed heavily on seagrass epiphytes (Loneragan et al., 1997).

Mangroves detritus is probably more important as a substrate for microbial activity and nutrient regeneration than it is as a direct food for detritivores. Wafar et al. (1997) analyzed energy and nutrient fluxes between mangroves and estuarine waters and concluded that mangroves contribute significantly to the estuarine carbon budget. However, they contribute little to nitrogen and phosphorus budgets. It is not clear whether any of these substances are exported from the mangal in sufficient quantities to make significant contributions to energy flow and the ecology of the broader ecosystem. Mangrove sediments efficiently uptake, retain and recycle nitrogen. Resident bacteria and benthic algae rapidly assimilate available ammonium and prevent its export (Kristensen et al., 1995; Middelburg et al., 1996a). The mangrove environment may, therefore, represent a nutrient and carbon sink rather than a source for adjacent habitats. Careful measurements and creative experimentation will be necessary to clarify the role these habitats plays in larger-scale food webs and energy fluxes.

Mangroves habitats and prawn/shrimp populations are tightly linked in many regions. Analyses of commercial prawn catches have repeatedly shown strong correlations between abundance and biomass of prawns and extent of the surrounding mangrove areas (Vance et al., 1996). Robertson and Blaber (1992) proposed three explanations for this relationship. First, organic detritus exported directly from the mangrove provides food and habitat for juvenile penaeids in offshore areas. Second, the waters in the numerous channels and creeks of the mangrove receive high levels of terrestrial runoff, rich in nutrients. Export of these nutrients contributes to productivity. This productivity, in turn, may support offshore penaeid populations. Third, the mangrove waterways directly serve as nursery ground for juvenile penaeids that move offshore and enter the commercial fishery as they mature. This hypothesis is strongly supported by surveys of larval, postlarval and juvenile penaeids in nearshore habitats (Vance et al., 1990). As the shrimp grow, they may eventually leave the mangal. In the Matang mangroves of Malaysia, Chong et al. (1994) measured prawn densities of 4092 individuals ha^{-1} in the mangal but only 2668 individuals ha^{-1} in the adjacent mudflats.

Crabs are characteristic members of the invertebrate mangrove fauna and have received much attention. Mangrove crabs can be divided into distinct guilds based on their feeding mode. Some species are detritivores that extract their food from sediments while others are opportunistic scavengers. There are also a number of active predators. It is unclear what factors are responsible for these preferences. Micheli (1993) found that preferences were not affected by tannins, water content or leaf toughness. Many of herbivorous crabs store the leaves in their burrows for some time. However, the nutritional value of the leaves does not increase during the time they are stored, indicating that the crabs are simply storing the leaves and not gardening them to encourage bacterial or fungal growth (Micheli, 1993). Given that the mangrove leaves, in general, have low nutritional value and the crabs do not have a mechanism to promote bacterial or fungal growth, it may be very important for them to get the maximum food value out of the leaves they eat. This may contribute to their specific preferences. Burrows enhance aeration, facilitate drainage of the soils, and promote nutrient exchange between the sediments and the overlaying tidal waters. Smith et al. (1991) removed burrowing crabs from a mangal and observed significant increase in soil sulphide and ammonium levels relative to control sites. These chemical changes led to decrease mangrove growth and reproduction.

Mangroves also host a rich and diverse assemblage of fish. For example, in the mangrove of Embley river (Australia) alone, Robertson and Blaber (1992) found 197 species of fish. Similar results were found in the mangrove waters of Vietnam with 260 species (Hong and San, 1993). Abundances of fish can also be very high with biomasses ranging from 10 to 29 g m^{-2} (Arancibia et al., 1993; Robertson and Blaber, 1992).

Insects constitute a significant portion of the fauna in many mangrove communities. For example, Veenakumari et al. (1997) found 276 insect species in the mangals of Andaman and Nicobar Islands of India; 197 of these were herbivores, 43 were parasites and 36 were predators. Similar levels of diversity and abundance have been found in the fauna of Thailand’s Ranong mangroves (Murphy, 1990). Many of the insects reported in mangals are only temporary visitors. As results, they provide linkages between the mangal and other environments (Annanda et al., 1998).

Mangroves provide important habitat for landbirds, shorebirds and waterfowl. The birds in the mangal may be permanent residents that forage and nest in the mangroves and mangrove waters or they can be temporary visitors. Lefebvre et al. (1994) measured bird abundances and grouped species according to their diet and the frequency with which they use mangrove habitats. Distributions and abundances of the feeding guild were consistent with the abundance and distribution of their invertebrate prey. About 315 species of birds are known from the Sunderbans of Bangladesh (Hussain and Acharya, 1994). Alves et al. (1997) counted 32 birds species in the mangroves of Jequiaman, Brazil and 77 bird species have been recorded in the Pacific mangroves of Colombia (Naranjo, 1997).

1.3.3 Mangrove ecosystem productivity

The most widely used proxy of mangrove productivity is annual litter fall, which is known to show a latitudinal gradient being highest close to the equator (e.g., Twilley et al., 1992). Typical global average litter fall rates range from 68 to 92 TgC yr^{-1} (Twilley et al., 1992; Jennerjahn and Ittekkot, 2002; Bouillon et al., 2008). It must be stressed, however, that this underestimates the total net CO_2 fixation by mangroves, since (1) it does not incorporate the wood and belowground biomass production (Middleton and McKee, 2001; Bouillon et al., 2008), (2) it does not take account of the leaf damage or direct consumption by herbivores that represent a formal component of NPP, and (3) nor DOC release through root exudates. Estimates indicate that belowground biomass makes up a substantial part (10-55%) of the total mangrove biomass (Matsui, 1998; Alongi and Dixon, 2000; Bouillon et al., 2008). A number of recent direct measurements of photosynthesis rates indeed suggest that NPP is significantly higher than litter fall estimates, the latter representing only ~30% (range: 14-41%) of the net canopy production (Alongi et al., 2005a). An alternative approach to estimate the NPP is to include the (scarce) estimates of wood and root production. Bouillon et al. (2008) estimated a global average rate wood production of 67 TgC yr^{-1}. Similarly, they estimated the fine root production of 82 TgC yr^{-1}. Combining these data, the total NPP (litter fall, wood and fine root production) can be estimated to be roughly 218 TgC yr^{-1}. This suggest that litter fall comprises no more than ~ 30% of the total NPP, consistent with the estimates presented by Alongi et al. (2005a). So far, budgeting and productivity studies in mangrove area have primarily been based on litter fall (e.g., Jennerjahn and Ittekkot, 2002), which obviously leads to underestimates of carbon dynamics.

The efficiency of mangrove systems in trapping suspended material from the water column likely depends on a range of factors such as the particle size, salinity, tidal pumping and areal extent of the intertidal zone, but can be very high: 15-44% (Victor et al., 2004), 30-60% (Kitheka et al., 2002), and up to 80% (Furukawa et al., 1997). The origin of the organic fraction in the water column is highly variable, and may include a mixture of marine and freshwater plankton, C3 or C4 terrestrial matter, mangrove litter and seagrass-derived material. The organic content of suspended matter is low, typically in the 2-4% range (Bouillon et al., 2003b), which is comparable to or lower than that of mangrove sediments.

Rates of benthic primary production by microphytobenthos have been reported from different mangrove ecosystems, and range between 7 and 73 mol C m^{-2} yr^{-1} (Gattuso et al., 1998; Kristensen and Alongi, 2006). The inputs from microalgae are generally considered to be low due to light limitation or inhibition by tannins (Alongi, 1994). Productivity data for macroalgae are scarce, but some studies indicate that they may contribute significantly (e.g., 110-118 mol C m^{-2} yr^{-1} for lagoon systems; Koch and Madden, 2001). Phytoplankton densities and primary production have been found to be highly variable and it has been suggested that phytoplankton productivity may be significantly lower in estuarine mangrove areas (e.g., the Fly river delta, Papua New Guinea: 0.7-21 mol C m^{-2} yr^{-1}; Robertson et al., 1992) than in mangrove-lined lagoons (e.g., Ivory Coast: up to 146 mol C m^{-2} yr^{-1}; Robertson and Blaber, 1992). The relative importance of phytoplankton to the total mangrove ecosystem primary productivity is expected to vary with geomorphology, water current, turbidity and nutrient levels, e.g., ~20% for the Fly River delta, Papua New Guinea (Robertson et al., 1992), 50% in Terminos Lagoon, Mexico (Day et al., 1987), and far exceeding mangrove inputs in other sites (e.g. Wafar et al., 1997; Li and Lee, 1998). Despite a potentially high phytoplankton production in mangrove creeks, high turbidity and active microbial degradation within the water maintain many creeks as net heterotrophic systems, even during the day (Kristensen and Suraswadi, 2002).

1.3.4 Outwelling and dispersal of mangrove organic matter

About four decades ago, Odum (1968) proposed a groundbreaking hypothesis in coastal ecology according to which the outwelling of litter from coastal wetlands was a major source of energy that supported much of the secondary production of estuaries and nearshore waters.

Because of the regular tidal flooding and draining in most mangrove areas, the material exchanges between the forests and coastal waters can be efficient (e.g. Dittmar and Lara, 2001a).

Many of the most productive mangrove forests in the world lose a significant fraction of their NPP to coastal waters (Robertson et al., 1992; Jennerjahn and Ittekkot, 2002). Large differences occur between mangrove forests with respect to litter production and export rates, and some largely retain detritus within their sediments (Woodroffe, 1992), which is then mineralized or buried. On a global average, however, numerous studies indicate that mangrove forests are a significant net source of detritus to adjacent coastal water, and the global export rate of mangrove litter has been estimated to 37 TgC yr^{-1} which is approximately half of the total litter production (Jennerjahn and Ittekkot, 2002).

While there are clear patterns of high particulate detritus export from most mangrove environments, the utilization of this organic matter in marine food webs seems variable. The large flux of mangrove detritus to the coastal ocean can have recognizable effects on aquatic foods webs in some areas (e.g., Alongi et al., 1989; Alongi, 1990), but the litter outwelling hypothesis has been challenged in other areas (Lee, 1995; Schwamborn et al., 1999). Some studies show that, as far as POC fluxes are concerned, mangrove forests and adjacent environments can strongly interact. For example, Hemminga et al. (1994), and Bouillon et al. (2007c) observed a tight coupling between mangrove forests and seagrass meadows in Gazi Bay (Kenya) where strong outwelling of particles from the mangrove environment is evident. During flood tides, however, reversed transport of organic particles from the seagrass zone to the mangrove forest can be observed. Respiratory CO_2 derived from mangrove detritus can be a major inorganic carbon source for the seagrass meadows as observed by Hemminga et al. (1994) in Gazi Bay and by Lin et al. (1991) for mangrove-seagrass system in Florida. In contrast to the tight coupling between mangroves and adjacent seagrasses, particle outwelling is often restricted to the reef line (Schwamborn et al., 1999) while nearby coral reefs can exist in relative isolation from mangrove influence (Hemminga et al., 1994; Bouillon et al., 2007c). Thus, the role of mangrove litter on sediment processes and the tight coupling with adjacent ecosystems is mostly restricted to the direct vicinity of the forests. A few kilometers offshore, however, mangrove litter usually contributes insignificantly to the organic matter accumulating in sediments or to the carbon consumed by organisms (Hemminga et al., 1994; Jennerjahn and Ittekkot, 2002).

Two major processes can explain the lack of a significant offshore impact of litter outwelling. 1) The distribution of exported mangrove litter largely depends on the local geomorphology and hydrodynamics. Many mangrove forests fringe semi-enclosed bays and estuaries. Water currents within these settings can efficiently trap suspended particles (Jay and Musiak, 1994) and cause enhanced sedimentation rates in direct vicinity of the mangrove environment. Lithogenic input from rivers can provide mineral ballast for the production of fast-sinking aggregates (Jennerjahn et al., 1999). Large scale boundary currents can also diminish the dispersion of terrigenous suspended particles off the continental margins (Jennerjahn and Ittekkot, 2002). 2) On the time scale of outwelling, a significant fraction of litter is lost as DOC. Within the first weeks of litter degradation in the water column or submersed sediments, >75% of organic carbon can be lost (Dittmar and Lara, 2001b; Schories et al., 2003), most of it to the dissolved pool (Benner et al., 1990b; Wafar et al., 1997).

Mangrove derived DOC is also released into the water column through the tidal pumping of DOC-rich pore waters, which can significantly add to the total organic carbon export (Bouillon et al., 2007b). DOC concentrations in mangrove pore waters vary considerably within and among forest, but levels as high as 9 mmol L^{-1} has been recorded (Marchand et al., 2006). Quantitative estimates from mangrove forests around the world almost consistently indicate that a significant fraction of NPP is indeed exported to coastal waters as DOC (Dittmar et al., 2006). Decomposition and leaching products of leaf litter are likely sources of the exported mangrove DOC (Dittmar et al., 2001), while the contribution of root exudates or decomposing belowground biomass is not known. The total export rate of organic carbon from mangrove forests may significantly exceed the estimates of litter export by Jennerjahn and Ittekkot (2002) (19 mol C m^{-2} yr^{-1}) if the export of DOC is taken account. Tidal DOC export from a Florida mangrove area (Twilley, 1985) was estimated to be 3.1-3.7 mol C m^{-2} yr^{-1}, while a mangrove tidal creek in Australia (Ayukai et al., 1998) was estimated to be 1.8 mol C m^{-2} yr^{-1}. These export estimates are usually based on small scale studies performed within or in direct vicinity of the mangroves. The only study performed so far on a continental shelf scale (Dittmar et al., 2006) indicates a significantly higher outwelling of DOC (12 mol C m^{-2} yr^{-1}) compared to previous small scale studies in the same region in northern Brazil (4 mol C m^{-2} yr^{-1}; Dittmar et al., 2001) or elsewhere in the world. The reason behind this discrepancy is probably that the gradual release of DOC from floating and suspended detritus in the water column was not accounted for in past studies. From the well developed mangrove forest in

Brazil about 13 mol C m^{-2} yr^{-1} of floating debris were exported through tidal creeks over the course of an annual sampling campaign (Schories et al., 2003). In addition to floating debris, POC was exported at the rate of 3 mol C m^{-2} yr^{-1} (Dittmar and Lara, 2001a,c).

Stable carbon isotope and lignin analyses indicate leaf litter as the primary source of the exported POC (Dittmar et al., 2001). The combined export of debris and POC accounts for ~40% of the total litter fall in this mangrove forest. Mangrove derived DOC is exported at a rate of 4 mol C m^{-2} yr^{-1} (Dittmar and Lara, 2001c). The combined export for all organic matter fractions (debris, POC, and DOC) is 20 mol C m^{-2} yr^{-1}. A major fraction (12 mol C m^{-2} yr^{-1}) of this organic matter is ultimately transported across the shelf in form of DOC, probably after extensive photochemical and microbial reworking (Dittmar et al., 2006).

Important master variables that control to a large degree the magnitude of organic matter outwelling and the partition between debris, POC and DOC outwelling are NPP, the abundance of litter-collecting fauna and tidal range. In the mangrove forest of Bragança (northern Brazil), the leaf-removing crab *Ucides cordatus* has a key-role for leaf litter turnover, significantly impacting litter export and decomposition (Schories et al., 2003). The main vehicle for DOC outwelling is tidally induced pore water flow from the upper sediment and litter horizon (Dittmar et al., 2001) which is largely controlled by tidal range.

Little is known about the fate of mangrove derived DOC in the ocean. The bulk of the leachable fraction from *Rhizophora mangle* leaves can be mineralized rapidly and assimilated into microbial biomass (Benner and Hodson, 1985). A significant fraction of mangrove derived DOC, however, is relatively resistant to degradation. Photodegradation and bio-incubation experiments indicate that a substantial fraction (~50%) of DOC in mangrove pore water is refractory on a time scale of weeks to years. Thus, it may be distributed over larger distances on continental shelves and beyond, depending mainly on local hydrodynamics at the sites of export. Slow mineralization of mangrove DOC could fuel aquatic secondary production far away from the mangroves areas, giving reason to revive the original outwelling hypothesis in a modified form. Mangrove derived DOC is present on the North Brazil shelf at distances >100 km offshore (Dittmar et al., 2006).

Mangroves probably contribute > 10% of the terrestrial derived, refractory DOC transported to the ocean (Dittmar et al., 2006), while they cover only < 0.1% of the continents' surface. Organic carbon export from mangrove areas to the ocean is more than one order of magnitude higher in proportion to their NPP than any major river (Kristensen et al., 2008a). The rapid decline (see section 1.3.8) in mangrove cover over the recent decades may have significantly impact the flux of terrigenous DOC to the ocean. The most recent global organic carbon input to the ocean is ~45 TgC yr^{-1} (Bouillon et al., 2008).

1.3.5 Burial and permanent storage of organic carbon in sediments

Mangrove ecosystems are able to store large amounts of organic carbon and in some mangrove ecosystems, organic rich sediments of several meters depth have been found (Twilley et al., 1992). The formation of old and refractory material in mangrove sediments can be observed visually as lignified and humified (spongy) litter fragments. Accordingly, Dittmar and Lara (2001b) estimated that the average age of organic carbon in the upper 1.5 m of the sediment in Furo do Meio mangrove forest, Brazil is between 400 and 700 years. Based on a compilation of available data, Duarte and Cebrián (1996) estimated that ~10% of the mangrove production is buried in the sedimentary pool, the remainder being exported (~ 30%), consumed (~9%), decomposed (~40%), or unaccounted (10%). However, the percentage of buried carbon strongly depends on the environmental conditions. As primary production increases with age, the efficiency of carbon burial in sediments increases, from 16% for a 5-year-old forest to 27% for an 85-yer-old stand (Alongi et al., 2004). Additionally, there is proportionally greater carbon burial in the low intertidal zone where sediment accumulation is greatest (Alongi et al., 2005b). Duarte et al. (2005) recently estimated the average global rate of carbon accumulation in mangrove systems at 10.8 mol m^{-2} yr^{-1}, which is similar to the 10.7 mol m^{-2} yr^{-1} estimated by Jennerjahn and Ittekkot (2002). There are, however, a number of caveats in such global estimates and it will likely require substantially more data to be able to constrain these budgets better.

The available global estimates of carbon accumulation are mainly calculated by difference using litter fall, export and consumption rates (Jennerjahn and Ittekkot, 2002) and many of the case studies used in the approach of Duarte and Cebrián (1996). This approach does not emphasize the fact that NPP is likely to be three to four times higher than litter fall rates, which may lead to a significant underestimate of burial rates. Also, other potentially important organic carbon sources derived from tidal water, such as seagrass detritus, phytodetritus and terrestrial material (Bouillon et al., 2003b; Marchand et al., 2003; Kennedy et al., 2004) are usually not considered in accumulation estimates, which may further accentuate the underestimate of carbon burial rates.

From that perspective, direct measurements of sediment and/or carbon accumulation rates hold a better potential, but unfortunately the number of such data are scarce (Chmura et al., 2003; Duarte et al., 2005) which raises the question as to whether these are representative enough for a global extrapolation. Looking into the datasets used by Duarte et al. (2005), the sediment carbon content of the mangrove sites considered was 8.5%, whereas a more exhaustive data compilation (Kristensen et al., 2008a) indicates that a representative global estimate of carbon content is likely to be close to 2.2%, suggesting that the data used in this bottom-up approach is biased towards organic rich systems and hence overestimates the global carbon accumulation in mangroves. The present global organic carbon burial rate in mangrove systems is ~18 TgC yr^{-1} (Bouillon et al., 2008).

1.3.6 Pathways of sedimentary organic carbon degradation

While the aerobic microbial community in mangrove environments consumes fresh litter and algal detritus deposited at or near the sediment surface, anaerobes are fuelled by detritus buried by accretion, by leaf-eating crabs and by belowground root production in the form of dead biomass and DOC excretion (Alongi, 1998; Kristensen and Alongi, 2006). Aerobic microorganisms have the enzymatic capacity for complete oxidation of organic carbon to CO_2, while anaerobic degradation processes occur stepwise involving several competitive types of prokaryotes. Aerobic degradation of labile materials near the surface of mangrove sediments is usually so rapid that O_2 rarely penetrates more than 2 mm into the sediment (Kristensen et al., 1994). The bulk sediment remains largely anoxic except for a network of narrow roots and infaunal burrows that translocate oxygen deep into the sediment (Kristensen and Alongi, 2006). Under anoxic conditions, large organic molecules are first split into small moieties by fermenting prokaryotes. These small molecules are then oxidized completely to CO_2 by a wide variety of anaerobic microorganisms using electron acceptors in the following sequence according to the energy yield: NO_3^-, Mn (IV), Fe (III) and SO_4^{2-}.

Aerobic respiration and sulphate reduction are usually considered the most important respiration processes in mangroves sediments (Alongi, 1998), with a share of 40-50% each. Consequently, most mangrove sediments contain high levels of reduced inorganic sulphur in the form of primarily pyrite (FeS_2) and elemental sulphur (S^0) and only negligible amounts of iron monosulphides (FeS) (Holmer et al., 1994). Denitrification, manganese reduction and iron reduction have traditionally been considered unimportant (Kristensen et al., 1998), although denitrification may be significant in areas polluted by sewage (Corredor and Morell, 1994). Recent evidence suggests, however, that the role of iron reduction in carbon oxidation may be comparable to, or higher than sulphate reduction in iron rich mangrove environments (Kristensen et al., 2008a). As sulphate reduction usually is hampered in the presence of more potent electron acceptors (e.g., O_2 and Fe (III); Canfield et al., 2005), this process becomes inferior to iron reduction when oxidizing roots and infaunal burrows increase the Fe (III) content in mangrove sediments (Nielsen et al., 2003). Recent results have shown that the proportion of anaerobic organic carbon degradation in mangrove sediments that is conducted via iron reduction (FeR) is significantly related to the concentration of reactive iron (Fe (III)) within the sediment (Kristensen et al., 2008a). Thus, when the concentration of the reactive Fe (III) exceeds about 35 µmol cm^{-3}, more than 80% of the anaerobic carbon degradation is mediated by microbial iron reduction. This relationship is similar to that generally found for other marine areas (Jensen et al., 2003).

When all electron acceptors are exhausted and electron donors are in surplus, CH_4 is produced by fermentative disproportionation of low molecular compounds (e.g. acetate) or reduction of CO_2 by hydrogen or simple alcohols (Canfield et al., 2005). Thus, a process like sulphate reduction can usually maintain concentrations of hydrogen and acetate at levels too low to fuel methanogens. In general, rates of methane production are low and highly variable in mangrove sediments and in some environments methanogenesis cannot be detected at all (Alongi et al., 2004; 2005b). Despite the presence of active methanogenesis, the concentration of methane in pore waters of near-surface sediments is usually very low due to simultaneous removal by anaerobic methane oxidation (Canfield et al., 2005). Emissions of CH_4 from mangrove sediments are therefore close to zero (range: 0 to 5 mmol m^{-2} d^{-1}). There is a general consensus that anthropogenic influence, i.e. higher nutrient and organic loading, strongly increases emissions of CH_4 from mangrove sediments by inducing severe oxygen stress and supplying labile organic carbon (e.g., Purvaja and Ramesh, 2001; Kreuzwiser et al., 2003; Alongi et al., 2005b). Nevertheless, our knowledge on factors controlling methanogenesis and methane emissions in mangrove environments is limited and relies primarily on a few recent studies.

In Tanzania mangrove forests, Kristensen et al. (2008b) showed that pneumatophores and crab burrows enhance CH_4 emission to the atmosphere. These structures act as channels through which CH_4 from deep sediment layers escape oxidation and rapidly diffuse to the atmosphere. Indeed, these authors noted that emission of CH_4 from the sediment was extensive when pneumatophores and burrows were abundant and these structures are responsible for 93-100% of the total. However, the magnitude of enhanced CH_4 emission was related to mangrove species (Kristensen et al., 2008b). It must be emphasized that CH_4 emitted from pneumatophores and burrows originate solely from methanogenesis in the surrounding sediment because plant roots and crabs residing inside burrows do not generate CH_4. Moreover, CH_4 emissions in the Tanzanian mangrove creeks were dependent on tidal level and wind speed. Lowest emission occurred during high tide (10-80 µmol m^{-2} d^{-1}) and highest during low tide (100-350 µmol m^{-2} d^{-1}) when supersaturated runoff from the forest floor and pore water seepage reach the creek waters. Overall, CH_4 emissions in the Tanzania mangrove ecosystems do not contribute significantly to the carbon gas balance. Thus, carbon emitted as CH_4 accounts for only 0.1-0.2% and 0.8-1.2% of the CO_2 contribution during low and high tide, respectively.

Rates of microbial carbon oxidation and partitioning of electrons acceptors within typical marine sediments are usually dependent on the quantity and the reactivity of organic matter, sediment grain size, and bioturbation activity (Kristensen, 2000). However, in mangrove sediments other factor are equally important; these include forest age, physiological activities of the root system, extent of water logging and intensity of faunal burrowing activities. It has been observed that sulphate reduction account for 20-30% in young *Avicennia marina* and *Rhizophora apiculata* forests, while this process is responsible for most carbon degradation in old forests (Alongi et al., 2000b). Oxidized conditions with dominance of aerobic and iron respiration prevail in sediments beneath young *Rhizophora* stands characterized by low plant biomass and high exposure to tidal effect on well-aerated sandy substratum. As forests age, the organic carbon inputs becomes stronger, and the increasing amount of fresh organic matter leads to a prevalence of sulphate reduction. The effect of *Avicennia marina* roots on sediment biogeochemistry, on the other hand, appears contradictive. Oxygen leaching by roots keeps the rhizosphere deep in the sediment oxidized and enriched in Fe (III) for use by iron reducers. At the same time, leaching of labile DOC from roots appears to stimulate bulk sulphate reduction (Kristensen and Alongi, 2006).The impact of water logging is evident in mature *Avicennia* forests. When the water table is low during the dry season, oxygen penetrates deeper into the sediment through crab burrows and cracks in the sediment and adds to the oxidizing effect of the rhizosphere, allowing suboxic (e.g. iron reduction) oxidation of organic carbon. Conversely, during the rainy season, prolonged water logging prevents oxidation of the sediment and sulphate reduction becomes the dominant pathways (Clark et al., 1998; Marchand et al., 2004). Animal burrows are a major conduit for subsurface movement of water (Ridd, 1996). They allow the supply of oxygen and oxidized elements below the depth at which oxygen usually penetrate, resulting in the development of oxidized halos around burrows (Clark et al., 1998). Thus, Kristensen et al. (2000) observed that sulphate reduction in a burrowed mudflat is reduced to half of that in adjacent vegetated and almost fauna-free sediments.

1.3.7 Mineralization and export of inorganic carbon

Mineralization is generally considered to be a major fate of plant production in coastal ecosystems (Duarte and Cebrián, 1996). However, when based on sediment CO_2 fluxes, benthic mineralization only represents ~15% of the total mangrove NPP. For a number of reasons, however, these CO_2 emission rates are unlikely to serve as appropriate proxies for mineralization: 1) core incubations typically use sediments which are free of pneumatophores and crab burrows. Recent data, however, indicate that these structures are important as vectors for enhancing CO_2 exchange, and add considerably to the total CO_2 flux from the sediment (Kristensen et al., 2008a). Crab burrows can be very complex, abundant, and deep structures, and thus greatly enhance the surface area of sediment-air or sediment-water interface where exchange of CO_2 or DIC can take place (Thongtam and Kristensen, 2003; Kristensen et al., 2008b). Similarly, CO_2 emission rates were found to be greatly enhanced when *Sonneratia* or *Avicennia* pneumatophores were included in the measurements, with CO_2 emission rates equivalent to 0.2-0.7 mmol CO_2 d^{-1} per individual pneumatophore (Bouillon et al., 2008; Kristensen et al., 2008b). 2) An unknown part of CO_2 released from pneumatophores and rooted sediments might represent plant respiration rather than heterotrophic respiration (i.e., mineralization). Since mangrove carbon budget is generally based on NPP, the CO_2 release due to autotrophic respiration is not included (Lovelock et al., 2006). This stresses the need for novel methodological approaches that allow quantitative estimates of the partitioning of measured CO_2 fluxes between autotrophic and heterotrophic respiration. 3) Lateral transport of DIC resulting from mineralization via pore water drainage is not taken into account using the standard approach used to estimate sediment mineralization: the latter is based on the assumption that efflux of CO_2 equates with depth-integrated mineralization. Mangroves pore waters are typically rich in TAlk and DIC (e.g., Ovalle et al., 1990; Borges et al., 2003; Bouillon et al., 2007a), indicating that build-up of inorganic carbon resulting from mineralization occurs. Lateral transport of DIC-enriched mangrove pore water to creeks thus results in an underestimation of mineralization rates if based on sediment-water CO_2 effluxes only. The impact of mineralization in intertidal sediments and subsequent lateral transfer on the DIC dynamics in mangroves creeks has been demonstrated in a number of studies (e.g., Ovalle et al., 1990; Borges et al., 2003; Bouillon et al., 2007c).

In order to assess the potential magnitude of lateral CO_2 transport, Bouillon et al. (2008) evaluated the water column concentration of DIC and DOC along the salinity gradient in six mangrove systems. Because of lateral inputs into creek waters, DIC and DOC typically show a non conservative pattern in the mangrove creek water column. The relative amounts of "excess" DIC and DOC (ΔDIC and ΔDOC) can thus be considered proportional to their relative export rates, on the condition that the tidal variations in both parameters are similar, so that their overall relative fluxes are not influenced by the variations in flow rates during the tidal cycle (e.g., Dittmar and Lara, 2001c). Based on these assumptions ΔDIC/ΔDOC ratios reported in the literature ranged from ~3 to ~10 (Bouillon et al., 2008). This implies that DIC export should exceed DOC export to the same degree based on the assumption that both originate mainly from the tidal exchange and therefore follow the same tidal variations (Bouillon et al., 2007c). Thus, tidal export of DIC would represent 178 ± 165 TgC yr^{-1}. For comparison, the overall global NPP based on litter fall, wood production and fine root production of mangroves is estimated at 218 ± 72 Tg C yr^{-1}. Other processes may affect DIC and DOC after their export from the system boundaries (e.g., CO_2 efflux, mineralization or photodegradation of DOC), but data to assess this further are currently not available. It must be noted that the estimated tidal DIC export in principle includes the cumulated DIC released from mangrove sediments during tidal inundation, DIC released from permanently inundated sediments, and DIC from organic carbon degradation in the mangrove creek waters (which has been seldom measured). However, it does not include the sediment CO_2 emission during exposure or CO_2 exchange between the water column and atmosphere. Clearly, to date, there are insufficient data to fully constrain CO_2 emission from sediments and tidal DIC export. However, available data suggest that mineralization is severely underestimated, and the majority of carbon export from mangroves to adjacent waters occurs as DIC (Bouillon et al., 2008). CO_2 efflux from sediments and creek waters and tidal export of DIC appear to be the major sinks. These processes are quantitatively comparable in magnitude to the unaccounted carbon sink in current budgets, but are not yet adequately constrained with the limited published data available so far.

1.3.8 Mangroves and anthropogenic pressures

In recent years, anthropogenic pressures have significantly damaged the world's mangroves, with alarming levels of habitat loss. For example, Ramirez-Garcia et al. (1998) estimate a 32% decrease in mangroves in the Santiago river of Mexico in the past 23 years. Aksornkoae (1993) and Raine (1994) report more than a 50% reduction in the mangrove forest of Thailand. Approximately 45% of the mangroves in Indonesia have been heavily impacted by human activities (Choong et al., 1990). Some estimates put global mangrove loss rates at one 10^6 ha yr^{-1} (Mohamed, 1996). Such levels of destruction and habitat fragmentation raise concerns about conservation of biodiversity in the mangrove habitats and preservation of the mangals themselves. Ellison and Farnsworth (1996) classified anthropogenic disturbance into four types: extraction, pollution, reclamation, and changing climate. These disturbances are listed in the order of their increasing spatial scale, their increasing temporal scales, and the increasing time required for recovery. Research suggests that even relatively low impact human activities can affect the mangrove environment. For instance, boardwalks placed in the mangal around Sydney, Australia to provide access for educational and recreational activities have modified sediment composition and benthic invertebrate community structure (Kelaher et al., 1998). It may require fairly long periods for the mangal to recover from even minor disturbances (Snedaker et al., 1992).

Diversion of freshwater for irrigation and land reclamation has historically been a major cause of wide-scale mangrove destruction (Twilley et al., 1998). Throughout the world, mangroves and mangrove products have also been used for timber, fuel, food, clothing, perfume, dyes, tannins, and medicine. In the past several decades, extensive tracts of mangrove have been converted for aquaculture. Shrimp ponds have become particularly common in many former mangals. Menasveta (1997) reports that nearly 55% of the mangroves in Thailand were converted to shrimp ponds between 1961 and 1993. Pond culture now surpasses open ocean fishing as the major source of shrimp there. Unfortunately, ponds in many regions are unsustainable and up to 70% of them may be left idle after some period of production (Stevenson, 1997). Because of changes in the sediments caused by pond construction, the abandoned sites are difficult to revegetate with mangroves even after the shrimp farming has ceased. **Figure 1.10** sums up the longitudinal mangrove loss in the world from 1980 to 2000. Brazil and Pakistan had loss ~50% of their mangroves during the 1990's.

Three characteristics have long made mangrove habitats favored sites for sewage dumping: 1) flow through the habitat disperses wastes from a point source over vast areas, 2) the vegetation itself filters nutrients from the water, and 3) the mangrove soil, algae, microbes, and physical processes absorb large amount of the pollutants (Wong et al., 1997). Nutrients (primarily nitrogen and phosphorus) are often major components of the pollution. Tam and Wong (1995) have studied the ability of mangals to absorb nutrients and the effects of the pollutants on the mangal community as a whole. In general, mangrove soils efficiently trap wastewater-borne phosphorus, but are less effective at removing nitrogen. High level of organic pollution can contribute to disease, death, and changes in species composition within the mangal (Tattar et al., 1994). Mandura (1997) found that sewage discharge killed of *Avicennia marina* in the Red Sea. The loss of the pneumatophores decreased surface area for respiration and nutrient uptake and retarded the growth of the trees.

Oil pollution from oil or gas exploration, petroleum production and accidental spills severely damages mangrove ecosystems (Mastaller, 1996). One of the most immediate and obvious is defoliation of the trees. The toxicity of the oil may depend on environmental conditions; oil has the greatest effect on survival and growth of *Rhizophora mangle* when the trees are in hot, bright outdoor conditions. Toxicity may also differ among mangrove species. For example, along the coast of Sao Paulo, Brazil, an oil spill caused 26% defoliation of *Rhizophora mangle*, 43% defoliation of *Laguncularia racemosa*, and 65% defoliation of *Avicennia schaueriana* (Lamparelli et al., 1997). Differential mortality of the trees can potentially lead to long-term changes in the community structure. Grant et al. (1993) demonstrated that sediment oil can inhibit establishment and decrease survival of mangrove seedlings for several years. This residual toxicity may interfere with mangrove reforestation efforts (Zheng et al., 1997). Oil contamination can damage animals living in the mangal, both in the sediments and on submerged mangrove roots.

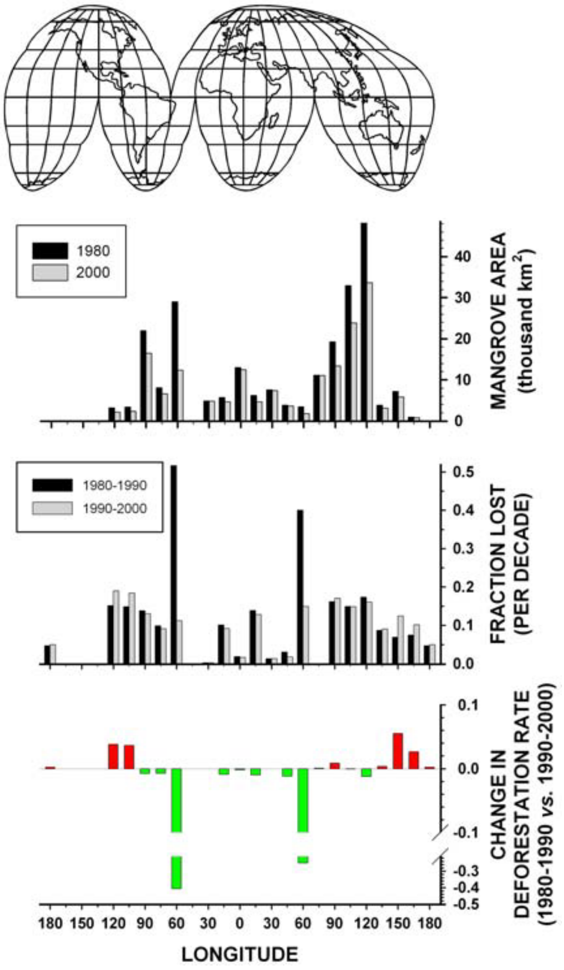

Figure 1.10: Loss of mangroves 1980-2000. The top graph shows estimated mangrove area per 15° of longitude in 1980 (black bars) and 2000 (grey bars). The middle graph shows the fraction of mangroves area lost per 15° of longitude between 1980-1990 (black bars) and between 1990-2000 (grey bars). The two extreme values are Brazil, which lost 56% of its mangrove area between 1980 and 1990, and Pakistan, which lost 40% of its mangrove area in the same decade. The bottom graph shows the change in deforestation rate between the two decades. The value shown is the simple difference between deforestation rates 1990-2000 and 1980-1990. A positive value (shown in red) indicates a faster deforestation rate, and a negative value (shown in green) indicates a slower deforestation rate in 1990-2000 than in 1980-1990. All data are derived from 113 country-by-country summaries (Ellison, 2008).

Five years after the *Galeta* oil spill in Panama, there was a 60% decrease in the number of isopods on submerged *Rhizophora mangle* prop roots and a 40-50% drop in the number of spring lobsters (Levings et al., 1994). Oyster populations dropped 65% along mangrove channels and 99% in mangrove streams.

Efforts are being made to rebuild damage mangrove ecosystems in many parts of the world (Field, 1998). The programs are called regeneration, reclamation, rehabilitation, or eco-development. Finding adequate supplies of viviparous seedlings for use in such reforestation projects is a challenge and more effective methods are needed. Living seedlings can be cut and the cuttings induced to produce roots and shoots. However, success of the cuttings depends on how they are done. In vitro micropropagation methods have been developed for *Excoecaria agallocha* (Rao et al., 1998). These techniques hold promise for mangrove regeneration.

1.3.9 Mangroves and global changes

Increasing concentrations of atmospheric CO_2 and other greenhouse gases will bring changes in the global climate. Global mean sea level has been rising. From 1993 to 2003, the average rate of sea level rise estimated from observations with satellite altimetry was 3.1 ± 0.7 mm yr^{-1} (IPCC, 2007). However, sea level change is highly non uniform spatially, and some regions are up to several times the global mean rise, while in other regions sea level is falling. Moreover, the rise in global mean sea level is accompanied by considerable decadal variability (IPCC, 2007). Because of their location at the interface between land and sea, mangroves are likely to be strongly affected by global changes. Most mangrove habitats will experience increasing temperature, changing hydrologic regimes (e.g., changes in rainfall, evapotranspiration, runoff and salinity), rising sea level and increasing tropical storm magnitude and frequency. Davis et al. (1994) have developed a framework for assessing risks to mangrove ecosystems in the context of a changing global climate but the seriousness of the effects will be strongly site-specific. Small increase in air temperature may have little direct effect on the mangroves, but if temperatures exceed 35°C, root structures, seedling establishment and photosynthesis will all be negatively affected. The broader effects of temperature increases may be in modifying large-scale distribution and community structure, increasing species diversity in higher latitude mangals and promoting spread of mangroves into sub-tropical saltmarsh environments (Ellison, 1994). Because they are so specialized, and may live so close to their tolerance limits, mangroves are particularly sensitive to minor variation in hydrological or tidal regimes (Blasco et al., 1996). Reduced rainfall and runoff would produce higher salinity and greater seawater-sulphate concentrations. Both would decrease mangrove production (Snedaker, 1995). The most important effects, however, would come from rising sea levels, but responses will vary among locations and will depend on the local rate of the rise and the availability of sediment to support reestablishment of the mangroves (Woodroffe, 1999). For example, in the Caribbean, mangrove seedlings are very sensitive to low sediment availability, suggesting that mangroves will not survive on Caribbean coral island if sea levels increase as predicted (Ellison, 1996).

Predicted global changes in atmospheric CO_2 are likely to have strong effects on mangroves. Farnsworth et al. (1996) grew *Rhizophora mangle* under double ambient CO_2 for one year. Growth rate, net assimilation, and photosynthetic rate all increased significantly. Seedlings in the enhanced CO_2 treatment had greater biomass, longer stems, more branching, and more leaf area than control seedlings. They also became reproductive after only one year (2 years sooner than under normal conditions). Ellison (1994) found that, in addition to stimulating productivity, increased CO_2 led to more efficient use of water as a result of reduced stomatal conductance. However, the effects of increased CO_2 may vary with other physical and chemical conditions. For instance, *Rhizophora apiculata* and *Rhizophora stylosa* both benefit from increased CO_2, but the stimulatory effect is much greater under low salinity conditions (Ball et al., 1997). Snedaker and Araújo (1998), for example, studied the effects of a 6-34% increase in CO_2 concentration on four mangrove species in south Florida (*Rhizophora mangle*, *Avicennia germinans*, *Laguncularia racemosa*, and *Conocarpus erectus*). Elevated CO_2 reduced stomatal conductance and transpiration and significantly increased instantaneous transpiration efficiency in all of these species. However, it did not increase net primary productivity in any species and actually reduced the productivity of *Laguncualria racemosa*.

High methane levels can be associated with anoxia in mangrove environments. The methane flux from the sediments is strongly influenced by freshwater loading and nutrient input. Fluxes may also vary along tidal gradients being generally low on the landward fringe and high in the seaward transition zone between *Avicennia* and *Rhizophora* communities (Ye et al., 1997). Mangrove species with pneumatophores may be best equipped to deal with high methane loads. The pneumatophores themselves may be conduits for release of methane gas. Pneumatophore-bearing species also release more methane through their leaves than do those lacking pneumatophores (Lu et al., 1998).

1.3.10 Description of mangroves from Ca Mau Province (Vietnam)

The Ca Mau Province is characterized by a strong bimodal rainfall pattern, with a clearly defined rainy season extending from May to November, and very little rainfall during the rest of the year, and an annual average rainfall of about 2400 mm (Clough et al., 2002). Approximately 46 species of mangrove trees have been identified in the region and the forested species are mainly in the families of Rhizophoraceae (10 species), Sonneratiaceae (3 species) and Verbennaceae (4 species) (Binh et al., 1997). The tidal amplitude ranges between 0.5 m and 0.8 m, and the water in the mangrove creeks is either brackish (salinities of 24-26 during the rainy season) or saline (salinities of 30-32 during the dry season), and there is no distinct terrestrial source of freshwater in the area (Binh et al., 1997).

Prior to the Vietnam-American war, Ca Mau Province was covered extensively by mangrove forests, most of which were destroyed by defoliants during the war leading to the destruction of 80% of the of mature Rhizophora forests (Clough et al., 2002). Following the Vietnam reunification in 1975, natural regeneration and extensive replanting, mainly with monocultures of *Rhizophora apiculata*, led to the partial recovery of mangrove vegetation. Recent and rapid expansion of shrimp aquaculture has contributed to the loss of more than half the mangrove forest that existed in Ca Mau and Bac Lieu provinces in 1982. Under the current forest management policy, *Rhizophora apiculata* is planted at an initial density of 20000 ha^{-1}, with thinnings by 20-30% at 5, 10 and 15 yr, and the final harvest at 20 yr (Clough et al., 2002).

1.4 Lagoons

1.4.1 Definition and formation

Lagoons are inland water bodies, found on all continents, usually oriented parallel to the coast, separated from the ocean by a barrier, connected to the ocean by one or more restricted inlets which remain open at least intermittently, and have water depths which seldom exceed a few meters (Kjerfve, 1985). They owe their origin largely to eustatic sea level rise. With the onset of an interglacial stage near the end of the Pleistocene 15 000 years ago, sea level rose 130 m at a rapid but variable rate (Nichols and Biggs, 1985) and flooded river valleys and low-lying coastal depressions. Sea level reached its approximate present elevation 5000 years ago, but has undergone fluctuations of a few meters since then. As a result of coastal processes, barriers formed that now constitute the margins of lagoons (Lankford, 1976). The combined action of marine and fluvial processes caused trapping and infilling of semi-enclosed coastal systems, including lagoons, and the reshaping of seaward boundaries. Lagoons also formed in marginal depressions behind barriers of reworked in deltaic sediments in active river delta systems (Nichols and Allen, 1981). Such lagoons are often oriented normal rather than parallel to the coast, as in the case of Lake Calcasieu, Louisiana, and Lagoa Feira, Brazil. Lagoons occupy 13% of coastal areas worldwide, with the percentage being even larger for tropical coastlines bordered by mangrove forests and coral reefs (Boynton et al., 1996), and are often impacted by both natural and anthropogenic influences. Depending on local climatic conditions, lagoons exhibit salinities which range from completely fresh to hypersaline. Lagoons usually act as net material sinks, although mature systems can serve as a source of organic materials to the adjacent ocean. They are often subject to rapid sedimentation, and will eventually evolve into other types of environments through sediment infilling, tectonic activity, eustatic change in sea level, and land use activities (Kjerfve, 1985). The time scale of this environmental transition is geological rapid and can be expected to occur within decades to centuries, and can be accelerated by human activities. Lagoons experience forcing from river input, wind stress, tides, precipitation to evaporation balance, and surface heat balance, and respond differently to these forcing functions. Water and salt balances, lagoons water quality, and eutrophication depend critically on lagoon circulation, salt and material dispersion, water exchange through the ocean canal (s), and turnover, residence, or flushing times.

Kjerfve (1985) sub-divided lagoons into three geomorphic types according to water exchange with coastal ocean (**Figure 1.11**). The rate and magnitude of oceanic exchange reflects both the dominant forcing function(s) and the time scale of hydrologic variability. The divisions represent three points along a spectrum of lagoon variability. These points are:

1.4.1.1 Choked lagoons

Choked lagoons are characterized by a single entrance channel and a small ratio of entrance channel cross-sectional area to surface area of the lagoon. They are dominated by the hydrologic/riverine cycles; have long residence times; are wind forced; and experience limited short-term marine variability. They are most common on coasts with high wave energy and low tidal range. Strong coastal wave action in combination with available sediment produces littoral drift, which builds the barrier that separates lagoon and ocean. If the littoral drift is substantial, the lagoon may temporarily become closed off the ocean. For example, on the west coast of Mexico, the closing and opening of lagoon entrance channels is a seasonal cycle (Moore and Slinn, 1984). These choked lagoons are closed off from the sea during the dry season. As they are filled by runoff during the rainy season, the channel reopens. In arid climates, closed-off lagoons may turn into salt flats. Occasional heavy rains and flood runoff can refill the lagoon basin, percolate through the barricade entrance, and eventually weaken and break through the barrier. As fresh water input dwindles, salt water will intrude and evaporation will greatly exceed combined runoff and rainfall. As the channel is blocked off by littoral drift, the lagoon will again turn into a salt flat. Tidal influence in choked lagoons is usually confined to the entrance channel. As a consequence, variability of current and water level is largely related to wind forcing. Many choked lagoons experience seasonal water level changes with a range exceeding 1 m in response to onset of the rainy season. A system can change seasonally over the entire range from fresh water lagoon to hypersaline lagoon, to salt flat in extreme cases.

1.4.1.2 Restricted lagoons

Restricted lagoons are usually located on low/medium wave energy coasts with a low tidal range. They are usually connected to the ocean by two or more channels which typically remain open at all times. Tidal water level and current variability are readily transmitted into the lagoon without excessive filtering. As a result, restricted lagoons exhibit well defined tidal circulation, which is modified by wind forcing and fresh water runoff. Restricted lagoons are less likely to undergo dramatic fluctuations in salinity as compared to choked lagoons. They are usually well mixed vertically. Fresh to brackish water is found near the river mouths. During flood discharge the entire restricted lagoon may turn fresh or brackish. Because of the small tidal range and the occurrence of near uniform salinity over large areas, semidiurnal/ diurnal tidal salinity variations are minimal except in the entrance channels and tidal passes.

1.4.1.3 Leaky lagoons

Leaky lagoons are connected to the ocean by wide tidal passes (rather than entrance channels) that transmit oceanic effects into the lagoon with a minimum of resistance. The separating barrier can be either a series of sand islands, or sections of a barrier reef. A reef can be either of coral origin as in the case of the Great Barrier Reef in Australia or of sandstone origin as in the case of the reefs along the coast of north-eastern Brazil or Western Australia

(Allison and Grassia, 1979). Leaky lagoons are located along the coasts with variable tidal and wave characteristics. However, tidal currents must be sufficiently energetic to keep wave-generated littoral drift from closing off the passes. In areas of high tidal range, leaky lagoons exist despite with wave energy conditions. On coasts with low tidal range, leaky lagoons may still exist as long as wave energy conditions are low. Leaky lagoons are usually characterized by near-oceanic salinities. However, in regions of a lagoon where river runoff is significant in comparison to local tidal exchange, estuarine salinities may persist. Tidal circulation patterns in leaky lagoons are usually well defined but are sometimes modified dramatically by wind forcing. Leaky lagoons are readily flushed. Most large leaky lagoons are oceanic, rather than estuarine in regard to salinity.

1.4.2 Lagoons and eutrophication

Because of their position as an interface between the terrestrial and marine environments, lagoons are subject to both continental and marine influences. Thus, they are highly dynamic environments. The continental inputs in the lagoons are mainly characterized by river water and sometime, by ground water or rain water that drain the surrounding soils. These waters not only carry large amounts of particulate material in the form of clay particles and organic detritus but also dissolved material in the form of DOC and nutrients arising from human activity in the vicinity of the lagoons (fertilizers, domestic and industrial effluents …). Most of these materials are deposited and concentrate in the lagoons. Nutrient and organic inputs, together with shallow water conditions, good light penetration and good mixing lead to high primary production. It is widely accepted that the rates of primary production in lagoons are among the highest measured for natural ecosystems (Castel et al., 1996). According to Duarte (1995), primary production in lagoons is 10-15 times higher than those of continental shelves. This is the result of intense bacterial activity which ensures ready mineralization of DOC and recirculation of nutrients, including those in the sediments. The bulk of the primary production is due to macrophytes (*Rupia*, *Zostera*) and macroalgae (*Enteromorpha*, *Ulva*). However, significant production by microphytes (epiphytic and/or epibenthic) have also been recorded. According to Castel et al. (1996) the benthic compartment largely controls the functioning of the ecosystem in lagoons. The superficial film of sediment on the lagoon bed is generally covered by a blanket of unicellular organisms (cyanobacteria, dinoflagellates, diatoms). Through the intense browsing action of herbivorous fauna such as small gastropods and crustaceans, this vegetal material is converted into increasingly fine debris which is quickly colonized by a large number of microorganisms (microalgae, bacteria) and small-sized invertebrates (meiofauna, crustaceans, annelids). In most lagoons, it is known that the anaerobic bacterial community is dominated by sulphate-reducing bacteria that can transform up to 50% of the organic material (Jørgensen, 1983) but produce H_2S, a toxic compound that can accumulate as FeS_2 (pyrite) in the anoxic environments. However, sulphide does not usually reach the oxic zone unless sulphate reduction is very intensive. Indeed, it is well established that in the most of the coastal sediments studied so far, between 50 and 95% of the H_2S produced is oxidized, at the interface between the oxic and anoxic zones (Castel et al., 1996).

Etang du Prévost (France) is an example of an eutrophic lagoon that according to Castel et al. (1996), is regularly subject to dystrophic crises, locally called the “malaïgues”. Such dramatic events appear every year during the warm summer month for a period about 15 days. They have a dramatic consequence for aquaculture, particularly oyster culture that takes place in the lagoon. Macroscopically, the dystrophic crises are characterized by coloured waters (white, red or black waters). They originate from a perturbation of the sulphur cycle. In normal conditions, there is steady-state at the benthic level between sulphate reducing bacteria producing H_2S and bacteria oxidizing this reduced sulphur compounds or elemental sulphur. Sulphate reduction leads to the production of H_2S which then rapidly oxidized to sulphate in the presence of oxygen. After an increase in organic load these sulphate reduction accelerate, and under anoxic conditions white waters can be observed together with the production of H_2S. They usually occur when the light intensity is low. Under certain conditions, red waters can be observed. They are due to the development of phototrophic sulphur oxidizing bacteria. The conditions for their development are: a sufficient light intensity, a pH value near 8 and a H_2S concentration < 1 ppm.

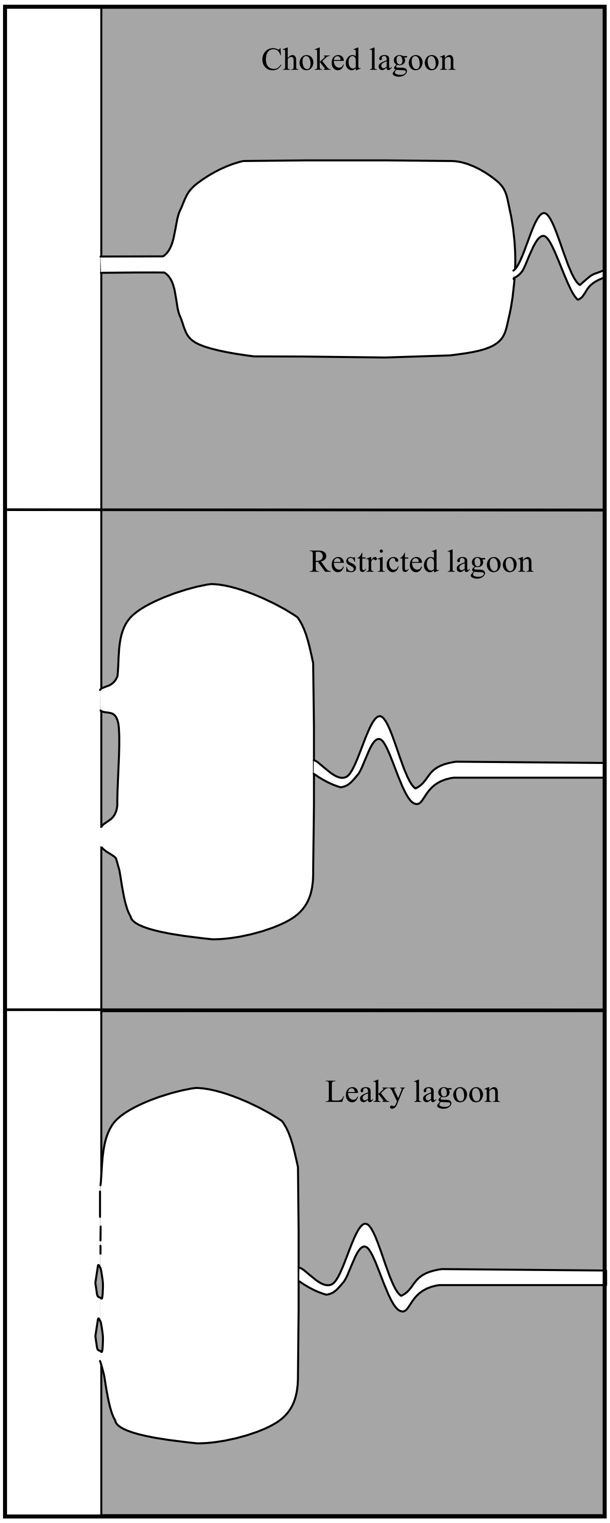

Figure 1.11: the 3 schematic types of lagoons (adapted from Kjerfve, 1985).

In West Africa, one of the most polluted lagoons is the Korle lagoon (Accra, Ghana). This lagoon serves as a cesspool for most of Accra's industrial and municipal wastes. Its stench travels far to engulf the adjoining shantytowns, which are home to thousands of people, who for lack of sanitation facilities have turned the shores of the lagoon into a giant latrine (Kwasi and Markku, 2002). Due to the lack of sanitation facilities in various communities in the immediate area, people continue to use the isolated bushes along the lagoon for open range defecation. The excess loads of nutrients in the lagoon have caused serious eutrophication, and the growth of blue-green algae. The resultant fall in oxygen levels within the lagoon has led to the extinction of most aquatic life forms and an ecological imbalance within the lagoon and along its shore.

1.4.3 Lagoons from Ivory Coast

Lagoons are the most prominent coastal ecosystems of Ivory Coast (**Figure 1.12**) covering an area of 1200 km^2, which corresponds to a large fraction of the surface area of lagoons in West Africa (5000 km^2; Binet et al. 1995). The Ebrié and Grand-Lahou lagoon systems fall under the "restricted lagoon" class while Aby lagoon system falls under the "choked lagoon" class, according to the Kjerfve (1985) classification. They are gathered in three systems (Ebrié, Grand-Lahou and Aby) and stretch along some 300 km of the coastline. The density of the riparian population is variable ranging from 3.5 inhabitants km^{-2} around the Aby lagoon system to ~100 inhabitants km^{-2} around the Ebrié lagoon system (Jallow et al. 1999).

The climate is close to equatorial, with an annual rainfall ranging from 1500 to 1800 mm, characterized by two rainy seasons and two dry seasons (Durand and Skubich, 1982). The high dry season extends from January to March, the high rainy season from early April to late July, the low dry season from August to September, and the low rainy season from October to December. The rivers flowing into these lagoons have two different hydrological regimes (Iltis and Lévêque, 1982; Jallow et al., 1999). The Tanoé, the Bia, the La Mé and the Agnéby rivers have an equatorial transition regime with two flooding periods in June-July and October-November. The Comoé and Bandama rivers have a mixed regime with only one flooding period during September-October. The lithology of the drainage basin of the three rivers is different: in the Comoé it is composed of 63% plutonic acids, 26% of Precambrian basement and 11% consolidated siliciclastic rocks; in the Bia it is composed of 67% of

Precambrian basement, 17% plutonic acids and 16% semi- to unconsolidated sedimentary; in the Tanoé it is exclusively composed of Precambrian basement (Dürr et al., 2005).

The Ebrié lagoon system (**Figure 1.12**) is the largest lagoon in West Africa (Adingra and Arfi, 1998). It is an elongated lagoon system with a total area of 566 km^2 and it stretches for ~130 km, with a maximum width of ~7 km. The average depth is of 4.8m, with a few deep areas especially around Abidjan (27 m south of Boulay Island). It is divided into three lagoons: Potou, Aghien and Ebrié, and receives freshwater from the Comoé, Agnéby and La Mé rivers (**Figure 1.12**; **Table 1.8**). Annual freshwater inputs from Comoé river is estimated to ~7 km^3 that represents ~3 times the total volume of the lagoon system (**Table 1.8**), while the flow of seawater is ~14 times this volume (Durand and Guiral, 1994). Salinity in the system varies between 0 and 35. Before 1951, the Ebrié lagoon system was only connected to the Atlantic Ocean through the Bassam inlet in the far east of the lagoon system (40 km away from Abidjan). The Vridi Channel was built in 1951 allowing a connection to the sea closer to Abidjan, greatly modifying the hydrological environment since the Bassam inlet has progressively closed, and nowadays the Comoé discharges into the lagoon system rather than directly to the sea. The Ebrié lagoon system is strongly polluted by domestic and industrial waste water inputs (Kouassi et al., 1995; Adingra and Arfi, 1998). The waters around Abidjan are highly eutrophicated leading to frequent oxygen depletion, massive fish kills and repelling sulphuric smells (Kouassi et al., 1995; Scheren et al., 2004), and have been included in the recent compilation of coastal “dead zones” (Diaz and Rosenberg, 2008). Total annual nitrogen loads to the lagoon for 2000 was estimated at 33 kilotons (kt), of which 45% from urban sources, 42% from land runoff and 13% from atmospheric deposition. Estimate for phosphorus are 2.5 kt, 39%, 48% and 13%, respectively (Scheren et al., 2004). The analysis of various scenarios has shown that autonomous growth, without pollution reduction measures, will result in an estimated five-fold increase in nutrient loads to the lagoon over the period 1980-2050, primarily from domestic and agricultural sources (Scheren et al., 2004). The consequential increase in nutrient concentrations would approximately be 3.5 fold, which would escalate to a dramatic level of eutrophication for the complete system.

The Aby lagoon system consists of the main Aby lagoon, the Tendo lagoon and Ehy lagoon, and receives freshwater from the Bia and Tanoé rivers, respectively, in the northwest and in the east (**Figure 1.12**). It is located in the far east of Ivory Coast, and forms a natural border with Ghana, extends over 30 km of the coastline and occupies over an area of 424 km^2.

The main Aby lagoon (hereafter Aby lagoon) is the largest and covers 305 km^2, with a total shoreline of 24.5 km and a maximal width of 15.5 km. The Tendo lagoon has a length of 22 km and a width varying between 1.5 km and 3.5 km, and a surface area of 74 km^2. The Ehy lagoon has a mean depth of 1.5 m and a surface area of 45 km^2. The Aby and Tendo lagoons are characterized by permanent haline stratification unlike the other 2 lagoon systems that are seasonally stratified. Thus, the bottom waters are anoxic and rich in H_2S while the surface layers are oversaturated with oxygen due to the high primary production (Chantraine, 1980). The population of ichtyofauna in the Aby lagoon system has been estimated at around of 60 species, among which the *Etmalosa fimbriata* is by far the most represented. It constitutes 60% to 80% of the catch (Konan, 1999). Crabs and shrimps are also very abundant particularly in the southern part of the lagoon close to mangrove forests from “The Parc National des îles Ehotilés”. Moreover, this lagoon system provides important habitat for landbirds, shorebirds and waterfowl.

The Grand-Lahou lagoon system (Tagba and Tadio lagoons) is located in the far west of the coast and is the smallest of the Ivory Coast lagoon systems with an area of 190 km^2 (**Figure 1.12; Table 1.8**). It receives freshwater from the Bandama river, and from the smaller Gô and Boubo rivers. The principal basin is elongated with an axis oriented E-W and is 50 km long, parallel to the coast. The system is fringed by mangrove forests. Similarly to Aby lagon system, crabs, shrimps and fishes are very abundant in the Grand-Lahou lagoon system particularly from July to October. The average migration rate of the mouth of Bandama river about ~ 10m per month was observed during our sampling period due to tide actions.

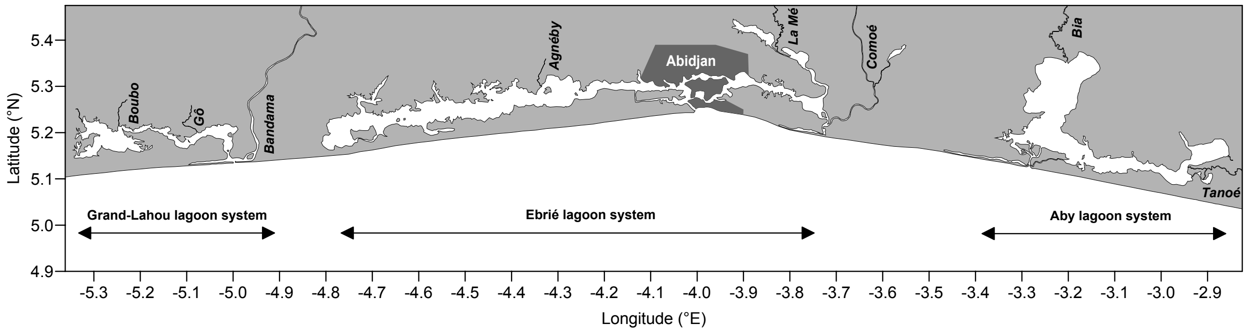

Figure 1.12: Map showing the three major lagoon systems and rivers in Ivory Coast.

Table 1.8: Some relevant characteristics of the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons (from West to East), and of the main rivers (Tanoé, Bia, Comoé, La Mé, Agnéby and Bandama) flowing into these lagoons, based on Chantraine (1980), Durand and Chantraine (1982), and Durand and Skubich (1982).

Lagoons	Area (km^2)	Volume (km^3)	Mean depth (m)	Surface salinity	Rivers	Total length (km)	Drainage area (km^2)	Mean water discharge ($m^3 s^{-1}$)
Tendo	74	0.2	2.7	0-8	Tanoé	625	16000	132
Aby	305	1.3	4.2	1-8	Bia	290	9650	59
Ebrié	524	2.6	4.8	0-35	Comoé	1160	78000	224
					Agnéby*	200	8900	27
Potou	22	0.03	2.7	0-6	La Mé*	140	4300	47
Grand-Lahou	190	0.5	2.0	0-26	Bandama*	1050	97000	298

2 General objectives

Tropical and subtropical freshwater and coastal ecosystems have been largely understudied in terms of the dynamics of CO_2 and CH_4, two major greenhouse gases, despite the fact that about 60% of global freshwater inputs, 80% of total organic and 45% of total inorganic carbon burial take place at these latitudes (Ludwig et al., 1996; Mackenzie et al., 2004).

Several coastal ecosystems are encountered in these zones; some of them are restricted to these latitudes. Among them, mangroves form a conspicuous habitat in many tropical estuaries, lagoons and deltas, and their high productivity could have a major influence on the carbon budget of the coastal zone (see section 1.3). However, the actual amount of mangrove-derived C inputs to the coastal zone remains an open question since local mineralization and subsequent efflux of CO_2 to the atmosphere appears to be quantitatively important but poorly studied.

There is also a lack of information on CO_2 and CH_4 fluxes in some coastal ecosystems, such as lagoons where the few studies of the carbon cycle have focussed solely on the ecosystem metabolism (e.g., Boucher et al. 1994; Carmouze et al. 1998; Sidinei et al. 2001; McGlathery et al. 2001; Hung and Hung, 2003). These ecosystems are found on all continents from the tropics to Polar Regions but are particularly prominent in the low latitudinal zone (Kjerfve, 1985). In West Africa, they cover approximately 5000 km^2 (Binet et al., 1995) in which lagoons from Ivory Coast alone cover a surface area about 1200 km^2. No studies on the DIC distribution and behaviour have been taken in any of these lagoons. Similarly, no CH_4 data are available in these lagoons. Therefore, the present work aims to:

- ♦ Describe the seasonal variability of DIC and related parameters in the waters surrounding two forested mangrove sites (Tam Giang and Kiên Váng) located in the Ca Mau Province (South-West Vietnam). Mangrove forests of the Ca Mau Province are significantly damaged due to the rapid expansion of shrimp aquaculture
- ♦ Assess and compare the spatial variability within each of the two mangrove forests
- ♦ Compute air-water exchanges of CO_2 in the two forested mangrove sites

♦ Investigate the seasonal variability of CO_2 and CH_4 fluxes and related parameters (nutrients and chlorophyll-a) in the five largest lagoons from Ivory Coast. These lagoons are contrasted in terms of geomorphology, of freshwater and seawater inputs, and riparian population and related anthropogenic pressure. Thus, the studied lagoons are representative of most lagoons that can be encountered in West Africa.

♦ Assess the seasonal variability of CH_4 and CO_2 fluxes and related parameters (nutrients and chlorophyll-a) in three rivers from Ivory Coast. These rivers flow into the lagoons and have two different hydrological regimes and contrasting drainage areas. Two rivers (Bia and Tanoé) are entirely located in forest zones and have an equatorial regime with two flooding periods in June-July and October-November; while the third river (Comoé) is mostly located in savannah zone and is characterized by a mixed regime with only one flooding period during September-October. Moreover, these rivers are seasonally covered by floating macrophytes that can be transported quickly to the adjacent lagoons depending on the water discharges.

3 Material and Methods

3.1 Sample collection and handling.

Subsurface waters (depth ~30 cm) were sampled with a 1.7 L Niskin bottle. pH and O_2 were measured immediately after collected while CH_4 were sampled in serum bottles, poisoned and sealed. Salinity and water temperature were measured in situ using a portable thermosalinometer (WTW Cond-340) with a precision of ±0.1 and ±0.1°C, respectively. Samples for the other quantities were stored and preserved; they were analyzed in Belgium, except for CH_4 that was analyzed at the University of Bordeaux 1, and for chlorophyll-a that was analyzed at the University of Abobo-Adjamé.

3.2 The measurement of pH

pH was measured with a combination electrode (Metrohm 6.0232.100) calibrated on the U.S. National Bureau of Standards scale as described by Frankignoulle and Borges (2001b), with a precision and estimated accuracy of respectively ±0.001 and ±0.005 pH units (for more details for pH refer to section 1.1.3.). We used two standards buffer solutions for the calibration of the pH electrode: NBS_4 ($C_8H_5KO_4$ 0.05 mol Kg^{-1}, pH = 4.002 at 25°C) and NBS_7 (KH_2PO_4 0.025 mol kg^{-1} and Na_2HPO_4 0.025 mol kg^{-1}, pH= 6.881 at 25 °C)

3.3 Measurement of total alkalinity (TAlk)

Samples for the determination of TAlk were filtered through 0.2-µm pore size polysulphone filters, and were stored at ambient temperature in polyethylene bottles. TAlk was measured on 50-mL samples by automated Gran-electro-titration with 0.1 M HCl as titrant, with a reproducibility of ± 1 µmol kg^{-1}. HCl was added to the samples by increments of 0.05 ml and at each HCl increment, pH was measured and from pH 4.2 (beyond the second equivalence-point of carbonic acid) to pH 3.0, a Gran (1952) function was calculated to compute the equivalence point

3.4 pCO_2 and DIC computations

The pCO_2 and DIC values were computed from pH and TAlk measurements using the carbonic acid constants given by Mehrbach et al. (1973) on the NBS scale and the CO_2 solubility coefficient by Weiss (1974). The estimated accuracy was about ±4 µmol kg^{-1} for DIC and ±4 ppm for pCO_2.

3.5 The measurement of methane (CH_4)

Duplicate 40-mL serum bottles were sampled taking care to avoid formation of bubbles that were poisoned with $HgCl_2$ and sealed. CH_4 concentrations were determined by gas chromatography with flame ionization detection, after creating a 30-mL headspace with N_2, as described in Abril and Iversen (2002). Certified CH_4:N_2 mixtures at 10 and 500 ppm CH_4 were used as standards (Air Liquide). Precision was better than 5%. Dissolved methane concentration was calculated with the solubility coefficient of Yamamoto et al. (1976).

3.6 The measurement of dissolved oxygen

Oxygen saturation level (%O_2) was measured immediately after collection with a polarographic electrode (WTW Oxi-340) calibrated on saturated air, with an accuracy of ±1%.

3.7 Measurement of nutrients

Water samples for nutrient measurements were filtered through cellulose acetate filters (Sartorius), re-filtered through 0.2 µm pore size polysulphone filters and preserved with $HgCl_2$ (for NO_3^- and PO_4^{3-}) and HCl for Si. NO_3^- concentrations were measured on a Technicon Auto Analyser II (Tréguer and Le Corre, 1975), with an estimated accuracy of ±0.1 µmol L^{-1}. PO_4^{3-} and Si concentrations were obtained by using the standard colorimetric methods (Grasshoff et al., 1983), with an estimated accuracy of ±0.01 µmol L^{-1} and ±0.1 µmol L^{-1}, respectively.

3.8 The measurement of chlorophyll-a

The concentrations of chlorophyll-a were determined using the spectrophotometric method (Lorenzen, 1967). Water samples were filtered on GF/F glass fibber filters (volume 250 to 500 mL) and preserved frozen (-40 °C) until analysis. The pigments were extracted between 12 hours and 24 hours in approximately 15 mL of 90% at 4 °C. After a short centrifugation, absorbance was measured at 665 and 750 nm before and after acidification with 100 μL of HCl 0.1 M.

3.9 The measurement of total suspended matter (TSM)

Total suspended matter (TSM) data were obtained by filtering a known volume (250 to 500 mL) of water on pre-weighted glass fibber filters (Whatman GF/F), rinsed with deionised water to avoid salt contributions (for lagoon samples) and subsequently dried. Then, they were weighted again and the differences of mass were used to compute TSM concentrations.

4 Dissolved inorganic carbon dynamics in the waters surrounding forested mangroves of the Ca Mau Province (Vietnam)

Foreword

Although the mangrove ecosystem as a whole (aquatic, below and above ground compartment) is net autotrophic, aquatic primary production is often limited by high turbidity, canopy shadow and large changes in salinity. In addition, the water column and sediments receive important quantities of leaf and wood litter from the overlying canopy. Hence, the water column and the sediment metabolism are largely heterotrophic and mangrove surrounding waters should act as a net source of CO_2 to the atmosphere, although data are so far limited. In this chapter, we report DIC and data obtained in the waters surrounding two mature (about 10 yr) forested mangrove sites located in the Ca Mau Province (South-West Vietnam) during the dry and rainy seasons. We show that spatial and seasonal variations of pCO_2 in mangrove surrounding waters were marked.

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Dissolved inorganic carbon dynamics in the waters surrounding forested mangroves of the Ca Mau Province (Vietnam)

Y.J.-M. Koné, A.V. Borges*

Unité d'Océanographie Chimique, Institut de Physique (B5), Université de Liège, MARE, B-4000 Sart-Tilman, Belgium

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Abstract

Dissolved inorganic carbon (DIC) and ancillary data were obtained during the dry and rainy seasons in the waters surrounding two 10-year-old forested mangrove sites (Tam Giang and Kiên Vàng) located in the Ca Mau Province (South-West Vietnam). During both seasons, the spatial variations of partial pressure of CO_2 (pCO_2) were marked, with values ranging from 704 ppm to 11481 ppm during the dry season, and from 1209 ppm to 8136 ppm during the rainy season. During both seasons, DIC, pCO_2, total alkalinity (TAlk) and oxygen saturation levels (%O_2) were correlated with salinity in the mangrove creeks suggesting that a combination of lower water volume and longer residence time (leading to an increase in salinity due to evaporation) enhanced the enrichment in DIC, pCO_2 and TAlk, and an impoverishment in O_2. The low O_2 and high DIC and pCO_2 values suggest that heterotrophic processes in the water column and sediments controlled these variables. The latter processes were meaningful since the high DIC and TAlk values in the creek waters were related to some extent to the influx of pore waters, consistent with previous observations. This was confirmed by the stochiometric relationship between TAlk and DIC that shows that anaerobic processes control these variables, although this approach did not allow identifying unambiguously the dominant diagenetic carbon degradation pathway. During the rainy season, dilution led to significant decreases of salinity, TAlk and DIC in both mangrove creeks and adjacent main channels. In the Kiên Vàng mangrove creeks a distinct increase of pCO_2 and decrease of %O_2 were observed. The increase of TSM suggested enhanced inputs of organic matter probably from land surrounding the mangrove creeks, that could have led to higher benthic and water column heterotrophy. However, the flushing of water enriched in dissolved CO_2 originating from soil respiration and impoverished in O_2 could also have explained to some extent the patterns observed during the rainy season. Seasonal variations of pCO_2 were more pronounced in the Kiên Vàng mangrove creeks than in the Tam Giang mangrove creeks. The air–water CO_2 fluxes were 5 times higher during the rainy season than during the dry season in the Kiên Vàng mangrove creeks. In the Tam Giang mangrove creeks, the air–water CO_2 fluxes were similar during both seasons. The air–water CO_2 fluxes ranged from 27.1 mmol C m^{-2} d^{-1} to 141.5 mmol C m^{-2} d^{-1} during the dry season, and from 81.3 mmol m^{-2} d^{-1} to 154.7 mmol m^{-2} d^{-1} during the rainy season. These values are within the range of values previously reported in other mangrove creeks and confirm that the emission of CO_2 from waters surrounding mangrove forests are meaningful for the carbon budgets of mangrove forests.

Keywords: coastal ocean; mangroves; carbon dioxide; dissolved inorganic carbon; total alkalinity

1. Introduction

The exchange of carbon dioxide (CO_2) between coastal waters and the atmosphere could lead to a major revision of budgets of CO_2 fluxes at regional (Frankignoulle and Borges, 2001a; Borges et al., 2006) or global scales (Tsunogai et al., 1999; Thomas et al., 2004; Borges, 2005; Borges et al., 2005). Marginal seas have been estimated to act on the whole as a sink for atmospheric CO_2 ranging from −0.4 PgC yr^{-1} to −1.0 PgC yr^{-1} (Tsunogai et al., 1999; Thomas et al., 2004; Borges, 2005; Borges et al., 2005) that would lead to a major revaluation of the oceanic sink for atmospheric CO_2, since open oceanic waters are a CO_2 sink of about −1.6 PgC yr^{-1} (Takahashi et al., 2002). Near-shore coastal systems (estuaries, saltmarsh waters, mangrove waters, coral reefs, and coastal

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* Corresponding author.
E-mail address: alberto.borges@ulg.ac.be (A.V. Borges).

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upwelling systems) act as sources of CO_2 and a preliminary upward scaling suggests that the overall emission of CO_2 from these systems could be as high as $+0.4$ PgC yr^{-1}, thus balancing the CO_2 sink associated to marginal seas (Borges, 2005; Borges et al., 2005). However, the air–water fluxes of CO_2 from coastal environments are highly uncertain and in large part this reflects data coverage that is spatially biased towards the temperate latitudes of the Northern Hemisphere (Borges, 2005; Borges et al., 2005). Importantly, there is a scarcity of air–water CO_2 flux data in coastal environments at subtropical and tropical latitudes that receive about 60% of the global freshwater discharge and an equivalent fraction of riverine organic carbon inputs (e.g. Ludwig et al., 1996). Coastal environments at these latitudes are then highly dynamic in terms of carbon cycling and are expected to be characterised by considerable exchanges of CO_2 with the atmosphere.

Mangrove forests are intertidal habitats that occupy a major part of the tropical and sub-tropical coastlines but their surface area has been largely reduced in the past decades due to human activities. The most recent estimates show a decrease in surface area from 198×10^3 km^2 in 1980 to 146×10^3 km^2 in 2000 (FAO, 2003). High population pressure in coastal areas has led to the conversion of many mangrove areas to other uses, including infrastructure, aquaculture, rice growing and salt production. In South-East Asia, mangrove clearance has mainly been driven by the development of shrimp aquaculture. Vietnam has reportedly lost more than 80% of its mangrove forests over the last 50 years, and shrimp aquaculture is thought to be the single largest threat to those that remain (Thornton et al., 2003). Mangrove forests are characterised by high above-ground primary production, efficient nutrient recycling and a permanent exchange with terrestrial and marine ecosystems. The low ratio of sediment respiration to canopy primary production makes mangroves highly efficient in the sequestration of carbon into above and below ground plant biomass (e.g. Jennerjahn and Ittekkot, 2002). Carbon burial is in the order of 23 TgC yr^{-1}, which makes up about 15% of the organic carbon accumulating in modern marine sediments (Jennerjahn and Ittekkot, 2002; Duarte et al., 2005). The organic carbon supplied to mangrove sediments and creek waters has several sources, either local (mangrove detritus, and microphytobenthos) or allochthonous (phytoplankton, seagrass-derived material, and terrestrial non-mangrove), but the relative contribution of these sources varies considerably from one site to another (Bouillon et al., 2004; Bouillon and Boschker, 2006). Due to this organic carbon supply, the aquatic compartment and the sediments of mangroves are largely net heterotrophic (e.g. Gattuso et al., 1998), and as a consequence, the aquatic compartment associated to mangrove forests acts as a source of CO_2 to the atmosphere (Borges et al., 2003; Bouillon et al., 2003, 2007a,b,c), although the range of the CO_2 fluxes reported so far encompasses one order of magnitude. The sediments of human impacted mangroves are known to be more acid than natural ones (Middelburg et al., 1996), while the dominant diagenetic organic carbon degradation pathway of recently reclaimed mangroves is different than in natural (old) ones (Alongi et al., 1998). The impact of these processes on dissolved inorganic carbon (DIC) dynamics of the adjacent waters and related air–water CO_2 fluxes has not yet been investigated.

We reported DIC and ancillary data obtained during the dry and rainy seasons in the waters surrounding two 10-year-old forested mangrove sites (Tam Giang and Kiên Vàng) located in the Nam Can and Ngoc Hien Districts (Ca Mau Province, South-West Vietnam, Fig. 1). We aim to describe spatial and temporal distributions and inter-site variability of DIC and ancillary data in mangrove creeks and compare the range of values of these forested mangroves to the non-forested systems studied so far.

2. Materials and methods

2.1. Study area

The Ca Mau Province is characterised by a strong bimodal rainfall pattern, with a clearly defined rainy season extending from May to November, and very little rainfall during the rest of the year, and an annual average rainfall of about 2400 mm (Clough et al., 2002). Approximately 46 species of mangrove trees have been identified in the region and the forested species are mainly in the families of Rhizophoraceae (10 species), Sonneratiaceae (3 species) and Verbennaceae (4 species) (Binh et al., 1997). The tidal amplitude ranges between 0.5 m and 0.8 m, and the water in the mangrove creeks is either brackish (salinities of 24–26 during the rainy season) or saline (salinities of 30–32 during the dry season), and there is no distinct terrestrial source of freshwater in the area (Binh et al., 1997).

Prior to the Vietnam–American war, Ca Mau Province was covered extensively by mangrove forests, most of which were destroyed by defoliants during the war leading to the destruction of 80% of the of mature Rhizophora forests (Clough et al., 2002). Following the Vietnam reunification in 1975, natural regeneration and extensive replanting, mainly with monocultures of *Rhizophora apiculata*, led to the partial recovery of mangrove vegetation. Recent and rapid expansion of shrimp aquaculture has contributed to the loss of more than half the mangrove forest that existed in Ca Mau and Bac Lieu provinces in 1982. Under the current forest management policy, *Rhizophora apiculata* is planted at an initial density of 20,000 ha^{-1}, with thinnings by 20–30% at 5, 10 and 15 years, and the final harvest at 20 years (Clough et al., 2002).

2.2. Sampling and analytical techniques

Two sampling cruises were carried out on 10–14 April, 2004 (dry season) and 23–25 October, 2005 (rainy season) in two mangrove forests (Tam Giang and Kiên Vàng). The sampling strategy was aimed: (1) to describe the seasonal variability of DIC and related parameters within each of the two mangrove forests, (2) to assess the spatial variability within each of the two mangrove forests with a more or less regular grid, and (3) to compare the temporal and spatial variability between the two mangrove forests. Sampling was carried in the main (wider) channels adjacent to the mangrove forests

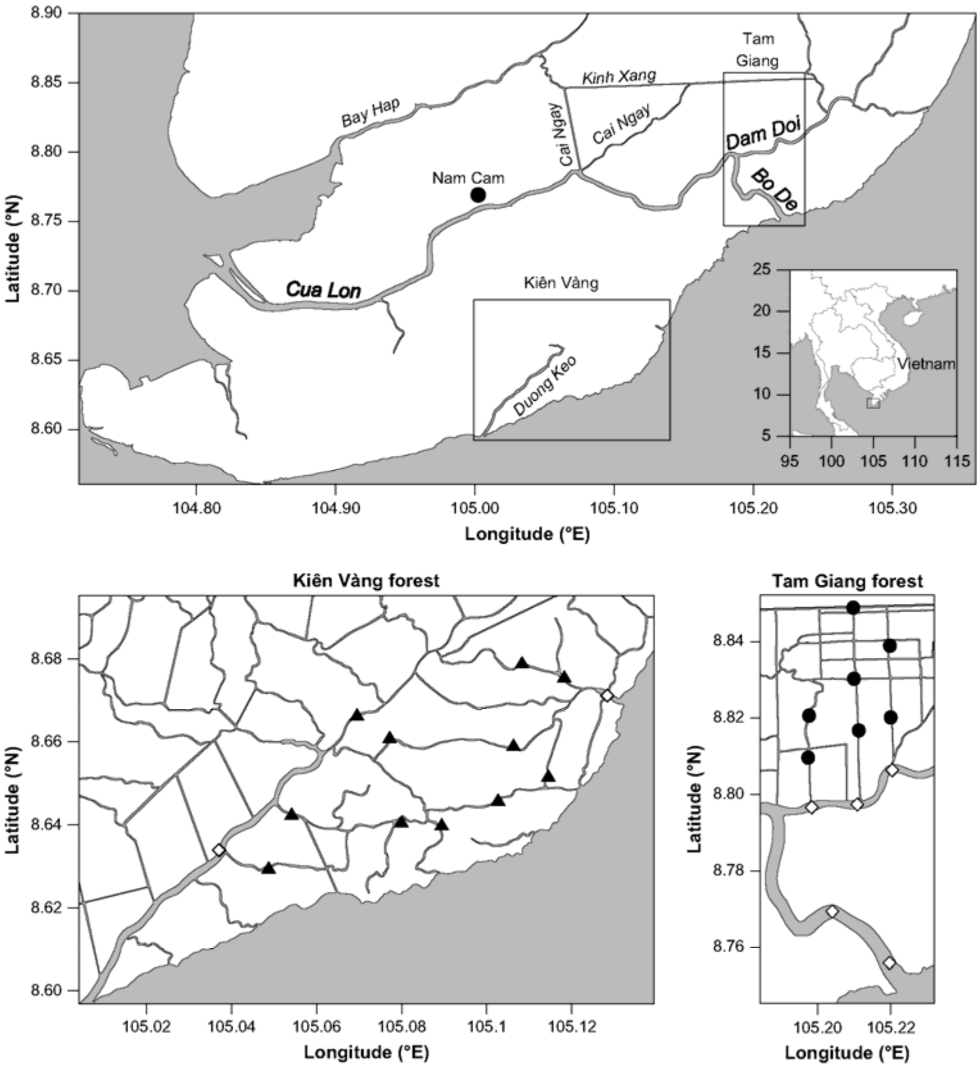

Fig. 1. Location of the sampling stations in Tam Giang (solid circles) and Kiên Vàng (solid triangles) mangrove creeks and in adjacent main channels (open diamonds).

(hereafter "adjacent main channels") and a range of mangrove creeks of different width and of variable distance from the adjacent main channels. Due to logistic constrains, the various stations were sampled (only once) at different tidal stages.

Subsurface waters (top 30 cm) were sampled with a 1.7-L Niskin bottle, and oxygen and pH measurements were carried out immediately after collection. Salinity and water temperature were measured in-situ using a portable thermosalinometer (WTW Cond-340) with a precision of ±0.1 and ±0.1 °C, respectively. The oxygen saturation level (%O_2) was measured with a polarographic electrode (WTW Oxi-340) calibrated on saturated air, with an accuracy of ±0.1%. pH was measured with a combination electrode (Metrohm 6.0232.100) calibrated on the U.S. National Bureau of Standards scale as described by Frankignoulle and Borges (2001b), with a precision and estimated accuracy of respectively ±0.001 and ±0.005 pH units. A volume of about of 100 ml was filtered through 0.2-µm pore size polysulphone filters, and was stored at ambient temperature in polyethylene bottles for the determination of total alkalinity (TAlk), within 1 week after sampling. TAlk was measured on 50-ml samples by automated Gran electro-titration with 0.1 M HCl as titrant, with a reproducibility of ±1 µmol kg^{-1}. Measurements TAlk and pH were used to compute the partial pressure of CO_2 (pCO_2) and DIC, with an estimated accuracy of ±4 ppm and ±4 µmol kg^{-1}, respectively (for details refer to Frankignoulle and Borges, 2001b). Total suspended matter (TSM) measurements were obtained by filtering a known volume of water on pre-weighted glass-fibre filters (Whatman GF/F). Wind speed was measured at each sampling station with a hand-held anemometer. Air–water fluxes of CO_2 were calculated according to:

$$F = \alpha \cdot k \cdot \Delta pCO_2$$

where α is the solubility coefficient of CO_2, k is the gas transfer velocity of CO_2 and ΔpCO_2 is the air–water gradient of pCO_2. We computed k using the wind speed field measurements, and the parameterisation as a function of wind speed given by Carini et al. (1996), that is assumed suitable under the considered environmental conditions (Borges et al., 2003).

The difference of the means of populations of variables (between sampling sites for one given season or between seasons for one given sampling site) were statistically analysed with a two-tailed unpaired Student t-test. The normality of distribution of the populations was tested with the Kolmogorov–Smirnov test, and all tested populations were found to be normally distributed. P values are not explicitly mentioned hereafter but "significant(ly)" refers to $P < 0.05$, "very significant(ly)" refers to $P < 0.01$, "highly significant(ly)" refers to $P < 0.001$, and "not significant(ly)" refers to $P > 0.05$ at the 0.05 level. Statistical analyses were carried out with Prism 4.00 (GraphPad).

3. Results and discussion

3.1. Spatial and seasonal variations of DIC and ancillary data

The spatial and temporal distributions of salinity, $\%O_2$, DIC, pCO_2, TAlk, and TSM in the surface waters of the mangrove creeks of the Tam Giang and Kiên Vàng forests and of the adjacent main channels are shown on Figs. 2–5, and average values for each site are reported in Table 1. In the Tam Giang mangrove creeks, salinity showed highly significant seasonal variations, and average values decreased from 33.1 during the dry season to 13.3 during the rainy season (Table 1). In the Kiên Vàng mangrove creeks and adjacent main channels a highly significant decrease of average salinity from the dry to rainy season was also observed. In the two mangrove creeks, during both seasons, the salinity spatial variations were of the same order of magnitude, of about 1 (Figs. 2–5). During the rainy season, the average salinity was significantly higher in the Kiên Vàng mangrove creeks than in the Tam Giang mangrove creeks, but average salinity was not significantly different in the two mangrove creeks during the dry season. Average salinity in the adjacent main channels was not significantly different than in the Tam Giang mangrove creeks during both seasons. In the adjacent main channels, average salinity was significantly to very significantly lower than in the Kiên Vàng mangrove creeks, during the rainy and dry season, respectively. This is due to higher effect of evaporation in the mangrove creeks that have a smaller water volume (narrower and shallower than the adjacent main channels) and probably a longer water residence time, particularly during the dry season.

Surface waters in the mangrove creeks and adjacent main channels were supersaturated with respect to atmospheric CO_2 during both seasons (Tables 1 and 2). The adjacent main channels were characterised by significantly to very significantly lower average pCO_2 compared to the two mangrove creeks during the dry and rainy season, respectively. In the Tam Giang mangrove creeks, average pCO_2 was not significantly different during both seasons, but pCO_2 values showed less spatial variability during the rainy season (Figs. 4 and 5). In the Kiên Vàng mangroves creeks, a significant twofold increase of average pCO_2 was observed from the dry to the rainy season, while spatial variability remained similar (Figs. 2 and 3). In the adjacent main channels, average pCO_2 showed a highly significant two fold increase from the dry season to the rainy season.

During both seasons, and in the two mangrove creeks, spatial variations of TAlk and DIC were apparent and similar in amplitude (Figs. 2–5). During both seasons, average TAlk and DIC values were significantly to highly significantly higher in the mangrove creeks than in the adjacent main channels. A highly significant decrease of average TAlk values during the rainy season compared to the dry season was observed in both mangrove creeks and in the main adjacent channels. The decrease of DIC from the dry to the rainy season was highly significant in the main adjacent channels and significant in both mangrove creeks. The decrease of TAlk and DIC is related to dilution.

The mangrove creeks and the adjacent main channels were characterised by low $\%O_2$ values during both seasons (Table 1), with significantly to highly significantly lower average values in the creek waters compared to the adjacent main channels. In the mangrove creeks and the adjacent main channels, $\%O_2$ values decreased by about 10% of level of saturation during the rainy compared to the dry season.

Average TSM values were significantly to very significantly higher in the Kiên Vàng mangrove creeks than in the Tam Giang mangrove creeks during the dry and rainy seasons, respectively. During both seasons, average TSM was significantly higher in the Kiên Vàng mangrove creeks than in the adjacent main channels. During the rainy season, average TSM was significantly lower in Tam Giang mangrove creeks than in the adjacent main channels, but was not significantly different during the dry season. Average TSM was very significantly higher in the Kiên Vàng mangrove creeks during the rainy season compared to the dry season. Average TSM was not significantly different in the Tam Giang mangrove creeks during the rainy season compared to the dry season.

The variation of pCO_2, DIC, TAlk, $\%O_2$ and TSM as a function of salinity, during the dry and rainy season are shown on Figs. 6 and 7, respectively. During both seasons, an increase in pCO_2, DIC and TAlk and a decrease of $\%O_2$ were observed in the mangroves creeks along the salinity gradient. TSM values were scattered but roughly showed an increasing trend with salinity. These trends were more pronounced in the Tam Giang mangrove creeks than in Kiên Vàng mangrove creeks, during the dry season, and similar in amplitude in both mangrove creeks during the rainy season. During both seasons, pCO_2

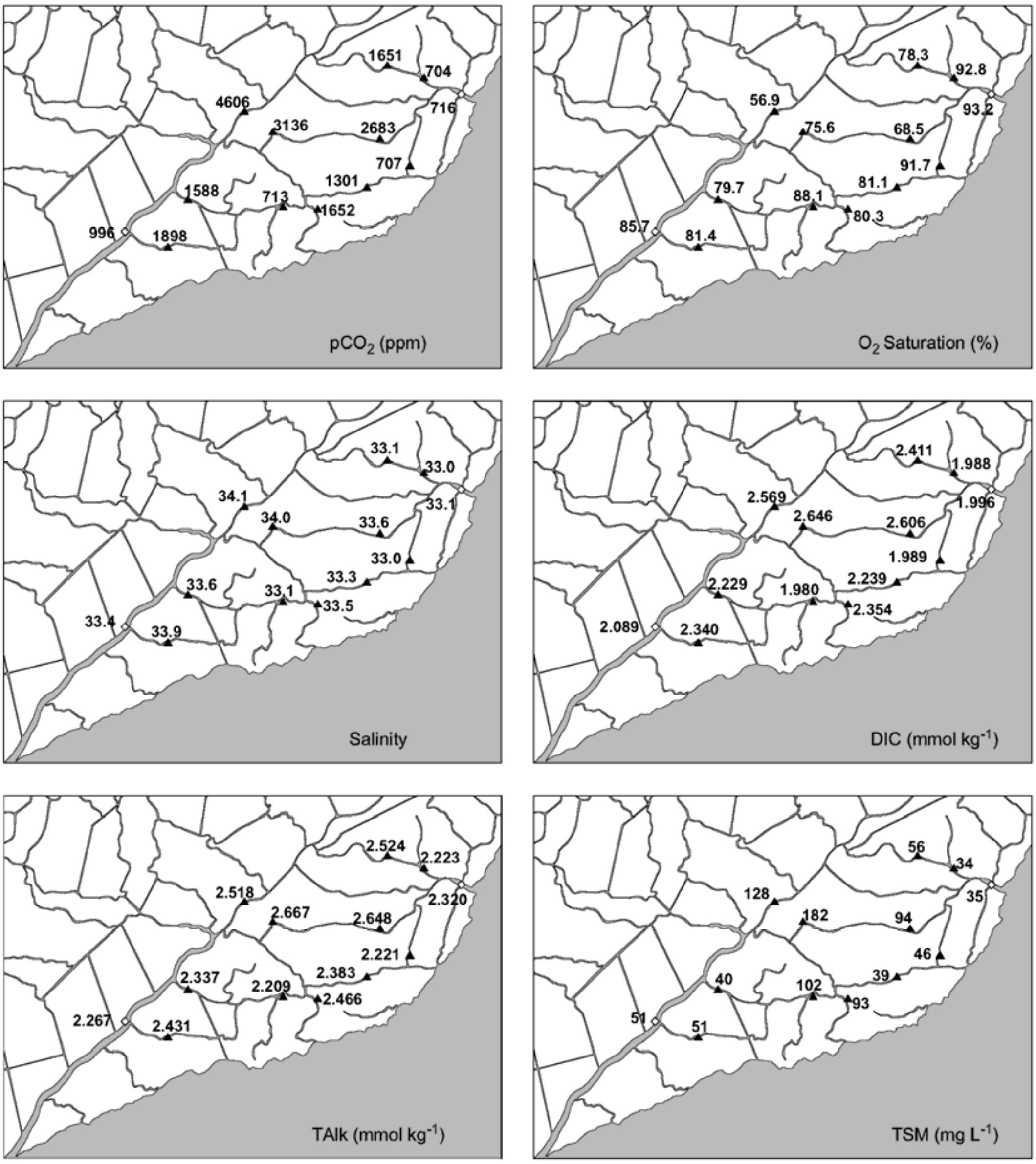

Fig. 2. Spatial distribution of pCO_2 (ppm), $\%O_2$ (%), salinity, TAlk (mmol kg^{-1}), DIC (mmol kg^{-1}) and TSM (mg L^{-1}) in the Kiên Vàng mangrove creeks (solid triangles), and adjacent main channels (open diamonds) during the dry season.

and $\%O_2$ were well correlated suggesting that these variables were controlled by biological process; values of pCO_2 above atmospheric equilibrium (365 ppm) coinciding with $\%O_2$ values below saturation imply that heterotrophic processes were dominant.

Higher values of pCO_2, DIC and TAlk in the mangrove creeks than in the adjacent aquatic systems are consistent with previous observations by Borges et al. (2003) in Papua New Guinea and the Bahamas, by Bouillon et al. (2003) in the Gautamani Godavari delta (India), by Bouillon et al. (2007a) in the Tana estuary (Kenya), by Bouillon et al. (2007b) in the Ras Dege mangrove creek (Tanzania), and by Bouillon et al. (2007c) in Gazi bay (Kenya). This can be related to several mechanisms: (a) mangrove tidal creeks are characterised by a long residence time of the water mass that favours a local degradation of organic matter provided by the canopy and/or allochthonous sources, and also promotes a stronger increase of salinity in the mangrove creeks compared to the adjacent water masses due to evaporation; and (b) the influx of pore water which mixes with the creek water

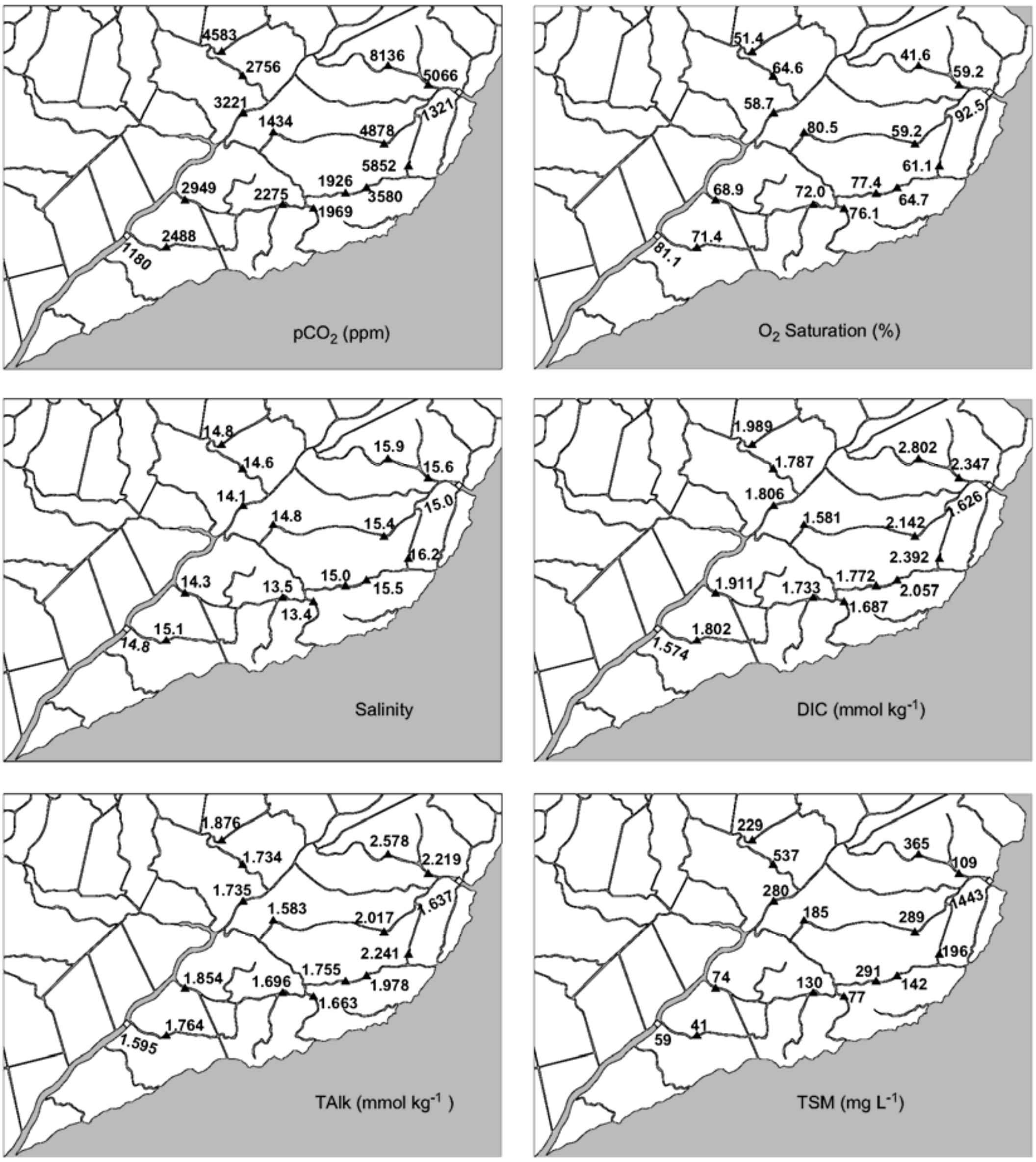

Fig. 3. Spatial distribution of pCO_2 (ppm), $\%O_2$ (%), salinity, TAlk (mmol kg^{-1}), DIC (mmol kg^{-1}) and TSM (mg L^{-1}) in the Kiên Vàng mangrove creeks (solid triangles), and adjacent main channels (open diamonds) during the rainy season.

substantially affects the chemical properties of the latter—this will also be enhanced in the creeks by a smaller water volume and by a longer residence time of the water mass.

Seasonal variations of remineralisation rates of mangrove canopy derived organic matter are expected to be minor due to the limited seasonal changes in temperature and in litter fall rates (Holmer et al., 2001; Kristensen et al., 2000). Alongi et al. (2001) showed that benthic respiration in mangrove ecosystems was more dependent upon allochthonous organic matter inputs rather than aboveground primary production, in agreement with benthic bacteria isotopic signatures (Bouillon et al., 2004; Bouillon and Boschker, 2006). This is also in agreement with recent findings by Bouillon et al. (2007a) in the mangrove dominated Tana estuary in Kenya that showed that water column particulate and dissolved organic matter were dominated by inputs from the non-mangrove drainage basin rather than from mangrove derived material. The increase of pCO_2 and decrease of $\%O_2$ in the mangrove creeks during the rainy season suggests an increase of heterotrophic activity in sediments and/or the water column, as also reported

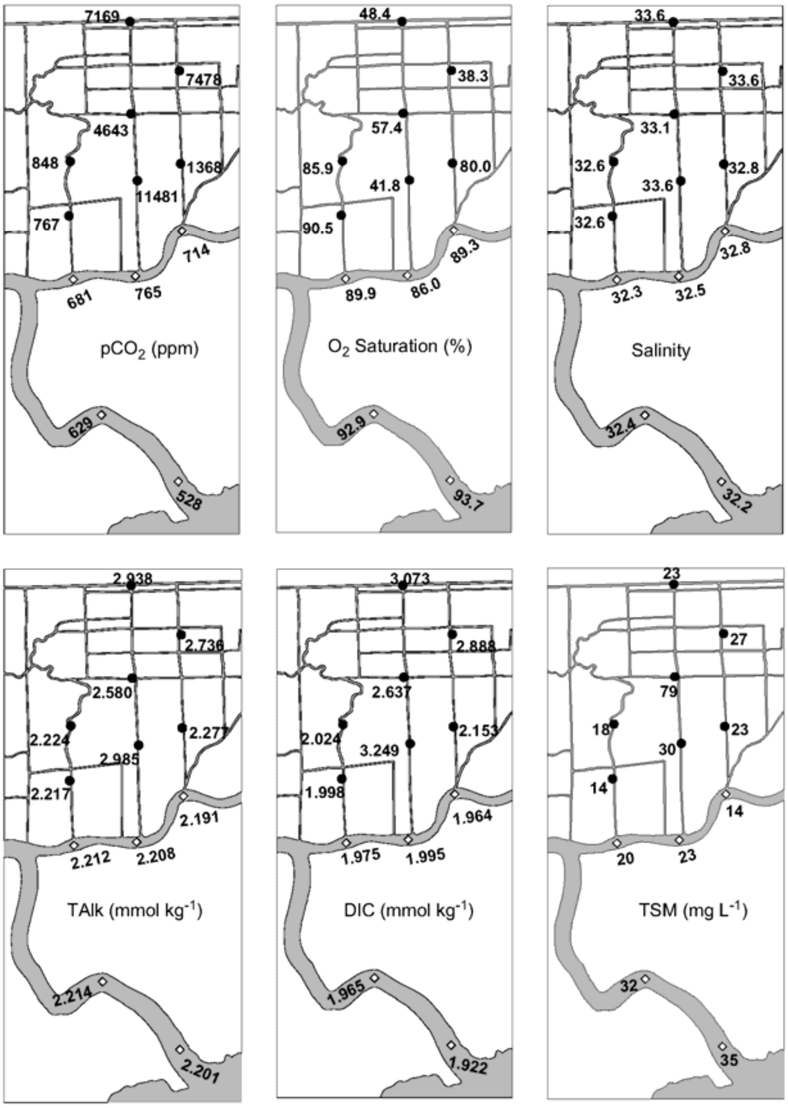

Fig. 4. Spatial distribution of pCO_2 (ppm), $\%O_2$ (%), salinity, TAlk (mmol kg^{-1}), DIC (mmol kg^{-1}) and TSM (mg L^{-1}) in the Tam Giang mangrove creeks (solid circles), and main adjacent channel (open diamonds) during the dry season.

in the Sundarban mangroves by Biswas et al. (2004). The increase of TSM also suggests an increase of soil flushing during the rainy season, probably from the land surrounding the mangrove forests. Such an additional input of non-mangrove organic matter is expected to fuel additional benthic and water column heterotrophy. Another process that could explain the higher pCO_2 and lower $\%O_2$ values during the rainy season is the increased input of mangrove porewaters, or from groundwater water enriched in CO_2 and impoverished in O_2 after flushing the soils from adjacent non-mangrove land. The influence of the input of mangrove porewaters on the CO_2 and O_2 dynamics in mangrove creeks has been documented (Ovalle et al., 1990; Borges et al., 2003; Bouillon et al., 2007b) and could be increased due to flushing by rain (Barnes et al., 2006), in analogy with freshwater systems where the flux of dissolved CO_2 originating from soil respiration is known to strongly contribute to the emission of CO_2 to the atmosphere (Kling et al., 1991; Jones and Mulholland, 1998; Cole and Caraco, 2001; Jones et al., 2003; Duarte and Prairie, 2005). The present data-set does not allow discrimination of these different causes of higher pCO_2 values during the rainy season that probably co-occur.

Diagenetic organic carbon degradation in mangroves has several anaerobic pathways (denitrification, manganese reduction, iron reduction, sulphate reduction and methanogenesis) that increase pore water TAlk (except methanogenesis).

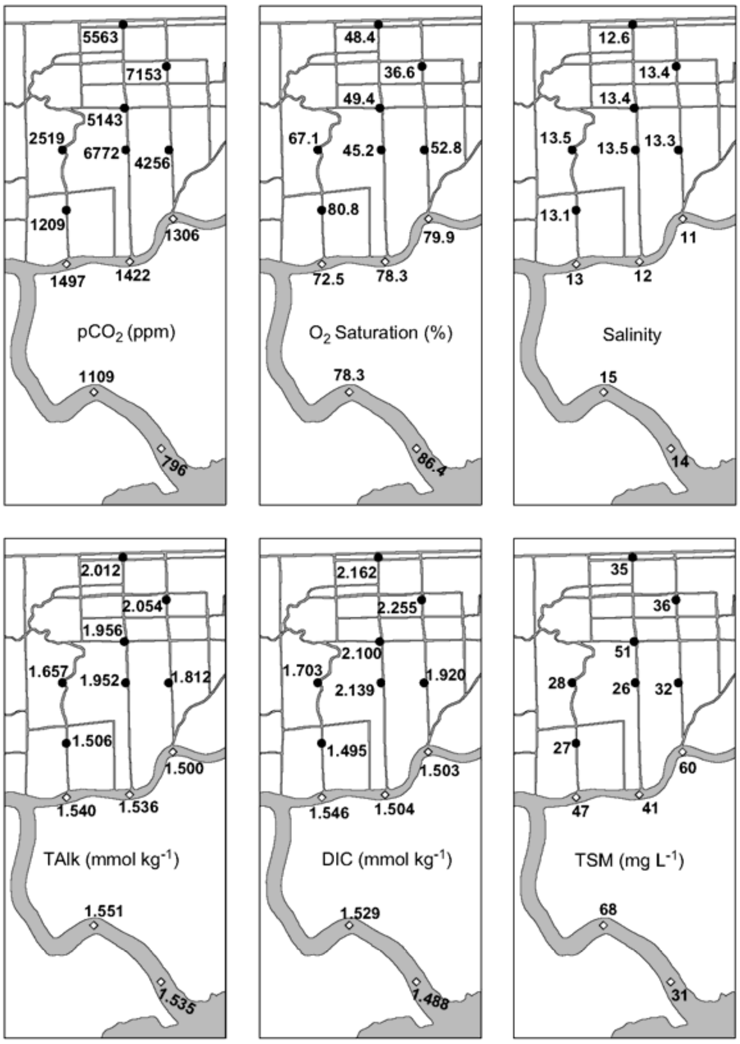

Fig. 5. Spatial distribution of pCO$_2$ (ppm), %O$_2$ (%), salinity, TAlk (mmol kg^{-1}), DIC (mmol kg^{-1}) and TSM (mg L^{-1}) in the Tam Giang mangrove creeks (solid circles), and adjacent main channels (open diamonds) during the rainy season.

Generally, sulphate reduction and aerobic respiration are the main pathways of organic matter degradation in mangrove sediments (Alongi et al., 2001). For instance, aerobic respiration accounted for 63–94% of total benthic organic carbon decomposition in *Rhizophora apiculata* plantations of the Mekong delta (Alongi et al., 2000a), while sulphate reduction represented 74% of benthic organic carbon decomposition in Western Australia mangroves (Alongi, 1998). According to

Table 1

Average ± standard deviation of salinity, pCO$_2$, TAlk, DIC, %O$_2$ and TSM in the Kiên Vàng and Tam Giang mangroves creeks and adjacent main channels, during the dry and rainy seasons

Sites	Season	Salinity	pCO$_2$ (ppm)	TAlk (mmol kg^{-1})	DIC (mmol kg^{-1})	%O$_2$ (%)	TSM (mg L^{-1})
Kiên Vàng	Dry	33.5 ± 0.4	1876 ± 1196	2.421 ± 0.163	2.305 ± 0.246	79.5 ± 10.3	79 ± 46
	Rainy	14.9 ± 0.8	3651 ± 1856	1.907 ± 0.276	1.986 ± 0.336	64.8 ± 10.7	210 ± 134
Tam Giang	Dry	33.1 ± 0.5	4822 ± 4105	2.565 ± 0.333	2.575 ± 0.519	63.0 ± 21.9	31 ± 22
	Rainy	13.3 ± 0.3	4698 ± 2187	1.850 ± 0.203	1.969 ± 0.278	54.3 ± 14.8	34 ± 9
Adjacent main channels	Dry	32.7 ± 0.4	718 ± 144	2.217 ± 0.025	1.987 ± 0.051	90.1 ± 3.3	29 ± 15
	Rainy	13.5 ± 1.6	1233 ± 234	1.556 ± 0.045	1.544 ± 0.046	81.3 ± 6.4	330 ± 622

Table 2

Average ± standard deviation of wind speed, air−water pCO_2 gradient, atmospheric CO_2 flux and the gas transfer velocity *k*, in the Kiên Vàng and Tam Giang mangrove creeks and adjacent main channels during the rainy and dry seasons

Sites	Season	Wind speed ($m\ s^{-1}$)	ΔpCO_2 (ppm)	Atmospheric CO_2 flux (mmol C $m^{-2}\ d^{-1}$)	*k* (cm h^{-1})
Kiên Vàng	Dry	1.6 ± 2.2	1511 ± 1196	32.2 ± 39.4	3 ± 4
	Rainy	3.0 ± 2.3	3286 ± 1856	154.7 ± 159.1	6 ± 5
Tam Giang	Dry	2.4 ± 1.3	4457 ± 4105	141.5 ± 117.8	5 ± 3
	Rainy	1.9 ± 1.1	4333 ± 2187	128.5 ± 110.0	4 ± 2
Adjacent main channels	Dry	5.5 ± 3.0	353 ± 144	27.1 ± 12.5	11 ± 6
	Rainy	5.3 ± 0.9	867 ± 234	81.3 ± 31.8	11 ± 2

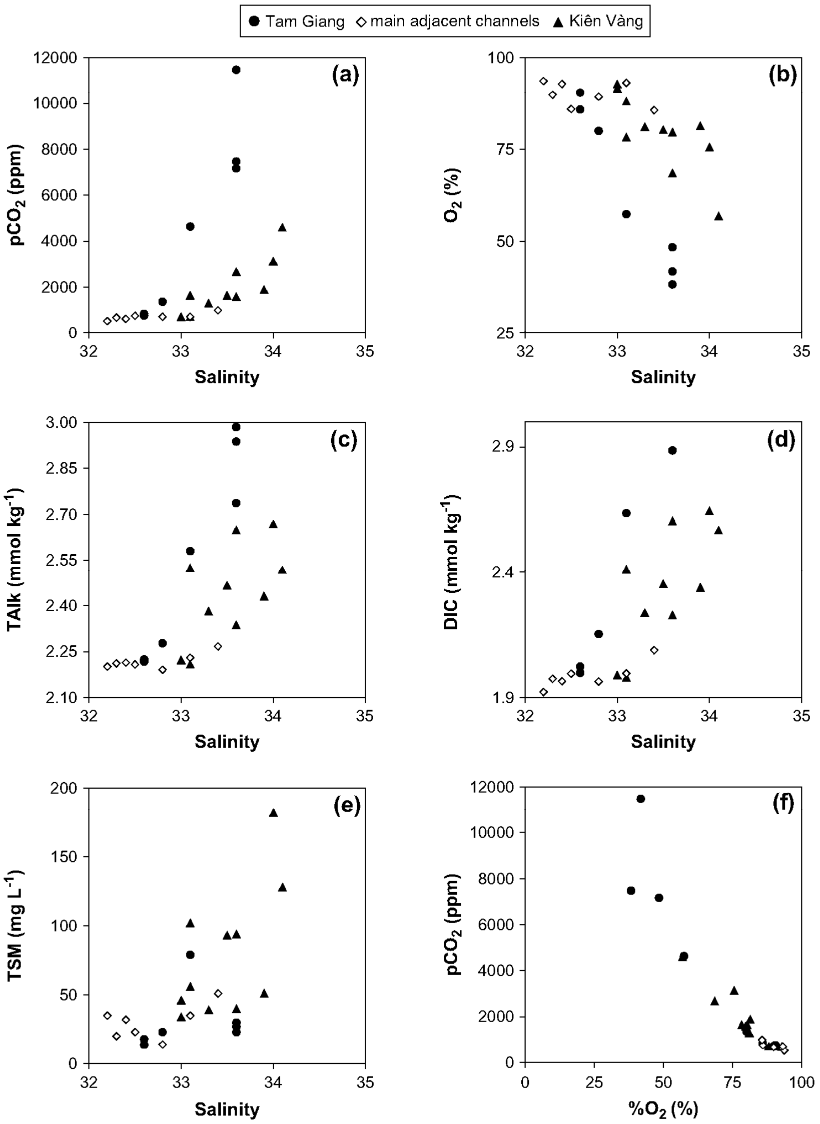

Fig. 6. Variation of pCO_2 (ppm), $\%O_2$ (%), TAlk (mmol kg^{-1}), DIC (mmol kg^{-1}) and TSM (mg L^{-1}) as a function of salinity in the mangrove creeks (Tan Giang, solid circles and Kiên Vàng, solid triangles) and adjacent main channels (open diamonds), and pCO_2 versus $\%O_2$ during the dry season.

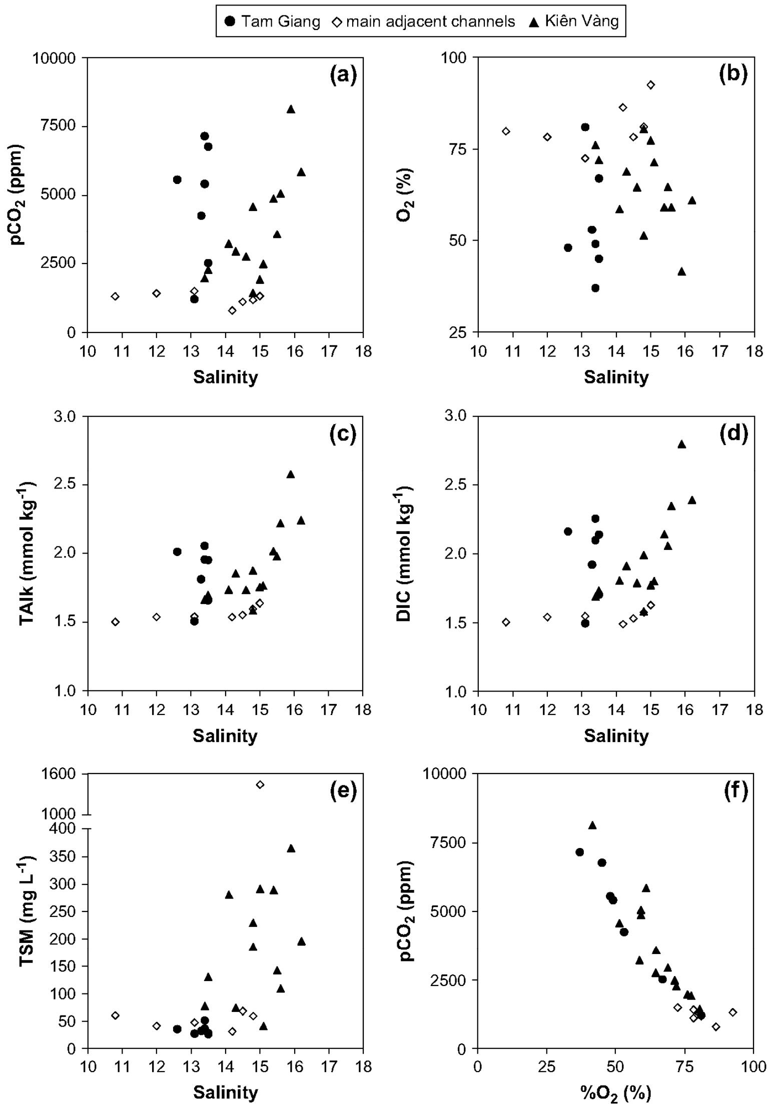

Fig. 7. Variation of pCO_2 (ppm), $\%O_2$ (%), TAlk (mmol kg^{-1}), DIC (mmol kg^{-1}) and TSM (mg L^{-1}) as a function of salinity in the mangrove creeks (Tan Giang, solid circles and Kiên Vàng, solid triangles) and adjacent main channels (open diamonds), and pCO_2 versus $\%O_2$ during the rainy season.

Alongi et al. (2000b), the magnitude of these processes depends of the dominant species of mangrove trees; these authors also reported that sulphate reduction rates were significantly correlated with live root biomass, aboveground biomass and forest net primary production. Denitrification is assumed to be a minor pathway for diagenetic organic carbon degradation and has only been observed in the oldest mangrove forests of the Mekong delta (Alongi et al., 2000a). Only in the Bangrong mangrove area (Thailand), iron reduction has been reported as the predominant diagenetic carbon degradation process (Kristensen et al., 2000), while in Matang mangrove forest (Malaysia), manganese reduction and denitrification—nitrification coupled with aerobic respiration, accounted for most organic matter degradation (Alongi et al., 1998). Finally, based on pore water chemistry in Gazi Bay (Kenya), Middelburg et al. (1996) suggested that the acidification of pore waters due to anaerobic diagenetic degradation processes led to the dissolution of calcium carbonates (also increasing TAlk).

Whatever the process that dominated diagenetic organic carbon degradation in Tam Giang and Kiên Vàng, the high TAlk and DIC values in the mangrove creeks were consistent with the enrichment of these quantities in the creek waters due to the influx of pore waters, during both seasons. The relative variation of TAlk normalised to a constant salinity (nTAlk) versus DIC normalised to a constant salinity (nDIC) is an indicator of the dominant biogeochemical process affecting directly or indirectly these quantities. TAlk and DIC were normalised to a constant salinity of 32 in order to minimise evaporation/dilution effects on these quantities. During the dry season, nTAlk and nDIC were well correlated in the Tam Giang mangrove creeks ($r^2 = 0.99$ of the linear regression) and the Kiên Vàng mangrove creeks ($r^2 = 0.93$ of the linear regression) with slopes of, respectively, 0.61 and 0.62 (Fig. 8). The values of the slopes were lower if sulphate reduction was the only biogeochemical process controlling these variables; this suggests that aerobic respiration and/or air–water exchange of CO_2 also strongly contributed to the variation of DIC in the water column. During the rainy season, nTAlk and nDIC were also well correlated in the Tam Giang mangrove creeks ($r^2 = 0.99$ of the linear regression) and the Kiên Vàng mangrove creeks ($r^2 = 0.99$ of the linear regression) with slopes of, respectively, 0.74 and 0.78 (Fig. 8). This suggests that during the rainy season, the enrichment of DIC and TAlk in the creek waters was also partly due to the influx of pore waters. The slopes were also consistent with a strong contribution by sulphate reduction, despite the fact that a decrease of this diagenetic process would have been expected due to the lower availability by sulphate due to dilution during the rainy season. During both seasons, no correlation was found between nTAlk and nDIC in the main adjacent channels and the range of variations was much smaller than in the tidal creeks (data not shown). This suggests that pore water influx did not affect DIC and TAlk in the main adjacent channels since the water volume is more important, and probably the water residence time shorter than in the mangrove creeks.

3.2. Air–water CO_2 fluxes

During the dry season, air–water CO_2 fluxes ranged from 27.1 mmol C m^{-2} d^{-1} to 141.5 mmol C m^{-2} d^{-1}, and the average air–water CO_2 flux was significantly higher in the Tam Giang mangrove creeks than in the Kiên Vàng mangrove creeks and than in the adjacent main channels, in accordance with ΔpCO_2 values (Table 2). During the dry season, average air–water CO_2 flux was not significantly different in the Kiên Vàng mangrove creeks and in the adjacent main channels. During the rainy season, the air–water CO_2 fluxes ranged from 81.3 mmol C m^{-2} d^{-1} to 154.7 mmol C m^{-2} d^{-1}, and the average air–water CO_2 flux highly significantly increased 5 fold in the Kiên Vàng mangrove creeks, and very significantly increased 3 fold in the adjacent main channels compared to the dry season. This increase can be explained by the significantly to highly significantly higher average ΔpCO_2 values during the rainy season, for, respectively, the Kiên Vàng mangrove creeks and the adjacent main channels. Indeed, in the Kiên Vàng mangrove creeks and in the adjacent main channels, wind speed was not significantly different between the two seasons. In the Tam Giang mangrove creeks, the average air–water CO_2 flux was not significantly different during both seasons in agreement with ΔpCO_2.

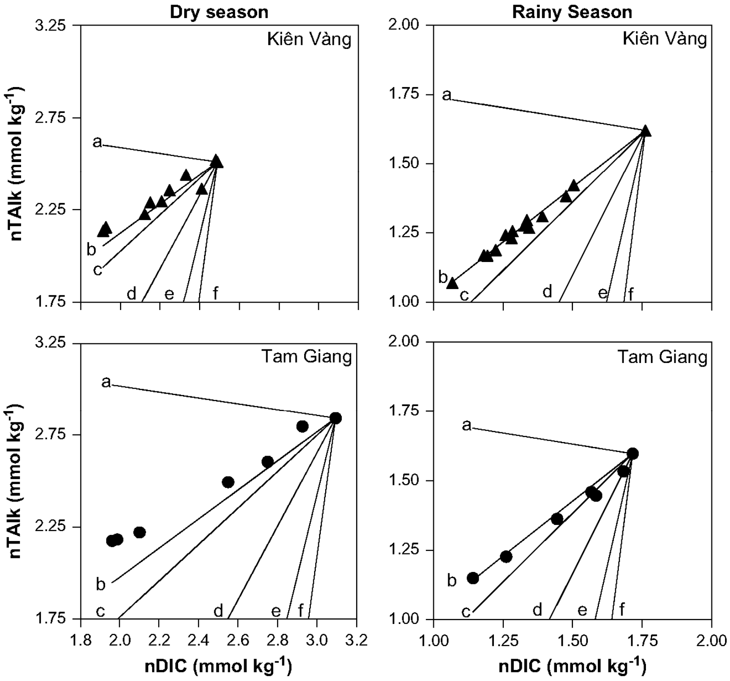

Fig. 8. Relative variation of TAlk normalised to a constant salinity of 32 (nTAlk, mmol kg^{-1}) versus DIC normalised to a constant salinity of 32 (nDIC, mmol kg^{-1}) in the Kiên Vàng (solid triangles) and Tam Giang (solid circles) mangrove creeks during the dry and rainy seasons. Solid lines correspond to the theoretical evolution to attain the highest nTAlk and nDIC values for the potential biogeochemical processes that can control these variables: a, aerobic respiration; b, denitrification; c, sulphate reduction; d, $CaCO_3$ dissolution; e, manganese reduction; f, iron reduction.

Table 3
Average ± standard deviation of wind speed, air−water pCO_2 gradient, atmospheric CO_2 flux and the gas transfer velocity k reported in literature. n.d., no data; LM86 = k parameterisation from Liss and Merlivat (1986)

Sites	Wind speed ($m\ s^{-1}$)	ΔpCO_2 (ppm)	Atmospheric CO_2 flux ($mmol\ C\ m^{-2}\ d^{-1}$)	k ($cm\ h^{-1}$)	References
Nagada Creek (Papua New Guinea)	3.0 ± 2.1	799 ± 357	43.6 ± 33.2	8 ± 6	Borges et al. (2003)
Norman's Pond (Bahamas)	5.5 ± 1.3	165 ± 86	13.8 ± 8.3	13 ± 3	Borges et al. (2003)
Gaderu Creek (India)	1.4 ± 1.9	2215 ± 864	56 ± 100.9	4 ± 5	Borges et al. (2003)
Saptamukhi Creek (India)	n.d.	2210 ± 1460	56.7 ± 37.4	4	Borges et al. (2003) based on Ghosh et al. (1987)
Mooringanga Creek (India)	n.d.	830 ± 363	23.2 ± 10.1	4	Borges et al. (2003) based on Ghosh et al. (1987)
Fringe of Sundarban forest (India)	n.d.	110 ± 321	0.4	LM86	Biswas et al. (2004)
Itacuraçá Creek (Brazil)	n.d.	3845 ± 3520	113.5 ± 104.4	4	Borges et al. (2003) based on Ovalle et al. (1990)
Florida Bay (USA)	n.d.	170 ± 200	4.6 ± 5.4	4	Borges et al. (2003) based on Millero et al. (2001)
Shark River (USA)	n.d.	1285 ± 1485	43.8 ± 52.1	4	Based on data available at http://www.rsmas.miami.edu/groups/jmc/fla-bay/fbay.html

Although during the dry season the average ΔpCO_2 was significantly 5 times lower in the adjacent main channels than in the Kiên Vàng mangrove creeks, the average air−water CO_2 flux was not significantly different, due to the very significantly higher wind speeds and k values in the adjacent main channels. This was due to the presence of trees and the narrowness of the tidal creeks that reduced the air−water CO_2 fluxes by limiting wind speed. This is in agreement with a recent analysis of air−water CO_2 fluxes in Gazi bay that shows a very large contribution of open waters compared to mangrove creek waters to the overall emission of CO_2 from the whole mangrove aquatic system (Bouillon et al., 2007c). The average k value in the Kiên Vàng and Tam Giang mangrove creeks ranged from 3 $cm\ h^{-1}$ to 5 $cm\ h^{-1}$ and from 4 $cm\ h^{-1}$ to 6 $cm\ h^{-1}$ during, respectively, the dry and rainy seasons. This confirms that the use of a constant k value of 4 $cm\ h^{-1}$ is adequate for sheltered mangrove creeks (Borges et al., 2003).

Our results are within the range of air−water CO_2 fluxes in aquatics systems associated to other mangrove forests (Table 3). The representativeness of the Millero et al. (2001) data for Florida's mangrove creeks is not straightforward, since they were obtained in the open waters of Florida Bay and some of the sampling stations were located about 30 km from the mangrove fringe. The data from Shark River are most probably more representative of the Florida Bay mangrove creeks than the values within the bay itself reported by Millero et al. (2001). Indeed, Ovalle et al. (1999) concluded that mangrove forests did not affect the chemistry of the shelf waters of Eastern Brazil, even at stations located 2 km away from the mangrove fringe. Similarly, Biswas et al. (2004) recently reported an annually integrated air−water CO_2 flux of 0.4 $mmol\ C\ m^{-2}\ d^{-1}$ at the fringe of the Sundarban mangrove forest that was much lower than the values in two creeks (Mooringanga and Saptamukhi) within the mangrove forest. This suggests that the export of DIC from mangroves does not seem to affect the air−water CO_2 fluxes in the adjacent aquatic ecosystems where the DIC is rapidly "diluted".

The air−water CO_2 fluxes computed for the Ca Mau mangrove creeks are consistent with previous estimates in mangrove surrounding waters (Table 3) and confirm that an overall value of 50 $mmol\ C\ m^{-2}\ d^{-1}$ given by Borges et al. (2003) was a reasonable first order general estimate. Based on data from Tables 2 and 3, we can re-evaluate the air−water CO_2 emission from mangroves to 72 $mmol\ C\ m^{-2}\ d^{-1}$ that upward scaled to the most recent surface area of mangrove forests ($146 \times 10^3\ km^2$ in 2000; FAO, 2003) provides a CO_2 emission of 0.046 $PgC\ yr^{-1}$. This emission corresponds to about 7% of the overall emission from open oceanic waters at sub-tropical and tropical latitudes (30° N−30° S, 0.71 $PgC\ yr^{-1}$, based on Takahashi et al. (2002)) and to 24% of the overall emission of about 0.19 $PgC\ yr^{-1}$ from coastal waters (including estuaries, marginal seas, coastal upwelling systems and coral reefs) at the same latitudes based on the compilation by Borges et al. (2005).

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5 Seasonal variability of carbon dioxide in the rivers and lagoons of Ivory Coast (West Africa)

Foreword

Lagoons are shallow water bodies relatively separated from the adjacent ocean, receiving large inputs of carbon and nutrients from land and highly productive. Lagoons are relatively closed basins and extremely vulnerable to nutrient input from the surrounding catchment, hence highly vulnerable to anthropogenic influences. They are commonly surrounded by mangrove forests and salt marshes, which are important sources of organic matter in addition to river inputs. Due to their shallowness, a large fraction of this organic matter accumulates locally and is not transported toward the adjacent ocean. Thus, they are expected to be significant sources of both CO_2 and CH_4 to the atmosphere, although so far not quantified. Furthermore, lagoons, exhibit great spatial and temporal variability in their physico-chemical characteristics due to sporadic inputs of freshwater, hence the cycling of CO_2 and CH_4 in these ecosystems is expected to show strong spatial gradients and high seasonality.

In this chapter, we report the first seasonal cycle of pCO_2 and related CO_2 fluxes in five lagoons and three rivers from Ivory Coast. We show that CO_2 fluxes in the 5 lagoons are very heterogeneous due variable physical settings that control the rate and fate of primary production. In the rivers, we show that seasonal variability of pCO_2 is governed by dilution processes. However, floating macrophytes that covers these rivers can be an additional CO_2 source to the atmosphere due to root respiration and organic matter degradation derived from these plants.

This chapter is in press (Koné, Abril, Kouadio, Delille & Borges. Seasonal variability of carbon dioxide in the rivers and lagoons of Ivory Coast (West Africa). Estuaries and Coasts)

Seasonal Variability of Carbon Dioxide in the Rivers and Lagoons of Ivory Coast (West Africa)

Y. J. M. Koné · G. Abril · K. N. Kouadio · B. Delille ·
A. V. Borges

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Abstract We report partial pressure of CO_2 (pCO_2) and ancillary data in three rivers (Bia, Tanoé, and Comoé) and five lagoons (Tendo, Aby, Ebrié, Potou, and Grand-Lahou) in Ivory Coast (West Africa), during four cruises covering the main climatic seasons. The three rivers were oversaturated in CO_2 with respect to atmospheric equilibrium, and the seasonal variability of pCO_2 was due to dilution during the flooding period. Surface waters of the Potou, Ebrié, and Grand-Lahou lagoons were oversaturated in CO_2 during all seasons. These lagoons behaved similarly to the oligohaline regions of macrotidal estuaries that are CO_2 sources to the atmosphere due to net ecosystem heterotrophy and inputs of riverine CO_2 rich waters. The Aby and Tendo lagoons were undersaturated in CO_2 with respect to the atmosphere because of their permanent haline stratification (unlike the other lagoons) that seemed to lead to higher phytoplankton production and export of organic carbon below the pycnocline.

Y. J. M. Koné · B. Delille · A. V. Borges (✉)
Unité d'Océanographie Chimique, Institut de Physique (B5),
Université de Liège,
4000 Liège, Belgium
e-mail: alberto.borges@ulg.ac.be

Y. J. M. Koné · K. N. Kouadio
Laboratoire d'Environnement et de Biologie Aquatique,
Université d'Abobo-Adjamé,
02 BP 801,
Abidjan 02, Ivory Coast

G. Abril
Département de Géologie et Océanographie, Environnements
et Paléoenvironnements Océaniques, Avenue des Facultés,
Université de Bordeaux 1,
33405 Talence, France

Keywords Carbon dioxide · Inorganic nutrients · Tropical lagoons · Tropical rivers · *Eichhornia crassipes*

Introduction

Despite the small surface area covered by coastal ecosystems (7% of the global ocean surface area), they host between 10% and 30% of the global marine primary production, and they account for 80% of oceanic organic matter burial (Gattuso et al. 1998; Wollast 1998). Overall continental seas are net sinks for atmospheric CO_2 although there are strong regional differences in the direction of the air–sea CO_2 fluxes, with tropical and subtropical systems acting as sources of CO_2 to the atmosphere and mid- and high-latitude systems acting as sinks for atmospheric CO_2 (Borges 2005; Borges et al. 2005; Cai et al. 2006; Chen and Borges 2008). However, near-shore coastal ecosystems are in general sources of CO_2 to the atmosphere due to the influence of inputs from land (Abril and Borges 2004; Borges 2005; Borges et al. 2005, 2006; Chen and Borges 2008). There is a scarcity of air–water CO_2 flux data in coastal environments at subtropical and tropical latitudes that receive about 60% of the global freshwater discharge and an equivalent fraction of riverine organic inputs (e.g., Ludwig et al. 1996a; Richey 2004). There is also a lack of information on air–water CO_2 fluxes in some coastal ecosystems, such as lagoons where the few studies of carbon cycling have focused solely on the ecosystem metabolism (e.g., Boucher et al. 1994; Carmouze et al. 1998; Sidinei et al. 2001; McGlathery et al. 2001; Hung and Hung 2003).

Lagoons are among the most common near-shore coastal environments occupying 13% of the World's coastline (Kjerfve 1985). These ecosystems are difficult to define, and there are no generally accepted criteria which unambiguously separate them from bays, estuaries, marshes, and other parts of the coastal zone. In general, they are characterized by their shallow depth (<5 m), limited exchanges with the adjacent ocean and a high net primary production (Boynton et al. 1996). Like the coastal zone of which they are an integral part, lagoons are subjected worldwide to increased nutrient inputs due to anthropogenic activities such as modification of land use, effluent disposal, and aquaculture (Caumette et al. 1996). The resulting eutrophication leads to the proliferation of macrophytes and the enhancement of phytoplankton blooms in lagoons (Sidinei et al. 2001). The decomposition of the increased plant biomass and of the anthropogenic carbon may lead to the emission of CO_2 to the atmosphere from lagoons.

The input of dissolved inorganic carbon (DIC) from rivers contributes to the CO_2 dynamics in estuaries and lagoons. Rivers are in general oversaturated in CO_2 with respect to atmospheric equilibrium (Kempe 1982; Cole and Caraco 2001) due to the input of soil CO_2 by rain and groundwater and to the in situ degradation of organic matter in excess of primary production. Dynamics of pCO_2 in rivers are modulated seasonally by primary production, temperature effect on the CO_2 solubility, dilution during flooding periods, and exchange of CO_2 with the atmosphere.

In the present work, we report DIC and ancillary data obtained in five lagoons (Tendo, Aby, Ebrié, Potou, and Grand-Lahou) in Ivory Coast (West Africa) and three rivers (Bia, Tanoé, and Comoé) flowing into these lagoons (Fig. 1), during the four characteristic seasons (Fig. 2). The three studied rivers are the most important in Ivory Coast in terms of freshwater discharge excepted for the Bandama (Table 1). The studied lagoons differ by the variable density of the riparian population, by different freshwater inputs (Table 1), and by physical settings (permanent or seasonal stratification). Hence, the studied lagoons are representative of most of the kinds of lagoons that can be encountered in West Africa and at tropical latitudes. The present study allows characterizing the differences in the cycling of CO_2 in a wide range of types of tropical lagoons, provides the range of seasonal variability of pCO_2 and air–water CO_2 fluxes over an annual cycle.

Material and Methods

Description of Study Area

Lagoons are the most prominent coastal ecosystems of Ivory Coast (Fig. 1) covering an area of 1,200 km^2, which corresponds to a large fraction of the surface area of lagoons in West Africa (5,000 km^2; Binet et al. 1995). They are gathered in three systems (Ebrié, Grand-Lahou, and Aby) and stretch along some 300 km of the coastline. The density of the riparian population is variable ranging from 3.5 inhabitants km^{-2} around the Aby lagoon system to ~100 inhabitants km^{-2} around the Ebrié lagoon system (Jallow et al. 1999).

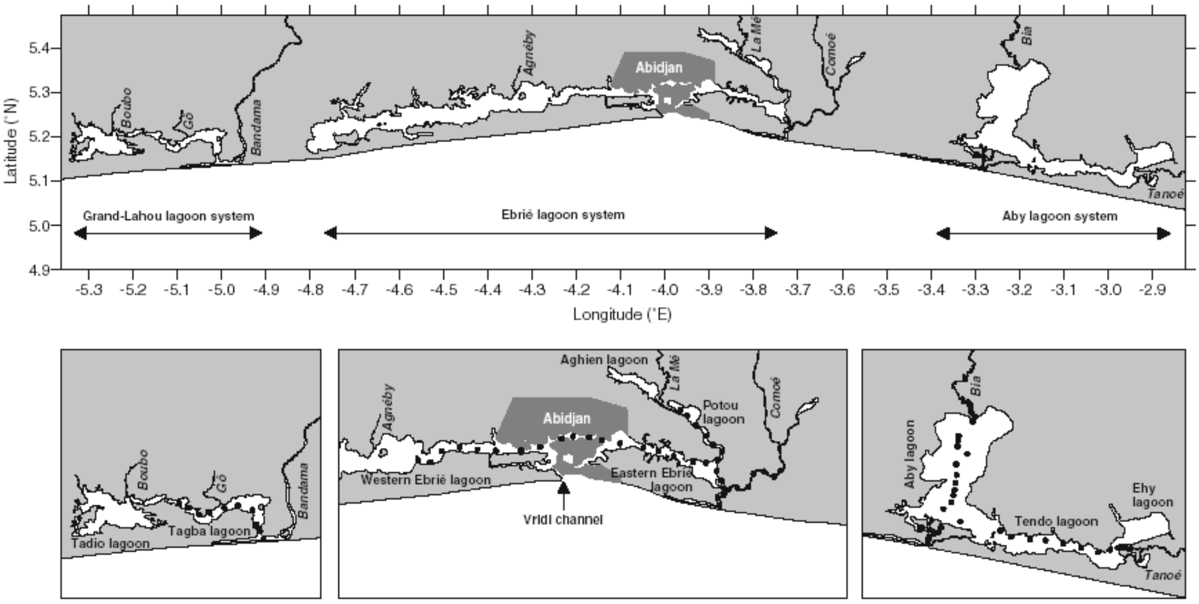


Fig. 1 Map showing the location of lagoons and rivers in Ivory Coast and the sampling stations (*bottom panels*)

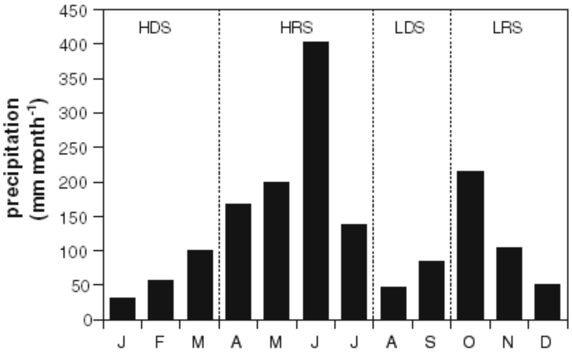


Fig. 2 Average monthly rainfall (mm month^{-1}) during 2000–2006 at Adiaké station (−3.3° E 5.28° N) close to Aby lagoon, obtained from the Direction Météorologique d'Adiaké. *HDS* high dry season, *HRS* high rainy season, *LDS* low dry season, *LRS* low rainy season

The climate is close to equatorial, with an annual rainfall ranging from 1,500 to 1,800 mm, characterized by two rainy seasons and two dry seasons (Durand and Skubich 1982). The high dry season extends from January to March, the high rainy season from early April to late July, the low dry season from August to September, and the low rainy season from October to December (Fig. 2).

The rivers flowing into these lagoons have two different hydrological regimes (Iltis and Lévêque 1982; Jallow et al. 1999). The Tanoé, the Bia, the La Mé, and the Agnéby rivers have an equatorial transition regime with two flooding periods in June–July and October–November. The Comoé and Bandama rivers have a mixed regime with only one flooding period during September–October. The lithology of the drainage basin of the three rivers is different: In the Comoé, it is composed of 63% plutonic acids, 26% of Precambrian basement, and 11% consolidated siliciclastic rocks; in the Bia, it is composed of 67% of Precambrian basement, 17% plutonic acids, and 16% semi- to unconsolidated sedimentary; in the Tanoé, it is exclusively composed of Precambrian basement (Dürr et al. 2005).

The Ebrié lagoon system (Fig. 1) is the largest lagoon in West Africa (Adingra and Arfi 1998). It is an elongated lagoon system with a total area of 566 km^2, and it stretches for ~130 km, with a maximum width of ~7 km. The average depth is of 4.8 m, with a few deep areas especially around Abidjan (27 m south of Boulay Island). It is divided into three lagoons—Potou, Aghien, and Ebrié—and receives freshwater from the Comoé, Agnéby, and La Mé rivers (Fig. 1; Table 1). Annual freshwater input from the Comoé river is estimated to ~7 km^3 that represents approximately three times the total volume of the lagoon system (Table 1), while the flow of seawater is ~14 times this volume (Durand and Guiral 1994). Salinity in the system varies between 0 and 35. Before 1951, the Ebrié lagoon system was only connected to the Atlantic Ocean through the Bassam inlet in the far east of the lagoon system (40 km away from Abidjan). The Vridi Channel was built in 1951 allowing a connection to the sea closer to Abidjan, greatly modifying the hydrological environment since the Bassam inlet has progressively closed, and nowadays, the Comoé river discharges into the lagoon system rather than directly to the sea. The Ebrié lagoon system is strongly polluted by domestic and industrial waste water inputs (Kouassi et al. 1995; Adingra and Arfi 1998). The waters around Abidjan are highly eutrophicated leading to frequent oxygen depletion, massive fish kills, and repelling sulfuric smells (Kouassi et al. 1995; Scheren et al. 2004) and have been included in a recent compilation of coastal "dead zones" (Diaz and Rosenberg 2008).

The Aby lagoon system consists of the main Aby lagoon, the Tendo lagoon, and the Ehy lagoon and receives freshwater from the Bia and the Tanoé rivers, respectively, in the northwest and in the east (Fig. 1). The Aby lagoon system is located in the far east of Ivory Coast and forms a natural border with Ghana, extends over 30 km of the coastline and occupies over an area of 424 km^2. The main Aby lagoon (hereafter Aby lagoon) is the largest and covers 305 km^2, with a total shoreline of 24.5 km and a maximal width of 15.5 km. The Tendo lagoon has a length of 22 km and a width varying between 1.5 and 3.5 km and a surface area of 74 km^2. The Ehy lagoon has a mean depth of 1.5 m and a surface area of 45 km^2. The Aby and Tendo lagoons

Table 1 Some relevant characteristics of the Tendo, Aby, Ebrié, Potou, and Grand-Lahou lagoons and of the main rivers (Tanoé, Bia, Comoé, La Mé, Agnéby, and Bandama) flowing into these lagoons, based on Chantraine (1980), Durand and Chantraine (1982), and Durand and Skubich (1982)

Lagoons	Area (km^2)	Volume (km^3)	Mean depth (m)	Surface salinity	Rivers	Total length (km)	Drainage area (km^2)	Mean water discharge (m^3 s^{-1})
Tendo	74	0.2	2.7	0–8	Tanoé	625	16,000	132
Aby	305	1.3	4.2	1–8	Bia	290	9,650	59
Ebrié	524	2.6	4.8	0–35	Comoé	1,160	78,000	224
					Agnéby	200	8,900	27
Potou	22	0.03	2.7	0–6	La Mé	140	4,300	47
Grand-Lahou	190	0.5	2.0	0–26	Bandama	1,050	97,000	298

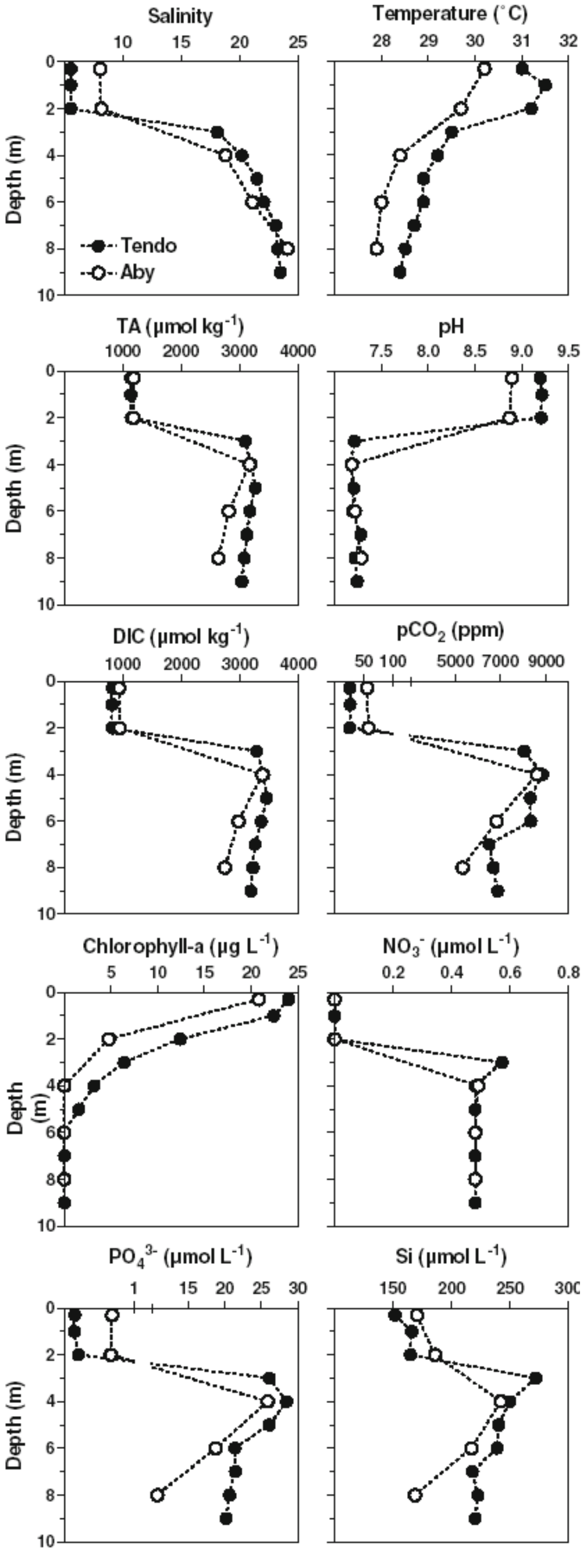


Fig. 3 Vertical profiles of salinity, temperature (°C), TA (mmol kg^{-1}), pH, DIC (mmol kg^{-1}), pCO_2 (ppm), chlorophyll-a (µg L^{-1}), NO_3^- (µmol L^{-1}), PO_4^{3-} (µmol L^{-1}), and Si (µmol L^{-1}) in Aby (−3.231° E 5.228° N) and Tendo (−3.110° E 5.142° N) lagoons during the high dry season (March)

are characterized by permanent haline stratification (Fig. 3) unlike the other two lagoon systems that are seasonally stratified.

The Grand-Lahou lagoon system (Tagba and Tadio lagoons) is located in the far west of the coast and is the smallest of the Ivory Coast lagoon systems with an area of 190 km^2 (Fig. 1; Table 1). It receives freshwater from the Bandama river and from the smaller Gô and Boubo rivers.

Sampling, Analytical Techniques, and Statistics

Four cruises were carried out (08 June to 07 July 2006, 06–22 September 2006, 24 November to 13 December 2006, 08–30 March 2007) to sample five lagoons (Tendo, Aby, Ebrié, Potou, and Grand-Lahou) and three rivers (Tanoé, Bia, and Comoé). The cruise in June–July is representative of the high rainy season, the cruise in September of the low dry season, the cruise in November–December of the low rainy season, and the cruise in March of the high dry season (Fig. 2). On average for each cruise, eight samples were obtained in the Comoé river, eight samples in the Bia river, eight samples in the Tanoé river, ten samples in the Grand-Lahou lagoon, 16 samples in the Aby lagoon, six samples in the Potou lagoon, 23 samples in the Ebrié lagoon, and eight samples in the Tendo lagoon (Fig. 1).

Subsurface waters (depth ~30 cm) were sampled with a 1.7-L Niskin bottle and pH measurements were carried out immediately after collection, with a combined electrode (Metrohm 6.0232.100) calibrated on the US National Bureau of Standards scale as described by Frankignoulle and Borges (2001), with a precision and estimated accuracy of ±0.001 and ±0.005 pH units, respectively. Salinity and water temperature were measured in situ using a portable conductivity meter (WTW Cond-340) with a precision of ±0.1 and ±0.1°C, respectively. A volume of 100 mL was filtered through 0.2 µm pore size polysulfone filters and was stored at ambient temperature in polyethylene bottles for the determination of total alkalinity (TA). TA was measured within 1 month after sampling, on 50 mL samples by automated Gran electro-titration with 0.1 M HCl as titrant, with a reproducibility of ±3 µmol kg^{-1}. Measurements of TA and pH were used to compute pCO_2 and DIC, with an estimated accuracy of ±4 ppm and ±4 µmol kg^{-1}, respectively (Frankignoulle and Borges 2001).

Air–water fluxes of CO_2 were calculated according to:

$$F = \alpha k \Delta pCO_2$$

where α is the solubility coefficient of CO_2, k is the gas transfer velocity of CO_2, and ΔpCO_2 is the air–water gradient of pCO_2.

We computed k using the wind speed field measurements and the "tracers only" parameterization given by Raymond and Cole (2001). Wind speed was measured at each sampling station with a hand-held anemometer.

Water samples for nitrate (NO_3^-), phosphate (PO_4^{3-}), and silicate (Si) measurements were filtered through cellulose acetate filters (Sartorius), refiltered through 0.2 µm pore size polysulfone filters, and preserved with $HgCl_2$ (for NO_3^- and PO_4^{3-}) and HCl for Si. Concentrations of NO_3^- were measured on a Technicon Auto Analyser II (Tréguer and Le Corre 1975), with an estimated accuracy of ±0.1 µmol L^{-1}. Concentrations of PO_4^{3-} and Si were measured with the standard colorimetric methods (Grasshoff et al. 1983), with an estimated accuracy of ±0.01 µmol L^{-1} and ±0.1 µmol L^{-1}, respectively.

Total suspended matter (TSM) data were obtained by filtering a known volume of water (250 to 500 mL) on preweighted glass fibber filters (Whatman GF/F), rinsed with deionized water to avoid salt contributions (for lagoon samples), and subsequently dried. Samples for chlorophyll-a concentrations were obtained by filtering a known volume of water (250 to 500 mL) on glass fibber filters (Whatman GF/F) that were frozen until analysis (−40°C). The pigments were extracted between 12 and 24 h in 15 mL of 90% acetone at 4°C, and after centrifugation, absorbance was measured at 665 and 750 nm, before and after acidification with 100 µL of HCl 0.1 M, according to the spectrophotometric method described by Lorenzen (1967). The estimated accuracy of chlorophyll-a concentration is ±5%.

Sample means were compared (across sampling sites in each season and across seasons within each site) statistically using a two-tailed unpaired Student t test, using Prism 4.00 (GraphPad). P values are not explicitly mentioned hereafter but "significant(ly)" refers to $P<0.05$, "very significant(ly)" refers to $P<0.01$, "highly significant(ly)" refers to $P<0.001$, and "not significant(ly)" refers to $P>0.05$ at 0.05 level.

Results and Discussion

Inorganic Carbon and Nutrient Dynamics in the Bia, Tanoé, and Comoé Rivers

Inorganic Nutrients and Suspended Matter Dynamics in the Three Rivers

Average Si concentration values in the three rivers ranged from 63 to 190 µmol L^{-1} (Fig. 4) in agreement with those reported in the same rivers by Iltis and Lévêque (1982). In the Tanoé and Bia rivers, average Si concentrations were very significantly to highly significantly higher during the high dry season than during the other seasons. In the Bia and Tanoé rivers, Si concentrations decreased during the flooding period due to dilution, while in Comoé river, Si concentrations increased during the flooding period. This different pattern could be due to the characteristic vegetation on the three drainage basins. The Comoé drainage basin is dominated by savannah and flooding most likely increases the export of vegetal debris that are rich in biogenic silica (phytoliths; Wilding et al. 1977; Conley et al. 2006). The Bia and Tanoé drainage basins are dominated by forests where there is a relatively efficient recycling and retention of silica by the vegetation (e.g., Conley 2002; Conley et al. 2006).

The average concentrations of NO_3^- and PO_4^{3-} in the three rivers ranged from 1.8 to 17.7 µmol L^{-1} and from 0.2 to 2.0 µmol L^{-1}, respectively (Fig. 4). Unlike Si, NO_3^- and PO_4^{3-} increased very significantly in the three rivers during the high rainy season (flooding) period due to increased leaching from soils. The average concentrations of NO_3^- were maximal in the three rivers during the high rainy season, while the average PO_4^{3-} concentrations showed a second seasonal maximum during the low rainy season in the Bia and Tanoé rivers but not in the Comoé river. This difference is related to the fact that the Comoé river has only one flooding period due to the more extended drainage basin, while the Bia and Tanoé rivers have two flooding periods. The average concentration of NO_3^- and PO_4^{3-} values are low compared to other rivers due to the fact that the Comoé, Bia, and Tanoé rivers do not receive domestic or industrial waste waters and because the use of agricultural fertilizers in the drainage basin is low.

TSM values in the three rivers ranged from 0 to 50 mg L^{-1} and were significantly to highly significantly higher during the flooding periods due to a substantial soil erosion (Fig. 4). In the three rivers, chlorophyll-a values were generally higher during the flooding periods, when inorganic nutrient availability was also higher. Chlorophyll-a showed a lower seasonal amplitude in the Tanoé and the Comoé rivers than in the Bia river. During the high rainy season and the low dry season, average chlorophyll-a concentrations were higher in the Bia river than in the Tanoé and the Comoé rivers. This is related to the fact that sampling in the Bia river was carried out 60 km downstream of the Ayamé dam. Hence, in the unregulated Comoé and Tanoé rivers, phytoplankton is flushed by the flow, while downstream of the Ayamé dam phytoplankton accumulates in the Bia river, due to a higher residence time of freshwater related to much lower (regulated) water discharge.

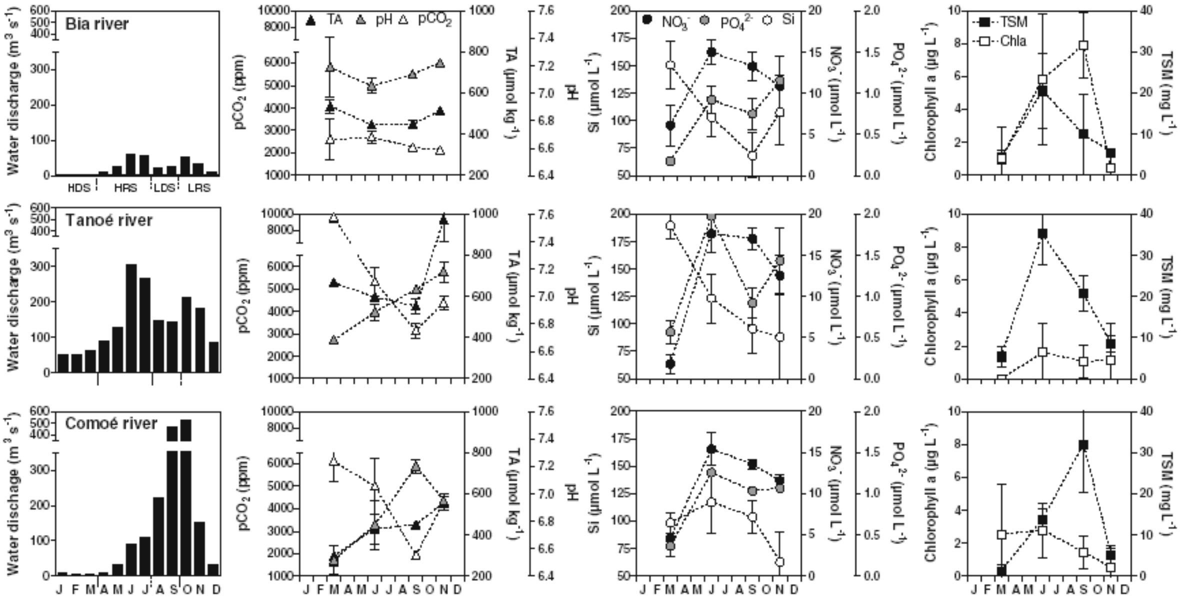


Fig. 4 Seasonal variations of average monthly freshwater discharge, TA (µmol kg^{-1}), pCO_2 (ppm), pH, NO_3^- (µmol L^{-1}), PO_4^{3-} (µmol L^{-1}), Si (µmol L^{-1}), chlorophyll-a concentration (µg L^{-1}), and TSM (mg L^{-1}) in the Bia (n=8), the Tanoé (n=8), and the Comoé (n=8) rivers, during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December). Average monthly freshwater discharge values during 2000–2005 measured at Bianou and Yakassé stations for Bia and Comoé rivers, respectively (data from the Direction de l'Eau d'Abidjan). Average monthly freshwater discharge values in Tanoé river are only available for 1978, at Alanda station (from the University of New Hampshire Global Runoff Data Centre database available at http://www.grdc.sr.unh.edu/). *Error bars* correspond to standard deviation on the mean

DIC Dynamics in the Three Rivers

The TA values in the three rivers were low (<1,000 µmol kg^{-1}; Fig. 4) due to the dominance of lateritic soils in the drainage basin (Mangin et al. 1966; Perraud, 1971), depleted in alterable minerals leading to low specific HCO_3^- fluxes, as in most tropical rivers (Ludwig et al. 1996b; Cai et al. 2008). During the high dry season (March), average TA values in the Comoé river were highly significantly lower than in the other two rivers. The Comoé river has no large tributaries, so during the high dry season, its small tributaries become dry or form ponds, resulting in a very low freshwater discharge compared for instance with the Tanoé river (Fig. 4). The TA varied inversely with water discharge in the Tanoé and Bia rivers due to dilution during the flooding period. In the Comoé river, TA increased with water discharge probably due to the different lithology of the drainage basins: The drainage basin of Comoé is dominated by acid plutonic rocks with a small contribution from consolidated siliciclastic rocks, while the Bia and the Tanoé drainage basins are dominated by Precambrian basement.

The average pH values in the three rivers ranged from 6.52 to 7.22, and pH followed the reverse temporal variations of pCO_2 except during the low rainy season (December) in the Tanoé river when both pH and pCO_2 increased compared to the value during low dry season (September; Fig. 4). This is related to the increase of the buffering capacity of the water due to almost twofold increase of TA values in the Tanoé river from the low dry season (September) to the low rainy season (December). The average values of pCO_2 in the three rivers ranged from 1,925 to 9,595 ppm, always above atmospheric equilibrium. Seasonal variations of pCO_2 were large in the Tanoé and Comoé rivers, with the highest average values obtained during the high dry season (highly significantly) and lowest values during the flooding period (highly significantly), due to dilution (Fig. 4). It is unlikely that planktonic primary production contributed to the decrease of pCO_2 during the flooding period because of relatively low seasonal variability of chlorophyll-a and relatively low values of chlorophyll-a (average <3 µg L^{-1}) in the Tanoé and Comoé rivers. Further, the lowest pCO_2 values did not coincide with the maximal chlorophyll-a values in these rivers. Also, pCO_2 values during the flooding period were highly significantly lower in the Comoé river (<2,000 ppm) than in the Tanoé river (~3,000 ppm) due to the twice higher freshwater discharge in the Comoé river. In the Bia river, the decrease of pCO_2 during the flooding period was much less marked than in the Comoé and the Tanoé rivers due to flow regulation by the Ayamé dam 60 km upstream of the sampling site. The dam strongly decreases the seasonal variations of freshwater discharge and smoothes over the annual cycle the impact of drainage of soil CO_2 by groundwater leading to lower amplitude of seasonal pCO_2 variations in the Bia compared to the other two rivers.

The seasonal cycle of pCO_2 in the Comoé and the Tanoé rivers followed the same pattern (strong decrease of pCO_2 during the flooding period due to dilution) as reported from the subtropical Xijiang river (pCO_2 range 600–7,200 ppm; Yao et al. 2007) and the tropical Niger river (pCO_2 range 1,210–6,310 ppm; Martin and Probst, 1991). This seasonal pattern is distinctly different from the one reported by Richey et al. (2002) in the Amazon where pCO_2 increases with rising water (up to 44,000 ppm) due to carbon inputs to the water during the inundation of the floodplain. The difference in seasonal patterns of pCO_2 between these subtropical and tropical rivers is related to the very large freshwater discharge of the Amazon river (~175,000 $m^3\ s^{-1}$) and very extensive floodplains (up to 20 times the surface area of the mainstream channel). Furthermore, the seasonal pCO_2 cycle in the Comoé and the Tanoé rivers is also distinctly different from temperate rivers, where pCO_2 can be maximal during low water (summer) due to the effect of temperature change on the CO_2 solubility like in the York river (Raymond et al. 1997), or where pCO_2 can be minimal in summer in highly eutrophied rivers like the Loire due to intense phytoplankton blooms (Abril unpublished).

Role of Floating Macrophytes on DIC and Inorganic Nutrient Dynamics in the Rivers

In tropical rivers, the respiration and decomposition from floating and emerged macrophytes can constitute an important source of CO_2 to the water column. For instance, in the Amazon river, root respiration from and decomposition of floating and emerged macrophytes contribute to 25% of CO_2 evasion to atmosphere from the water column (Richey et al. 2002; Engle et al. 2008). Different macrophytes are present in the Comoé, Bia, and Tanoé rivers, such as *Eichhornia crassipes*, *Pistia stratoties*, and *Salvinia molesta* (Guiral and Etien 1994). The biomass of these macrophytes is ~90 $gC\ m^{-2}$ in the rivers and ranges between ~90 and ~150 $gC\ m^{-2}$ in the lagoons (Guiral and Etien 1994) and can occupy between 1 and 100% of surface waters (Etien and Arfi 1996). The water hyacinth *E. crassipes* is an invasive species originating from the Amazon river with a capacity for growth and propagation that raises serious socioeconomic issues (Holm et al. 1991). *E. crassipes* affects water chemistry (temperature, pH, oxygen, and nutrients concentrations; Rai and Datta Mushi 1978) and organic matter flows (Poi de Neiffa et al. 1994).

During our sampling cruises, low densities of macrophytes were observed in the main stream and the inundation plains of the Bia and Comoé rivers. In the Comoé river, due to the large freshwater discharge, macrophytes are transported downstream to the adjacent lagoons, and in the Bia river, macrophytes accumulate upstream of our sampling site in Ayamé dam. In the Tanoé river, a strong proliferation of *E. crassipes* occurred during the high dry season (March), because of the low freshwater discharge, and macrophytes completely covered the mainstream of the river.

During the period of *E. crassipes* proliferation in the Tanoé, the average NO_3^- concentration was significantly lower (1.8±1.2 $\mu mol\ L^{-1}$; Fig. 4) than in the Bia and Comoé rivers at the same period (6.1±2.5 and 4.6±2.1 $\mu mol\ L^{-1}$, respectively), most likely due to the efficient uptake of nutrients from the water column by the macrophytes (Reddy and De Busk 1985; Petrucio and Esteves 2000). Also, the shading effect of the macrophytes on the water column lead to undetectable chlorophyll-a concentrations in the Tanoé compared to 1 and 2 $\mu g\ L^{-1}$ in the Bia and Comoé rivers, respectively, at the same period of the year. The combination of NO_3^- uptake by macrophytes and light limitation of phytoplankton production lead to a significantly higher Si/NO_3^- ratio (168) in the Tanoé than in the Bia and Comoé rivers at the same period of the year (52 and 31, respectively). The presence of macrophytes in the Tanoé river also lead to highly significantly higher pCO_2 values (~9,600 ppm) compared to the Comoé and Bia rivers during the same period (~6,100 and ~2,600 ppm, respectively), due to root respiration and degradation of macrophyte organic matter. The presence of these emerged macrophytes leads to a net built up of CO_2 in the water column, since photosynthesis fixes atmospheric CO_2, while root respiration and degradation of macrophyte organic matter lead to a release of CO_2 in the water column.

Inorganic Carbon and Nutrient Dynamics in the Aby, Tendo Potou, Ebrié, and Grand-Lahou lagoons

Salinity and TA Variations in the Five Lagoons

Surface salinity in the five lagoons was highly significantly lower during the high rainy season (June) than the high dry season (March; Table 2), due to the higher freshwater input during this period of the year. Yet, salinity in the Aby lagoon was highly significantly higher during the high rainy season (June) than during the low dry season (September) and the low rainy season (December), unlike the Tendo, Ebrié, and Grand-Lahou lagoons. This could be due to the fact that, in the Aby lagoon, the high freshwater inputs during the high rainy season (June) lead to an erosion of the pycnocline due to the turbulence from the flow and the partial mixing with surface waters of deep water with a much higher salinity (Fig. 3).

Whatever the season, surface salinity was significantly to highly significantly lower in the Potou, Aby, and Tendo lagoons than in the Ebrié and Grand-Lahou lagoons (except for the Aby lagoon during the high rainy season (June); Table 2). This is due to the fact that the Potou, Aby, and Tendo lagoons are in the direct continuation of the La Mé, Bia, and Tanoé rivers, respectively, hence strongly influenced by freshwater inputs, and they have a shallow connection with the adjacent marine systems. The surface salinity in the Grand-Lahou system was significantly to highly significantly higher than in the other lagoons during all seasons (except the high rainy season) because sampling was carried out close to the opening with the sea.

Surface salinity was high in the Ebrié lagoon (Table 2) because it is connected to the sea by the Vridi Channel. Surface salinity in the Ebrié lagoon had strong longitudinal gradients, with the highest salinities at the vicinity of the Vridi Channel (near Abidjan) and decreasing eastward due to the freshwater inputs from the La Mé and the Comoé rivers and westward due to the freshwater input from the Agnéby river (Fig. 5). The relative importance of the different freshwater inputs on the water masses in the Ebrié lagoon can be seen on the TA distribution as a function of salinity (Fig. 6). Whatever the season, TA was higher at a given salinity in the western side than in the eastern side of the Ebrié lagoon. This was due to the influence of the Agnéby river that had higher TA values than the Comoé and La Mé rivers. Indeed, the *y*-intercept of the linear regression of TA as a function of salinity for the western side of the Ebrié lagoon (indicative of TA in the Agnéby river) ranged from 670 to 777 µmol kg^{-1}, above the observed TA values in the Potou lagoon (influenced by the La Mé river) and the Comoé river (Fig. 6). In December and September, the TA values in the eastern side of the Ebrié lagoon, suggest that the Comoé river had a much larger influence on the oligohaline Ebrié lagoon than the La Mé river, in agreement with the very different average annual discharge values (47 and 224 $m^3 s^{-1}$, respectively). In June, the oligohaline region of the eastern Ebrié lagoon seemed to be a mixture of both the Comoé and La Mé river end members. Finally, in March when the freshwater inputs from the La Mé river were lowest, the Potou lagoon was dominated by brackish waters, and the *y*-intercept of the linear regression of TA as a function of salinity (381 µmol kg^{-1}) suggests that the La Mé river had a higher freshwater TA than the measured value in the Comoé river (268 µmol kg^{-1}).

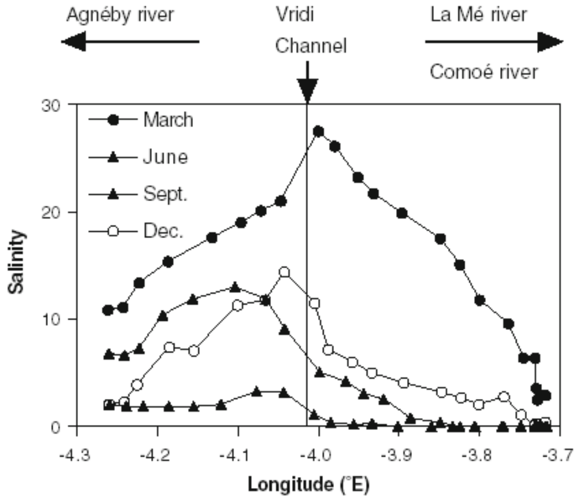


Fig. 5 Latitudinal variations of salinity in the Ebrié lagoon during the during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December)

Inorganic Nutrients and Suspended Matter Dynamics in the Five Lagoons

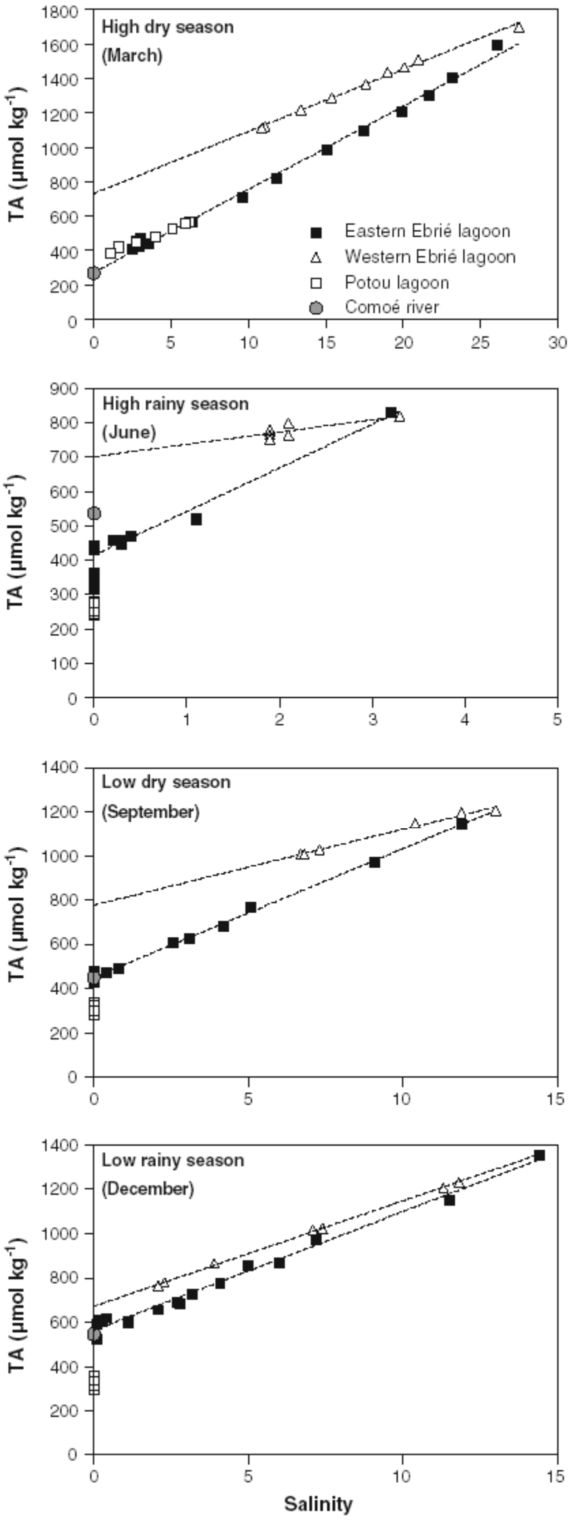
Average NO_3^- concentrations in the five lagoons were very significantly to highly significantly higher during the high rainy season (June) than the high dry season (March; Fig. 7) due to strong freshwater inputs (Table 2). Average NO_3^- concentrations in the Tendo, Ebrié, and Potou lagoons during the high rainy season (June) were also significantly to highly significantly higher than during the low dry season (September) and the low rainy season (December).

At a given salinity, whatever the season, NO_3^- and PO_4^{3-} were higher in the Ebrié, Potou, and Grand-Lahou lagoons

Table 2 Seasonal variations of the average salinity (±standard deviation) in surface waters in the Tendo (*n*=8), Aby (*n*=11), Ebrié (*n*=23), Potou (*n*=6), and Grand-Lahou (*n*=10) lagoons, during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December)

	High dry season (March)	High rainy season (June)	Low dry season (September)	Low rainy season (December)
Tendo	4.9±2.7	0.0±0.1	0.5±0.7	0.1±0.2
Aby	6.5±0.9	2.0±0.2	1.1±0.5	1.2±0.4
Ebrié	14.2±7.7	0.9±1.1	4.1±4.6	4.7±4.3
Potou	3.7±1.9	0.0±0.0	0.0±0.0	0.0±0.0
Grand-Lahou	19.4±5.0	0.6±0.3	8.0±1.6	9.2±3.5

Fig. 6 TA as a function of salinity in the Comoé river and in the Ebrié▶ and the Potou lagoons during the during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December). *Dotted line* indicate the regression lines of TA as a function of salinity for salinities >0. Note that the *x*-axis scale is variable from one season to another



than in the Aby and Tendo lagoons, except in March when strong NO_3^- depletion was observed in most lagoons (Fig. 8). In June and September, NO_3^- and PO_4^{3-} at a given salinity were higher in the eastern Ebrié lagoon than in the Grand-Lahou lagoon that is relatively pristine. In September, at a given salinity, both NO_3^- and PO_4^{3-} were higher in the eastern Ebrié lagoon than in the western Ebrié lagoon, and this was also the case of PO_4^{3-} in March. This was the case for the sampling stations in the eastern Ebrié lagoon in the vicinity of Abidjan showing the effect of eutrophication related to ~3.8 million inhabitants living in this city.

Average Si concentrations were always high in the five lagoons, and the seasonal cycles in the Tendo and Aby lagoons differed from that in the Ebrié lagoon (Fig. 7). In the Tendo and Aby lagoons, the average Si concentrations were highly significantly higher during the high dry season (March) because of the inputs from the Tanoé and the Bia rivers that were characterized during this period of the year by the highest Si concentrations (Fig. 4). In the Ebrié lagoon, average Si concentrations were very significantly to highly significantly higher during the high rainy season (June) than the other seasons due to the higher inputs of freshwater (Table 2) and because Si concentrations were highest at this period of the year in the Comoé river (Fig. 4). In the Potou and the Grand-Lahou lagoons, no clear seasonality was apparent in the average Si concentrations. The Si:NO_3^- ratios ranged between 2:1 and 5,691:1, and the Si/PO_4^{3-} ratios ranged between 16:1 and 1,800:1, well above the Redfield ratio for the average phytoplankton composition (1:16 and 1:1, respectively).

At a given salinity, Si concentrations in the Grand-Lahou lagoon were generally higher than in the Ebrié lagoon in June, September, and March (Fig. 8). In March, September, and December, Si concentrations were higher in the eastern side of the Ebrié lagoon than in the western side confirming the different influences of freshwater inputs from the Comoé and Agnéby rivers highlighted above from TA variations (Fig. 6).

During the high dry season (March) and the low dry season (September), the average TSM values were very significantly to highly significantly higher in the Ebrié lagoon (Fig. 7) than in the Comoé river and very significantly to highly significantly higher in the Aby lagoon (Fig. 7) than in the Bia river. In the five lagoons, average TSM values were not significantly different or in some cases significantly lower during the high rainy season

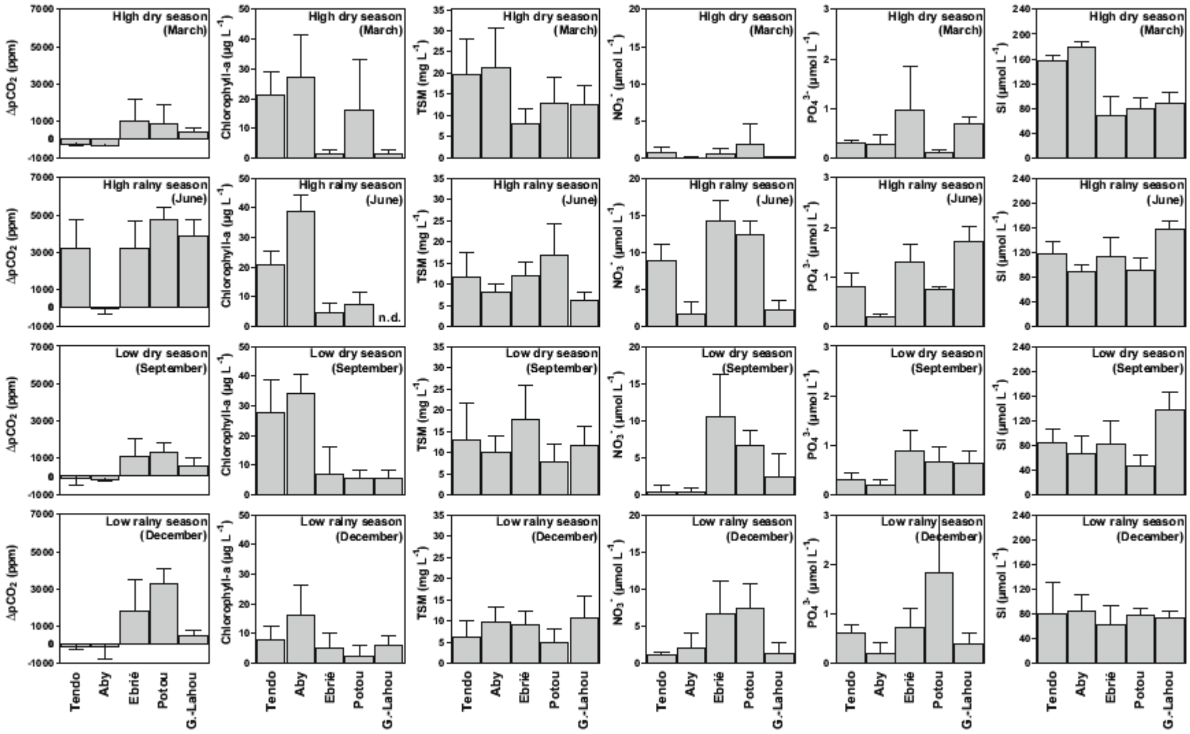


Fig. 7 Seasonal variations of average ΔpCO_2 (ppm), chlorophyll-a concentration (µg L^{-1}), TSM (mg L^{-1}), NO_3^- (µmol L^{-1}), PO_4^{3-} (µmol L^{-1}), and Si (µmol L^{-1}) in the Tendo (n=8), Aby (n=11), Ebrié (n=23), Potou (n=6), and Grand-Lahou (n=10) lagoons, during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December). *Error bars* correspond to standard deviation on the mean. *n.d.* no data, *G.-Lahou* Grand-Lahou

(June) than during the high dry season (March). This suggests that spatial and temporal variations of TSM in the lagoons were unrelated to riverine inputs of TSM. The TSM content in the lagoons was then related to sediment resuspension and coastal erosion. The comparison between the five lagoons of average TSM (Fig. 7) or as a function of salinity (Fig. 9) does not show any systematic patterns.

Whatever the season, the Aby lagoon was characterized by significantly to highly significantly higher average chlorophyll-a concentrations compared to the Ebrié, Potou, and Grand-Lahou lagoons (Fig. 7); this was also the case when chlorophyll-a concentrations in these lagoons are compared at similar salinities (Fig. 9). The average chlorophyll-a values in the Tendo lagoon were highly significantly higher than in the Ebrié and Grand-Lahou lagoons during all seasons, except during the low rainy season (December). The average chlorophyll-a values in the Tendo lagoon were also highly significantly higher than in the Potou lagoon during the high rainy season (June) and the low dry season (September).

The high chlorophyll-a concentrations in the Aby and Tendo seemed to be related to local production in the lagoons, rather than phytoplankton inputs from the rivers, since chlorophyll-a concentrations were four- to 44-fold higher according to the season in the Aby lagoon than in the Bia river and seven to 26-fold higher according to the season in the Tendo lagoon than in the Tanoé river. These two lagoons are permanently stratified (Fig. 3) unlike the other lagoons, and this probably enhances light availability for phytoplankton and leads to a higher primary production. The enhancement of light availability is probably related to a shallower mixed layer (~2 m deep; Fig. 3) than the other lagoons, since average TSM levels were similar for a given season in all five lagoons (Fig. 7). This is also consistent with the fact that in the Tendo and Aby lagoons, average NO_3^- values were very significantly to highly significantly lower (Figs. 7 and 8) than in the in the Ebrié and Potou lagoons, whatever the season, except in March when strong NO_3^- depletion was apparent in most of the lagoons (Figs. 7 and 8). Also, in the Tendo and Aby lagoons, average ΔpCO_2 were very significantly to highly significantly lower than the other three lagoons (Figs. 7 and 9), whatever the season, except during the high rainy season (June) when strong river runoff led to high pCO_2 values in the Tendo

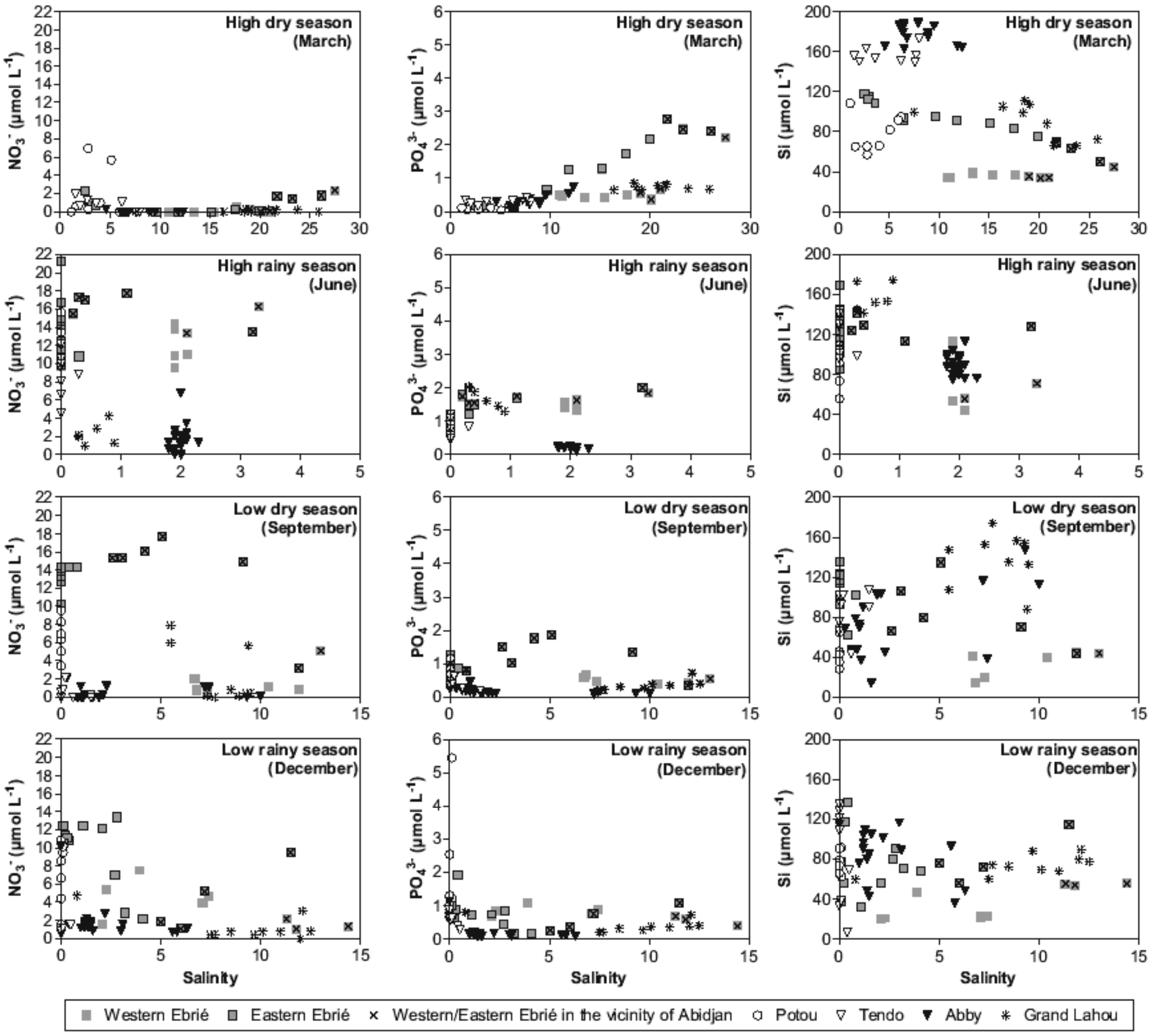


Fig. 8 NO_3^- (μmol L^{-1}), PO_4^{3-} (μmol L^{-1}), and Si (μmol L^{-1}) as a function of salinity in the Ebrié, Potou, Tendo, Aby, and Grand-Lahou lagoons during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December). Note that the *x*-axis scale is variable from one season to another

lagoon. This is due to the fact that in the permanently stratified Tendo and Aby lagoons, DIC and inorganic nutrient uptake by phytoplankton in the mixed layer is strongly decoupled from DIC and inorganic nutrient remineralization below the pycnocline, leading to strong vertical gradients of these quantities (Fig. 3). There was no clear seasonality in the chlorophyll-a concentration in the five lagoons. No clear difference in chlorophyll-a concentration was apparent between the eastern and western Ebrié lagoon, except in September when higher values were observed in the western side than in the eastern side.

DIC Dynamics in the Five Lagoons

In the Tendo, Ebrié, Potou, and Grand-Lahou lagoons, the average ΔpCO_2 values were very significantly to highly significantly higher during the high rainy season (June) than the other seasons (Fig. 7), due to strong inputs from the rivers that were oversaturated throughout the year (Fig. 4). The Ebrié, Potou, and Grand-Lahou lagoons were oversaturated in CO_2 whatever the season, as observed in the oligohaline and mesohaline regions of macrotidal estuaries worldwide (Frankignoulle et al. 1998; Abril and

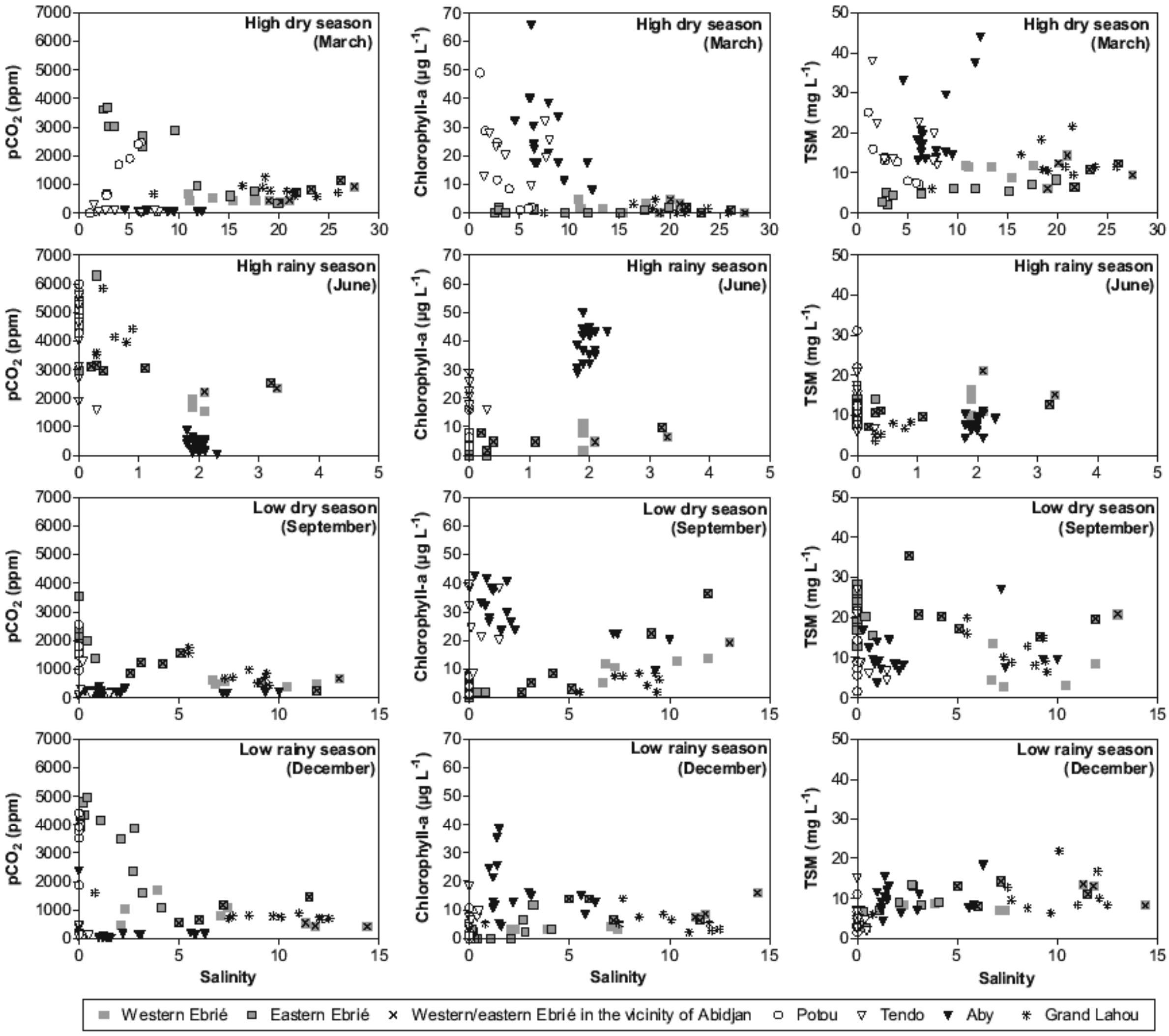


Fig. 9 pCO_2 (ppm), TSM (mg L^{-1}), and chlorophyll-a (µg L^{-1}) as a function of salinity in the Ebrié, Potou, Tendo, Aby, and Grand-Lahou lagoons during the high dry season (March), the high rainy season (June), the low dry season (September), and the low rainy season (December). Note that the *x*-axis scale is variable from one season to another

Borges 2004), while the Tendo and Aby lagoons were undersaturated in CO_2 through the year (except for the Tendo during the high rainy season (June) due the inputs from the Tanoé river).

The Aby lagoon is connected to the sea by a very shallow channel (<1 m) while the Grand-Lahou and the Ebrié lagoons are connected to the sea by much deeper channels that are used for navigation. This implies that wave and tidal action from the ocean do not propagate as intensely in the Aby lagoon system than in the Ebrié and Grand-Lahou lagoon systems, leading to a strong and permanent haline stratification (Fig. 3), resulting in anoxic conditions in bottom waters (Chantraine 1980). The freshwater residence time in the Aby lagoon is probably higher compared to the Ebrié and Grand-Lahou lagoons, due to the much shallower connection to the sea. The combination of permanent stratification and long freshwater residence time promotes the export from the mixed layer across the pycnocline of organic matter that is degraded in the bottom waters leading to an increase of DIC, pCO_2, inorganic nutrients, and the decrease of pH (Fig. 3). At the base of pycnocline (3–4 m), a maximum of DIC, pCO_2, and inorganic nutrients suggests an enhanced organic matter degradation due to the accumulation of organic matter sedimenting from the surface, as indicated by the presence of chlorophyll-a at these depths in the Tendo lagoon

(Fig. 3). The strong permanent haline stratification in the Aby lagoon probably also promotes light availability throughout the year when compared to the other seasonally stratified lagoons. This could lead to higher rates of primary production as suggested by the higher chlorophyll-a concentrations and lower inorganic nutrients in the Aby and Tendo lagoons when compared to the other three lagoons. This is in agreement with measurements of primary production based on O_2 incubations reported by Chantraine (1980) that yield annual averages of 3.8 g O_2 m^{-2} day^{-1} in the Tendo lagoon and 6.3 g O_2 m^{-2} day^{-1} in the Aby lagoon, well above the annual average of 2.5 g O_2 m^{-2} day^{-1} in the Ebrié lagoon (in the area we sampled). The combination of higher primary production and efficient export of organic matter across the pycnocline in the Aby and Tendo lagoons can explain why they were undersaturated in CO_2 throughout the year (except during the high rainy season (March) in the Tendo lagoon due to strong river inputs) unlike the other lagoons.

Values of pCO_2 in the Grand-Lahou lagoon and the eastern and western Ebrié lagoons were relatively similar whatever the season (Fig. 9). While evidence for the impact of the Abidjan population on the water quality was found for inorganic nutrients, this did not seem to be the case for pCO_2.

Air–Water CO_2 Fluxes in the Three Rivers and Five Lagoons

The average values of *k* and *F* obtained in the three rivers and the five lagoons are given per season and integrated on an annual basis in Table 3. The *u* and *k* values were generally higher in the wider Comoé river than in the narrower Bia and Tanoé rivers. The unregulated Tanoé and Comoé rivers were characterized by higher annual *F* values (137 and 170 mmol C m^{-2} day^{-1}, respectively) than the Bia river (49 mmol C m^{-2} day^{-1}) where the freshwater discharge is regulated by the Ayamé dam. Annual *F* values in the Comoé, Bia, and Tanoé rivers (ranging from 49 to 170 mmol C m^{-2} day^{-1}) are within the range reported by Cole and Caraco (2001) for worldwide rivers (20 to 1,026 mmol C m^{-2} day^{-1}) and for tropical rivers (60 to 1,026 mmol C m^{-2} day^{-1}).

The *F* values in the five lagoons showed strong seasonal variability in agreement with the seasonal changes of ΔpCO_2 (Table 3). The Ebrié, Potou, and Grand-Lahou lagoons were net sources of CO_2 to the atmosphere, since they were oversaturated in CO_2 throughout the year, and the annual *F* values (range from 51 to 101 mmol C m^{-2} day^{-1}) are consistent with those reported for macrotidal estuaries worldwide (range from 14 to 202 mmol C m^{-2} day^{-1}) and higher than those reported so far at subtropical and tropical latitudes (range from 14 to 39 mmol C m^{-2} day^{-1}; Frankignoulle et al. 1998; Abril and Borges 2004; Borges

Table 3 Seasonal variations of the mean (±standard deviation) of wind speed (u in m s^{-1}), gas transfer velocity (k in cm h^{-1}) and air–water CO_2 flux (F in mmol C m^{-2} day^{-1}) obtained in the rivers (Bia, Tanoé, and Comoé) and lagoons (Tendo, Aby, Ebrié, Potou, and Grand-Lahou)

		High dry season (March)			High rainy season (June)			Low dry season (September)			Low rainy season (December)			Annual F
		u	*k*	F	*u*	*k*	F	*u*	*k*	F	*u*	*k*	F	
Rivers	Bia	1.7±0.8	2.7±0.7	58.7±31.8	1.0±1.1	2.3±0.8	48.5±17.3	1.2±1.8	2.7±2.2	45.5±33.7	1.2±1.3	2.4±1.0	40.0±18.1	49.2±24.3
	Tanoé	1.5±2.1	2.8±1.9	233.1±141.6	1.2±1.5	2.5±1.4	119.3±79.4	1.6±1.4	2.8±1.4	72.7±44.3	0.7±0.7	2.0±0.4	73.5±16.9	137.4±97.1
	Comoé	4.3±1.2	6.0±2.3	311.4±88.7	2.4±1.3	3.5±1.2	148.1±71.4	3.5±1.8	5.1±2.5	73.7±37.7	0.7±0.6	2.0±0.4	73.1±16.4	170.4±112.8
Lagoons	Tendo	4.8±2.0	7.7±4.6	−17.7±12.6	1.8±1.1	2.8±0.8	75.5±29.3	5.3±0.7	7.8±1.6	−4.9±29.1	2.5±1.4	3.6±1.3	−3.0±4.9	19.3±45.0
	Aby	4.3±2.7	7.3±4.6	−20.0±13.2	3.7±2.6	6.4±4.8	1.2±16.4	4.7±1.7	7.3±4.0	−11.3±8.0	1.2±1.5	2.5±1.5	−4.1±12.9	−7.4±15.4
	Ebrié	4.5±2.1	7.7±5.7	56.4±59.8	2.8±2.0	4.3±2.6	109.4±61.3	4.3±2.4	7.2±4.9	61.9±63.7	2.1±1.2	3.1±1.1	48.0±47.0	72.9±62.3
	Potou	3.7±0.9	4.9±1.6	40.4±54.4	2.4±2.4	4.0±2.9	186.2±155.6	2.0±1.6	3.3±1.9	45.6±46.7	1.5±1.3	2.6±1.0	82.7±45.4	100.7±95.5
	Grand-Lahou	3.1±1.5	4.4±2.1	18.1±15.3	2.1±1.1	3.1±1.1	114.1±51.2	4.8±1.3	7.2±2.6	28.4±15.0	2.0±1.3	3.1±1.2	13.2 ±7.6	50.7±53.4

The annual *F* values (in mmol C m^{-2} day^{-1}) were integrated annually based on the average duration of the seasons (90 days for high dry season, 122 days for the high rainy season, 61 days for the low dry season, and 92 days for the low rainy season)

2005; Borges et al. 2005, 2006; Chen and Borges 2008). The Aby lagoon acted as a sink of atmospheric CO_2 (−7 mmol C m^{-2} day^{-1}) on an annual basis since undersaturation of CO_2 was observed throughout the year. The Tendo lagoon could be a net source of CO_2 to the atmosphere on an annual basis, although the annual efflux of CO_2 (19 mmol C m^{-2} day^{-1}) is driven by a large efflux during the high rainy season (June) of 76 mmol C m^{-2} day^{-1}, while the flux was negative the rest of the year (range from −3 to −18 mmol C m^{-2} day^{-1}).

The surface area weighted annual CO_2 flux in the five lagoons yields a net CO_2 emission to the atmosphere at a rate of 44 mmol C m^{-2} day^{-1}. This value is lower than the average values reported in other near-shore coastal ecosystems such as macrotidal estuaries (118 mmol C m^{-2} day^{-1}), mangrove surrounding waters (51 mmol C m^{-2} day^{-1}), and salt marsh surrounding waters (64 mmol C m^{-2} day^{-1}) compiled by Borges (2005).

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6 Seasonal variability of methane in the rivers and lagoons of Ivory Coast (West Africa)

Foreword

The previous chapter documented the seasonal and spatial variability of CO_2 fluxes in the lagoons and rivers from Ivory Coast. Fluxes of CH_4 (another greenhouse) in coastal and continental aquatic environments are generally significant. We show that although the two permanently stratified lagoons were a sink for atmospheric CO_2 (unlike the other 3 seasonally stratified lagoons that were sources of CO_2 to the atmosphere), they were stronger sources of CH_4 to the atmosphere (than the other 3 seasonally stratified lagoons that were lower sources of CH4 to the atmosphere).

This chapter is submitted for publication (Koné, Abril, Delille & Borges. Seasonal variability of methane in the rivers and lagoons of Ivory Coast (West Africa)).

Abstract

We report a data-set of dissolved methane (CH_4) in three rivers (Bia, Tanoé and Comoé) and five lagoons (Tendo, Aby, Ebrié, Potou and Grand-Lahou) of Ivory Coast (West Africa), during the four main climatic seasons (high dry season, high rainy season, low dry season and low rainy season). The surface waters of the three rivers were oversaturated in CH_4 with respect to atmospheric equilibrium (2216% to 38619%), and the seasonal variability of CH_4 seemed to be largely controlled by dilution during the flooding period. The strong correlation of CH_4 concentrations with the partial pressure of CO_2 (pCO_2) and dissolved silicate (Si) confirm the dominance of a continental carbon source (soils) for both CO_2 and CH_4 in these rivers. Diffusive air-water CH_4 fluxes ranged between 21 $\mu mol\ m^{-2}\ d^{-1}$ and 1379 $\mu mol\ m^{-2}\ d^{-1}$, and annual integrated values were 157±84 $\mu mol\ m^{-2}\ d^{-1}$, 267±259 $\mu mol\ m^{-2}\ d^{-1}$and 287±314 $\mu mol\ m^{-2}\ d^{-1}$ in the Bia, Comoé and Tanoé rivers, respectively. In the five lagoons, the surface waters were also oversaturated in CH_4 (ranging from 1574% to 51724%). Diffusive air-water CH_4 fluxes ranged between 18 $\mu mol\ m^{-2}\ d^{-1}$ and 3428 $\mu mol\ m^{-2}\ d^{-1}$, and annual integrated values were 84±48 $\mu mol\ m^{-2}\ d^{-1}$, 205±162 $\mu mol\ m^{-2}\ d^{-1}$, 238±235 $\mu mol\ m^{-2}\ d^{-1}$, 276±312 $\mu mol\ m^{-2}\ d^{-1}$ and 505±740 $\mu mol\ m^{-2}\ d^{-1}$ in the Grand-Lahou, Potou, Ebrié, Tendo and Aby lagoons, respectively. The largest CH_4 over-saturations and diffusive air-water CH_4 fluxes were observed in the Tendo and Aby lagoons that are permanently stratified systems (unlike the other 3 lagoons), leading to anoxic bottom waters favorable for a large CH_4 production. In addition, these two stratified lagoons showed low pCO_2 values due to high primary production, which suggests an efficient transfer of organic matter across the pycnocline. As a result, the stratified Tendo and Aby lagoons were respectively, a low source of CO_2 to the atmosphere and a sink of atmospheric CO_2 while the other 3 well-mixed lagoons were strong sources of CO_2 to the atmosphere but lower sources of CH_4 to the atmosphere.

6.1 Introduction

Methane (CH_4) is an atmospheric trace gas that contributes significantly to the anthropogenic enhancement of the greenhouse effect (~14%; Forster et al. 2007). The CH_4 atmospheric concentration has steadily increased since industrial revolution (~0.7 ppm) and has stabilized at ~1.8 ppm from 1999 to 2005 (Forster et al. 2007). An increase in the atmospheric growth of CH_4 during years 2006 and 2007 has been recently reported (NOAA News 2008), indicating that the sources and sinks of atmospheric CH_4 are dynamic and evolving.

Among the 500-580 $TgCH_4\ yr^{-1}$ emitted from the Earth surface to the atmosphere during the last 3 decades, nearly one half originated from wetlands, in majority from natural wetlands (145-230 $TgCH_4\ yr^{-1}$), but also artificial wetlands like rice paddies (30-110 $TgCH_4\ yr^{-1}$) and hydroelectric reservoirs (70 $TgCH_4\ yr^{-1}$) (Cicerone and Oremland 1988; St. Louis et al. 2000; Wuebbles and Hayhoe 2002; Mikaloff Fletcher et al. 2004, Denman et al. 2007; Khalil et al. 2007). Recently, lakes have also been indentified as a potentially significant additional source of CH_4 (8-48 $TgCH_4\ yr^{-1}$; Bastviken et al. 2004). The open ocean is a low source of CH_4 estimated at 4-15 $TgCH_4\ yr^{-1}$ (Wuebbles and Hayhoe 2002; Houweling et al. 2000). In contrast to the open ocean, the coastal ocean could significantly contribute to CH_4 sources. Indeed, at European scale alone, Bange (2006) evaluated the source of CH_4 from coastal waters to 0.75 $TgCH_4\ yr^{-1}$, among which 0.28 $TgCH_4\ yr^{-1}$ from continental shelves and 0.47 $TgCH_4\ yr^{-1}$ from estuarine environments. This coastal European source represents between 5% and 19% of the CH_4 source from the global open ocean. The global source of CH_4 from coastal environments could be severely under-estimated due to lack of data to adequately quantify estuarine CH_4 emissions and geological sources (Bange 2006).

Among the coastal environments, estuaries and lagoons are characterized by much higher CH_4 over-saturations with respect to atmospheric equilibrium (3643±2814% at European scale, Bange 2006) compared to continental shelves (224±142% at European scale, Bange 2006). The CH_4 oversaturation in estuarine waters is the result of a complex combination of methane sources, sinks and transport. In estuarine channels, *in situ* CH_4 production is generally low because oxic and suboxic respiration dominate (Abril and Borges 2004). Consequently, CH_4 in estuarine waters originates from inputs from two major sources: (1) rivers, which receive CH_4 from soils, groundwater, wetlands and floodplains on the watershed (De Angelis and Lilley 1987; Richey et al. 1988) and (2) tidal wetlands and mud flats, which are generally vegetalised and enriched in organic matter to support methanogenesis (Bartlett et al. 1987; Chanton et al. 1989; Kelley et al. 1995; Middelburg et al. 2002; Abril and Borges 2004). Major sinks of CH_4 in estuarine channels are the export to the adjacent coastal zone that dominates in the case of estuaries with a high freshwater discharge and a short residence time (Scranton and McShane 1991), the emission to the atmosphere and the bacterial oxidation in waters and sediments. The emission of CH_4 to the atmosphere usually dominates bacterial oxidation by a factor of 1 to 20 (De Angelis and Scranton 1993; Lilley et al. 1996; Abril and Iversen 2002; Abril and Borges 2004). In addition methanotrophic activity in estuaries is strongly inhibited by high salinity (Scranton and McShane 1991; De Angelis and Scranton 1993), but is enhanced by high turbidity (Abril et al. 2007). For that reason, methane oxidation is generally confined to the entrance of estuaries, where salinity is low and turbidity high, and where CH_4 concentrations are also often highest (Middelburg et al. 2002; Abril et al. 2007).

Lagoons are among the most common near-shore coastal environments occupying 13% of the World's coastline (Barnes 1990). At the interface between terrestrial and marine environments, lagoons are subject to both continental and marine influences (Castel et al. 1996). Lagoons usually act as net material sinks, although mature systems can serve as a source of organic material to the adjacent ocean. The continental inputs in the lagoons are mainly characterized by river water and sometimes, by ground water or rain water that drains the surrounding soils. This leads to the input of large amounts of particulate material in the form of clay particles and organic detritus but also dissolved material (dissolved organic carbon and nutrients) arising from human activity in the vicinity of the lagoons (fertilizers, domestic and industrial effluents, …). Most of these materials are deposited and concentrate in lagoons (Castel et al. 1996) where they can fuel intense mineralization (Sorokin et al. 1996) leading to the efflux of CO_2 to the atmosphere (Koné et al. 2008). A few studies have addressed CH_4 efflux from shallow or/and intertidal lagoon sediments to the atmosphere (Purvaja and Ramesh 2001; Verma et al. 2002; Hirota et al. 2007), but to our best knowledge, no studies have previously addressed the dynamics of CH_4 in surface waters of lagoons, and related air-water CH_4 fluxes.

In the present work, we report a dataset of CH_4 obtained in five equatorial lagoons (Grand-Lahou, Ebrié, Potou, Aby, and Tendo) in Ivory Coast (West Africa) and three rivers (Comoé, Bia and Tanoé) flowing into these lagoons (**Figure 6.1**), during the four characteristic seasons (**Figure 6.2**). The 3 studied rivers are the most important in Ivory Coast in terms of freshwater discharge excepted for the Bandama river (**Table 6.1**). The five studied lagoons differ by the wide range of riparian population density, of freshwater inputs (**Table 6.1**), and of physical settings (permanent or seasonal stratification). Hence, the lagoons studied here provide a large spectrum of biogeochemical settings for CH_4 dynamics that are representative of most of the kinds of lagoons encountered in West Africa, and at tropical latitudes.

6.2 Material and methods

6.2.1 Description of study area

The climate in Ivory Coast is close to equatorial, with an annual rainfall ranging from 1500 to 1800 mm, characterized by two rainy seasons and two dry seasons (Durand and Skubich 1982). The high dry season extends from January to March, the high rainy season from early April to late July, the low dry season from August to September, and the low rainy season from October to December (**Figure 6.2**).

The rivers in Ivory Coast have two different hydrological regimes (Jallow et al. 1999). The Tanoé, the Bia, the La Mé and the Agnéby rivers have an equatorial transition regime with two flooding periods in June-July and October-November. The Comoé and Bandama rivers have a mixed regime with only one flooding period during September-October. The lithology of the drainage basin of the three rivers is different: in the Comoé it is composed of 63% plutonic acids, 26% of Precambrian basement and 11% consolidated siliciclastic rocks; in the Bia it is composed of 67% of Precambrian basement, 17% plutonic acids and 16% semi- to unconsolidated sedimentary; in the Tanoé it is exclusively composed of Precambrian basement (Dürr et al. 2005).

Lagoons are the most prominent coastal ecosystems of Ivory Coast (**Figure 6.1**) covering an area of 1200 km^2, which corresponds to ~25% the surface area of lagoons in West Africa (Binet et al. 1995). They are gathered in three systems (Grand-Lahou, Ebrié and Aby) and stretch along some 300 km of the coastline. The Grand-Lahou lagoon system is the smallest of the Ivory Coast lagoon systems (190 km^2), is divided into two lagoons (Tagba and Tadio), and receives freshwater from the Bandama river, and from the smaller Gô and Boubo rivers. The Ebrié lagoon system is the largest lagoon in West Africa (566 km^2), is divided into three lagoons (Potou, Aghien and Ebrié), and receives freshwater from the Comoé, Agnéby and La Mé rivers. The Aby lagoon system (surface 424 km^2) consists of the main Aby lagoon (hereafter Aby lagoon), the Tendo lagoon and Ehy lagoon, and receives freshwater from the

Bia and Tanoé rivers. The main physical characteristics of the Ivory Coast lagoons and rivers are given in **Table 6.1**.

The Grand-Lahou lagoon system and the Ebrié lagoon system fall under the ecotype of “restricted lagoons” while the Aby lagoon system falls under the ecotype of “chocked lagoons” based on the classification of Kjerfve (1985). Chocked lagoons are connected to the sea by a very shallow channel hence there is a relatively low propagation of marine tidal and wave energy, unlike restricted lagoons that are connected to the sea by deeper channels. This strongly modulates the physical settings of the Ivory Coast lagoons, as the Aby lagoon system is permanently stratified by a strong vertical salinity gradient (Chantraine 1980) while the Grand-Lahou and Ebrié lagoon systems are well-mixed in shallow areas and seasonally stratified in deeper areas.

The density of the riparian population is variable ranging from 3.5 inhabitants km^{-2} around the Aby lagoon system to ~100 inhabitants km^{-2} around the Ebrié lagoon system (Jallow et al. 1999). Hence, the Grand-Lahou and Aby lagoon systems are relatively pristine, while the Ebrié lagoon system is strongly polluted by domestic and industrial waste water inputs (Kouassi et al. 1995; Adingra and Arfi 1998). The waters around Abidjan are highly eutrophicated leading to frequent oxygen depletion, and massive fish kills and repelling sulphuric smells (Kouassi et al. 1995; Scheren et al. 2004), and have been included in the recent compilation of coastal “dead zones” (Diaz and Rosenberg 2008).

6.2.2 Sampling, analytical techniques and statistics

Four cruises were carried out (08 June to 07 July 2006, 06-22 September 2006, 24 November to 13 December 2006, 08-30 March 2007) to sample five lagoons (Tendo, Aby, Ebrié, Potou and Grand-Lahou) and three rivers (Tanoé, Bia and Comoé). The cruise in June-July is representative of the high rainy season, the cruise in September of the low dry season, the cruise in November-December of the low rainy season, and the cruise in March of the high dry season (**Figure 6.2**). On average for each cruise, 8 samples were obtained in the Comoé river, 8 samples in the Bia river, 8 samples in the Tanoé river, 10 samples in the Grand-Lahou lagoon, 16 samples in the Aby lagoon, 6 samples in the Potou lagoon, 23 samples in the Ebrié lagoon and 8 samples in the Tendo lagoon (**Figure 6.1**).

Sampling was carried out with a 1.7 L Niskin bottle in subsurface waters at a depth of ~30 cm and a vertical profile was carried out in March 2007 in the Aby and Tendo lagoons. Duplicate 40-mL serum bottles were sampled taking care to avoid formation of bubbles that were poisoned with $HgCl_2$ and sealed. Concentrations of CH_4 were determined by gas chromatography with flame ionization detection, after creating a 30-mL headspace with N_2, as described in Abril and Iversen (2002). Certified CH_4:N_2 mixtures at 10 and 500 ppm CH_4 were used as standards (Air Liquide). Precision was better than 5%. Dissolved methane concentration was calculated with the solubility coefficient of Yamamoto et al. (1976). Salinity and water temperature were measured *in situ* using a portable thermosalinometer (WTW Cond-340) with a precision of ±0.1 and ±0.1°C, respectively. Wind speed was measured at each sampling station with a hand-held anemometer.

Diffusive air-water fluxes of CH_4 were calculated according to:

$F= k.\Delta[CH4]$

where k is the gas transfer velocity of CH_4 and $\Delta[CH_4]$ is the air-water gradient of CH_4.

We computed k using the wind speed field measurements, and the “tracers only” parameterization given by Raymond and Cole (2001), and we used a constant atmospheric CH_4 concentration of 1.8 ppm to calculate the flux.

Average monthly rainfall (mm month^{-1}) was obtained during 2000-2006 at Adiaké station (-3.3°E 5.28°N) close to Aby lagoon, from the Direction Météorologique d’Adiaké. Average monthly freshwater discharge values during 2000-2005 measured at Bianou and Yakassé stations for Bia and Comoé rivers, respectively, (data from the Direction de l’Eau d’Abidjan). Average monthly freshwater discharge values in Tanoé river are only available for 1978, at Alanda station (from the University of New Hampshire Global Runoff Data Centre database available at http://www.grdc.sr.unh.edu/). Hence, freshwater discharge and precipitation data in **Figure 6.2** are climatologically values for indicative purposes only, and preclude us of making a direct comparison with our field data, since freshwater discharge data contemporary to our sampling of are not available.

Sample means were compared (across sampling sites in each season and across seasons within each site) statistically using a two tailed unpaired Student t test, using Prism 4.00 (GraphPad). P values are not explicitly mentioned hereafter but “significant(ly)” refers to

P<0.05, “very significant(ly)” refers to P<0.01, “highly significant(ly)” refers to P<0.001, and “not significant(ly)” refers to P>0.05 at 0.05 level.

Table 6.1: Main physical characteristics of the studied lagoons, and of the main rivers flowing into these lagoons, based on Chantraine (1980), Durand and Chantraine (1982), and Durand and Skubich (1982).

Lagoons	Area (km²)	Volume (km^3)	Mean depth (m)	Surface salinity	Rivers	Total length (km)	Drainage area (km^2)	Mean water discharge (m^3 s^{-1})
Tendo	74	0.2	2.7	0-8	Tanoé	625	16000	132
Aby	305	1.3	4.2	1-8	Bia	290	9650	59
Ebrié	524	2.6	4.8	0-35	Comoé	1160	78000	224
					Agnéby*	200	8900	27
Potou	22	0.03	2.7	0-6	La Mé*	140	4300	47
Grand-Lahou	190	0.5	2.0	0-26	Bandama*	1050	97000	298

* Not sampled

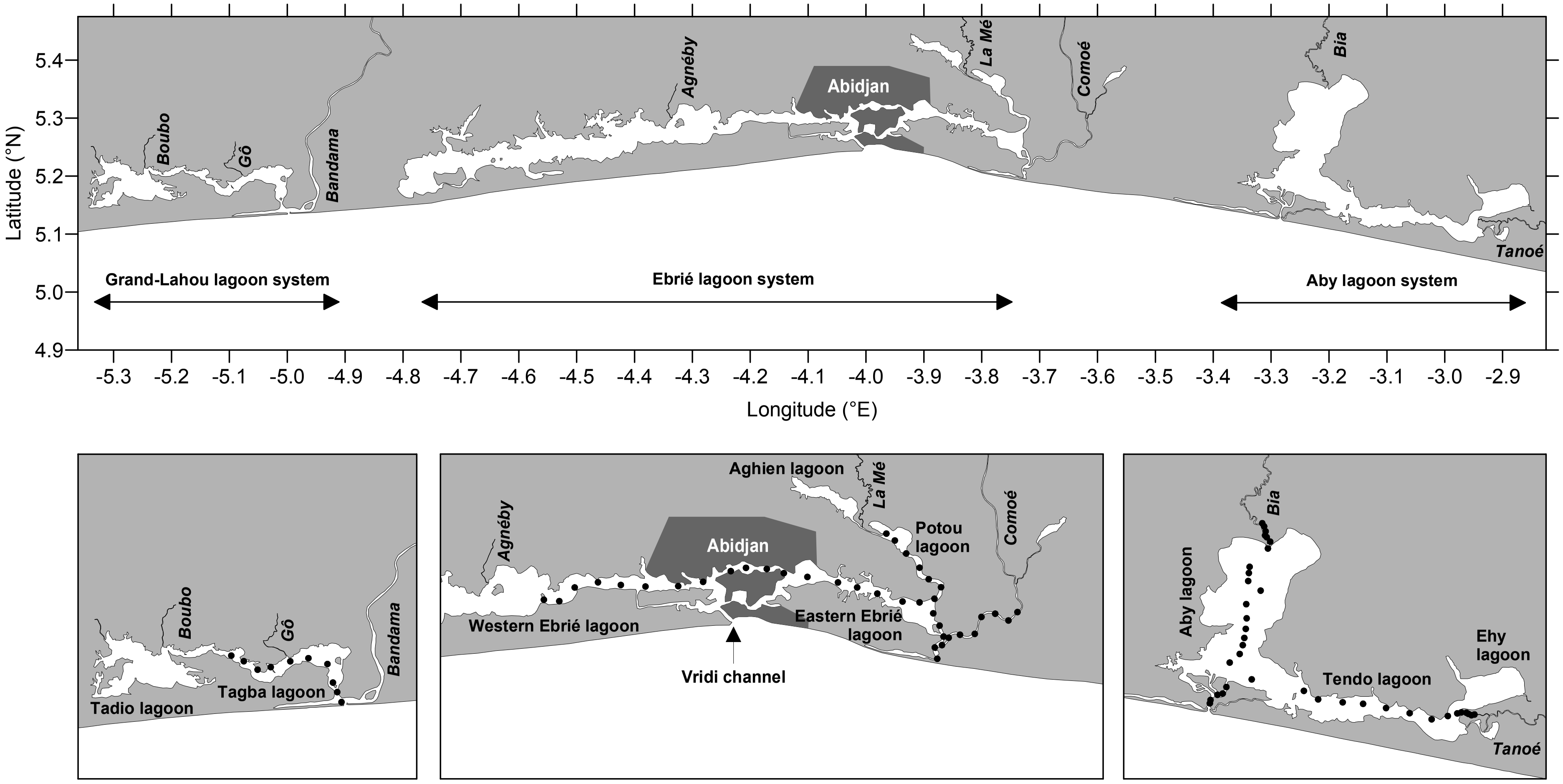

Figure 6.1: Map showing the location of lagoons and rivers in Ivory Coast, and the sampling stations (bottom panels).

6.3 Results and discussion

6.3.1 Dynamics of CH_4 in the three rivers

Figure 6.2 shows the seasonal variations of CH_4 in the Comoé, Bia and Tanoé rivers. Surface waters were always over-saturated in CH_4 with respect to equilibrium with the atmosphere, with CH_4 concentrations ranging from 48 nmol L^{-1} (i.e., 2216% of saturation) to 870 nmol L^{-1} (i.e., 38619% of saturation). These CH_4 over-saturations are within the range reported for temperate and tropical rivers ranging between ~260% and ~128420% (e.g., compilations by Upstill-Goddard et al. 2000 and by Middelburg et al. 2002). The amplitude of the seasonal variations of CH_4 was high, ~190 nmol L^{-1}, ~230 nmol L^{-1} and ~420 nmol L^{-1} in the Comoé, Bia and Tanoé rivers, respectively. An overall decrease of CH_4 concentrations variability occured in the 3 rivers from the low water period to the flooding period, suggesting that dilution due to increased freshwater discharge was a major driver of the seasonal cycle. Koné et al. (2008) analysed the behaviour of pCO_2 in these 3 rivers and concluded that it was mainly derived from drained soil CO_2, and that dissolved silicate (DSi) was derived from rock weathering. The seasonal cycles of these 2 quantities were strongly controlled by dilution during the flooding period. Similar seasonal trends with a summer CH_4 maximum have been observed in lower temperate European rivers (Middelburg et al. 2002; Abril et al. 2007). This trend might be due on the one hand to large dilution and probably high degassing rates (Hope et al. 2001) and, on another hand, limitation of in-stream methane production at high discharge (De Angelis and Scranton, 1993; Jones and Mulholland 1998b). In the Ivorian rivers we sampled, the positive relationship between the seasonal average CH_4 concentrations and seasonal average pCO_2 and DSi (**Figure 6.3**) suggests that drainage of soil CH_4 and dilution during the flooding period are the major drivers of CH_4 in these 3 rivers, as previously reported in several rivers (e.g., Hope et al. 2001; Middelburg et al. 2002; Upstill-Goddard et al. 2000).

Jones and Mulholland (1998b) have investigated in detail the spatial variations of riverine CH_4 concentrations in some natural US temperate rivers along gradients of stream size, elevation and soil organic carbon content. They found first a CH_4 maximum in small headwater streams at highest elevation and organic soil content, they attributed to large CH_4

groundwater inputs from organic soils. In contrast, in lowland rivers, summer CH_4 concentrations increased with river size and moving downstream, due, on the contrary to higher in-stream methane production (De Angelis and Lilley 1987; Jones and Mulholland 1998b). This spatial trend is also consistent with the seasonal CH_4 maximum at low discharge in many temperate rivers (Lilley et al. 1996; Middelburg et al. 2002; Abril et al. 2007). CH_4 in rivers originates from the combination of a terrestrial source, dominating at high river discharge when concentrations are lower or similar, and an aquatic source, dominating at low discharge, when concentrations can be much higher (De Angelis and Lilley 1987; Middelburg et al. 2002). As also suggested by Middelburg et al. (2002), river size is not the only important factor to explain differences in CH_4 concentrations across different rivers. In the Ivorian rivers we have sampled, during the high dry season (March) and the high rainy season (June), the average CH_4 concentrations (**Table 6.2**) were significantly to highly significantly higher in the smaller Bia river than in the larger Comoé river, (**Table 6.1**), confirming a terrestrial methane source.

The average CH_4 concentrations in our 3 studied rivers (**Table 6.2**) are quite high compared to other small tropical rivers such as Kaneohe River (Hawaii, 33 nm L^{-1}, Sansone et al. 1999), Sepik River (Papua New Guinea, (80-130 nmol L^{-1}, Wilkniss et al. 1978), or large river mainstems as the Orinoco River (Venezuela, 160-190 nmol L^{-1}, Smith et al. 2000), and Amazon River (Brazil, 44-62 nmol L^{-1} (Richey et al. 1988) 150-210 nmol L^{-1} (Barlett et al. 1990). However, the CH_4 concentrations in our 3 studied rivers are well below the CH_4 concentrations in the Amazon floodplains where CH_4 concentrations can be as high as 100000 nmol L^{-1} (Richey et al. 1988; Barlett et al. 1990) due to strong local production fuelled by organic carbon inputs from macrophytes and flooded forest.

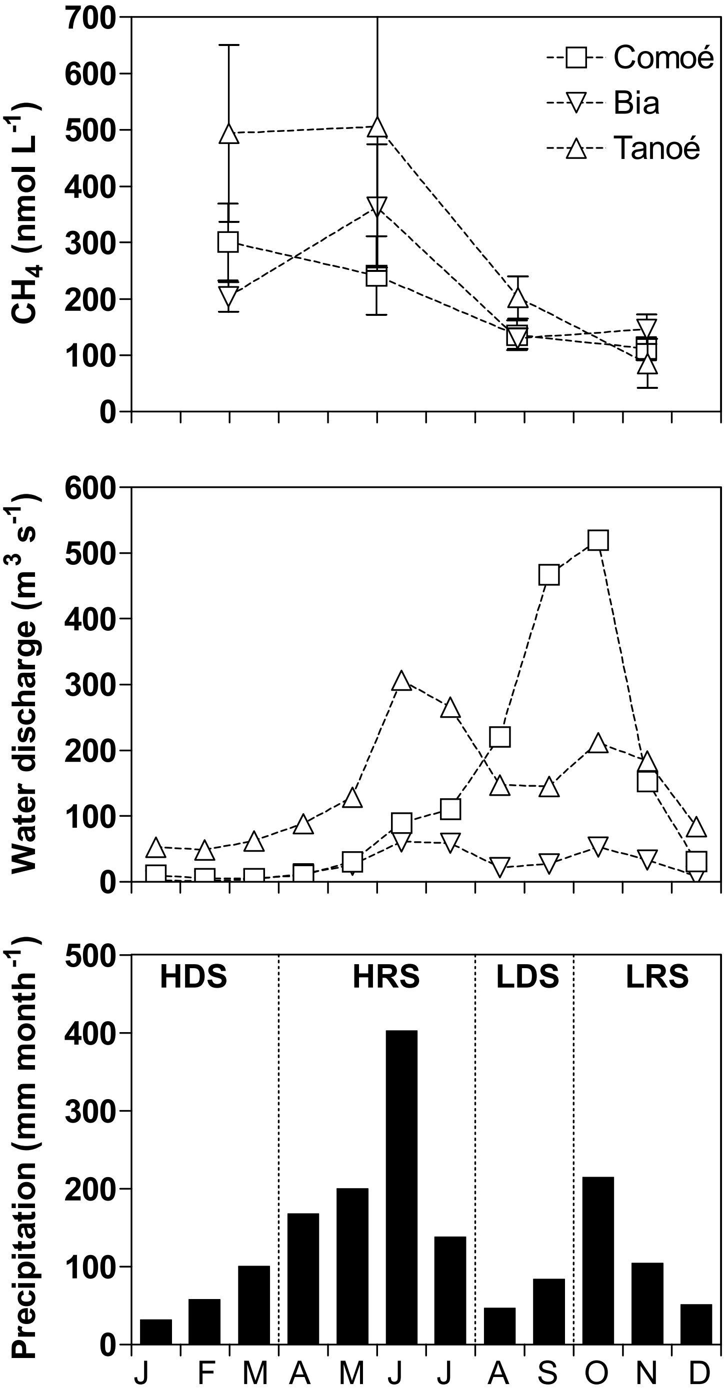

Figure 6.2: Seasonal variations of CH_4 concentration (nmol L^{-1}), average monthly freshwater discharge (m^3 s^{-1}) in the Bia (n=8), the Tanoé (n=8) and the Comoé (n=8) rivers, and average monthly precipitation (mm $month^{-1}$), during the high dry season (March), the high rainy season (June), the low dry season (September) and the low rainy season (December). Error bars correspond to standard deviation on the mean. HDS: high dry season; HRS: high rainy season; LDS: low dry season; LRS: low rainy season.

Table 6.2: Average (±standard deviation) of CH_4 concentration, percent of saturation (%CH_4), wind speed (u) and diffusive air-water CH_4 fluxes (µmol m^{-2} d^{-1}) in the Comoé, Bia and Tanoée rivers, and the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons, during the high dry season (March), high rainy season (June), low dry season (September) and low rainy season (December). Annually integrated values were computed using the average duration of the seasons (90 d for high dry season, 122 d for the high rainy season, 61 d for the low dry season, and 92 d for the low rainy season).

		Rivers			Lagoons				
		Comoé	Bia	Tanoé	Grand-Lahou	Ebrié	Potou	Aby	Tendo
High dry season (March)	CH_4	301±68	204±26	494±157	81±24	164±61	189±36	602±252	412±172
	%CH_4	14359±3268	9665±1285	23096±7180	4320±1073	8442±3089	9313±1761	30121±12919	20242±8
	u	4.3±1.2	1.7±0.8	1.5±2.1	3.1±1.5	4.6±2.1	3.7±1.1	4.9±2.4	4.8±2.0
	FCH_4	581±352	166±46	469±453	103±45	386±347	282±56	1495±958	780±217
High rainy season (June)	CH_4	241±69	362±112	506±250	86±42	180±88	252±44	162±36	109±55
	%CH_4	10922±3093	16535±5118	22527±11150	3837±1836	8315±4050	11474±2020	7644±1674	5052±25
	U	2.3±1.3	1.2±1.1	1.2±1.6	2.1±1.1	2.8±2.0	2.4±2.4	3.5±2.1	1.8±1.1
	FCH_4	225±99	232±60	402±345	72±38	220±183	289±223	249±142	81±29
Low dry season (September)	CH_4	136±26	130±18	203±37	66±8	141±85	144±32	68±21	91±60
	%CH_4	6226±1189	5800±794	8902±1630	3147±417	6490±3916	6557±1471	3073±935	4102±26
	U	3.5±1.8	1.2±1.8	1.6±1.4	4.8±1.3	4.3±2.4	2.1±1.6	4.9±1.8	5.3±0.7
	FCH_4	191±88	91±61	154±93	133±62	248±187	141±112	141±89	185±95
Low rainy season (December)	CH_4	112±21	146±26	86±43	56±18	127±61	81±41	124±45	87±17
	%CH_4	5249±951	6750±1231	3888±1936	2756±818	6139±3082	3815±1929	5925±2079	4178±80
	u	0.7±0.7	1.2±1.3	0.7±0.7	2.2±1.3	2.1±1.2	1.6±1.4	1.9±1.6	2.5±1.4
	FCH_4	67±20	102±45	46±21	50±19	111±58	61±24	111±55	98±40
Annually integrated	CH_4	206±91	238±131	345±237	74±29	156±77	175±76	246±242	176±162
	%CH_4	9547±4282	10839±5978	15655±10775	3567±1313	7488±3646	8171±3473	12013±12299	8437±80
	u	2.6±1.8	1.2±1.3	1.2±1.4	2.8±1.6	3.3±2.2	2.5±1.8	3.7±2.3	3.3±1.9
	FCH_4	267±259	157±84	287±314	84±48	238±235	205±162	505±740	276±312

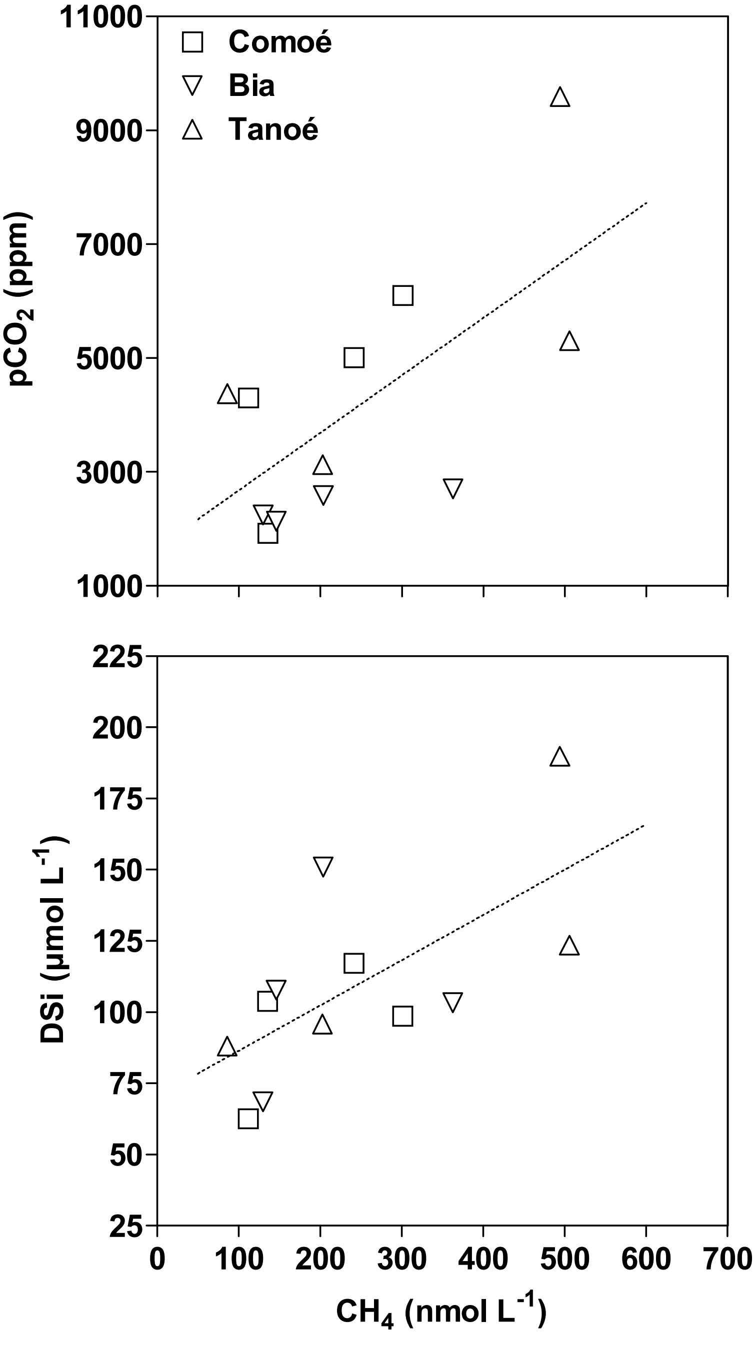

Figure 6.3: Comparison of seasonal averages of CH_4 concentrations (nmol L^{-1}) and partial pressure of CO_2 (pCO_2 in ppm) and dissolved silicate (DSi in µmol L^{-1}) in the Bia (n=8), the Tanoé (n=8) and the Comoé (n=8) rivers. The pCO_2 and DSi data were obtained at the same locations and same dates as the CH4 data (for details on analytical methods refer to Koné et al. 2008). Linear regression for pCO_2 (dotted line) yields r^2=0.43 and P=0.0201 for the DSi (dotted line) yields r^2=0.44 and P=0.0188.

6.3.2 Dynamics of CH_4 in the five lagoons

Figure 6.4 shows the seasonal and spatial variations of CH_4 in surface waters of the five sampled lagoons and associated rivers. Data are presented as a function of longitude for the Grand-Lahou, Ebrié and Tendo lagoons and as a function of latitude for the Potou and Aby lagoons. Surface waters were always over-saturated in CH_4 with respect to equilibrium with the atmosphere, with CH_4 concentrations ranging from 34 nmol L^{-1} (i.e., 1574% of saturation) to 1004 nmol L^{-1} (i.e., 51725% of saturation). These CH_4 over-saturations are within the range reported for temperate and tropical estuarine environments ranging between ~70% and ~160000% (Bange et al. 1994; Upstill-Goddard et al. 2000; Middelburg et al. 2002; Abril and Borges 2004; Bange 2006; Shalini et al. 2006).

The seasonal and spatial variations of CH_4 in the surface waters of the lagoons are the result of the balance between transport with water masses, outgassing to the atmosphere, and production and oxidation in waters and sediments of the lagoon. A net significant decrease in CH_4 concentrations at the river – lagoon transition was observed during several seasons: between the Comoé river and the Ebrié lagoon (Long -3.9°E to -3.6°E) in March, June and September; between the Bia river and the Aby Lagoon (Lat 5.3°N to 5.4°N) in June; between the Tanoé river and the Tendo lagoon (Long -3.0°E to -2.8°E) at all seasons except in December during the low rainy season (**Figure 6.4**). In contrast, during the low rainy season, CH_4 concentrations in the Comoé and Bia rivers were not significantly different from those in their respective lagoons (Ebrié and Aby) and the Tanoé river showed low CH_4 concentrations due to dilution (Figure 2). Finally, during the high dry season, the CH_4 concentrations were higher in the two stratified lagoons (Aby and Tendo), than in their respective river.

In some cases, the decrease of CH_4 between the river – lagoon transition occurred for zero or nearly zero salinity, as observed at the river – estuary transition (zero salinity region) of many estuaries like for instance the Hudson, the Columbia, the Parker, the Thames, the Gironde and the Randers Fjord (De Angelis and Scranton 1993; Sansone et al. 1999; Middelburg et al. 2002; Abril and Iversen 2002; Abril et al. 2007). This reflects the predominance of CH_4 outgassing and/or CH_4 oxidation over CH_4 production in these areas. The ratio between oxidation and outgassing is affected by many unconstrained environmental conditions such as high water depth and turbidity that favour oxidation, high salinity that limits it, and exposure to wind and tidal currents that enhances outgassing (De Angelis and

Scranton 1993; Abril and Iversen 2002; Abril et al. 2007). In some cases, an intermediate CH_4 maximum also appears in these regions were low hydrodynamics might favour local sedimentation of organic material and CH_4 production (Upstill-Goddard et al. 2000; Abril et al. 2007). In Ivory Coast, the entrance of the Tanoé river into the Tendo lagoon and the one of the Comoé river into the Ebrié lagoon are the regions of net CH_4 loss. Wind speed was always significantly higher in the lagoons than in rivers (**Table 6.2**), enhancing efflux of CH_4 to the atmosphere. Also, in the central Ebrié lagoon, tidal currents can reach ~0.9 m s^{-1} higher than near the mouth of the Comoé river of ~0.2 m s^{-1} (Brenon et al. 2004), and thus can increase gas transfer velocities (e.g. Borges et al. 2004), potentially enhance CH_4 outgassing.

The CH_4 distribution in the well mixed Grand-Lahou and Potou lagoons showed low spatial and seasonal variability, with concentrations always lower than 300 nmol L^{-1} and typical amplitudes of spatial variations of ~70 nmol L^{-1} and ~110 nmol L^{-1}, respectively (**Figure 6.4**). Such homogeneity in CH_4 distributions suggest stable conditions, with low CH_4 production and oxidation rates in these two well mixed lagoons (**Figure 6.5**).

In the Ebrié Lagoon, whatever the season, average CH_4 concentrations in the vicinity of the city of Abidjan were significantly to highly significantly higher than in western Ebrié lagoon and the adjacent eastern Ebrié lagoon (longitude < -3.8°E). This CH_4 maximum occurs at high salinity during the high dry season, at intermediate salinities during the low dry season and the low rainy season and at low salinities during the high rainy season (**Figure 6.5**). It is related to local production of CH_4 fuelled by wastewater inputs from the city of Abidjan (~3.8 million inhabitants). In addition, despite strong seasonal salinity variations, no significant seasonal differences were observed in average CH_4 concentrations in the vicinity of the city of Abidjan (**Figure 6.5**).

The highest CH_4 concentrations in surface waters were observed in the two permanently stratified Aby and Tendo lagoons. During the low rainy season (December), when CH_4 concentrations in the Bia river were lowest due to dilution (section 6.4.1), average CH_4 concentrations in the Bia river and the Aby lagoon were not significantly different. In contrast during the high dry season (March), average CH_4 concentrations in the Aby and Tendo lagoons were highly significantly higher than in the Bia and Tanoé rivers, indicating a local production of CH_4 in these stratified lagoons. The average CH_4 concentrations in the Aby and Tendo lagoons during the high dry season (March) were also very significantly to highly significantly higher than in the 3 other lagoons and than during the other 3 seasons in both the

Aby and Tendo lagoons. During the high dry season (March), CH_4 increased with salinity (**Figure 6.5**) in surface waters of the Aby (r^2=0.66, P=0.0001, n=16) and Tendo (r^2=0.84, P=0.0013, n=8) lagoons, clearly indicating a local production of CH_4. Vertical profiles in the water column of the Aby and Tendo lagoons in March (**Figure 6.6**) reveal very high CH_4 concentrations below the pycnocline, where anoxia prevails (Chantraine 1980). This anoxia favours the degradation of organic matter by methanogenesis in the anoxic hypolimnion or in the sediments and leads to the built up of high CH_4 concentrations below the pycnocline. Similar vertical CH_4 profiles have been reported in several permanently stratified marine systems and are typical for CH_4 production in the bottom layers, vertical transport across the oxicline and intense CH_4 oxidation in the surface layers (Ward et al. 1987; Fenchel et al. 1995). During the high dry season, the decrease of freshwater inputs to the Aby and Tendo lagoons leads to a shallower mixed layer (~3 m) compared to the other seasons (~4 m to ~6 m), and also to a lesser degree of stratification due to the decrease of the vertical salinity gradient (Chantraine 1980). This shallower mixed layer leads to higher surface CH_4 concentrations since diffusion of CH_4 across the pycnocline is enhanced by the lesser stratification. Moreover, the increase of salinity during the high dry season (March) (**Figures 6. 5 and 6.6**) might inhibit the activity of methanotrophic bacteria (De Angelis and Scanton 1993). Aerobic CH_4 oxidation in brackish and marine waters is known to be very sensitive to CH_4 concentrations (Sansone and Martens 1978; Scranton and McShane 1991). Furthermore, in the stratified Aby and Tendo lagoons, primary production is enhanced during high dry season compared to the other seasons due to the shallower mixed layer (enhanced light availability for a similar photic depth) and to a higher flux of inorganic nutrients from bottom waters across the pycnocline. Indeed, measurements of primary production reported by Chantraine (1980) were higher during the high dry season in the Aby (9.0 gO_2 m^{-2} d^{-1} in February 1979) and Tendo lagoons (5.4 gO_2 m^{-2} d^{-1} in February 1979) than the other seasons (5.4 gO_2 m^{-2} d^{-1} in July 1979 and 3.1 gO_2 m^{-2} d^{-1} in October 1979 in the Aby lagoon; 3.1 gO_2 m^{-2} d^{-1} in July 1979 and 2.2 gO_2 m^{-2} d^{-1} in October 1979 in the Tendo lagoon).

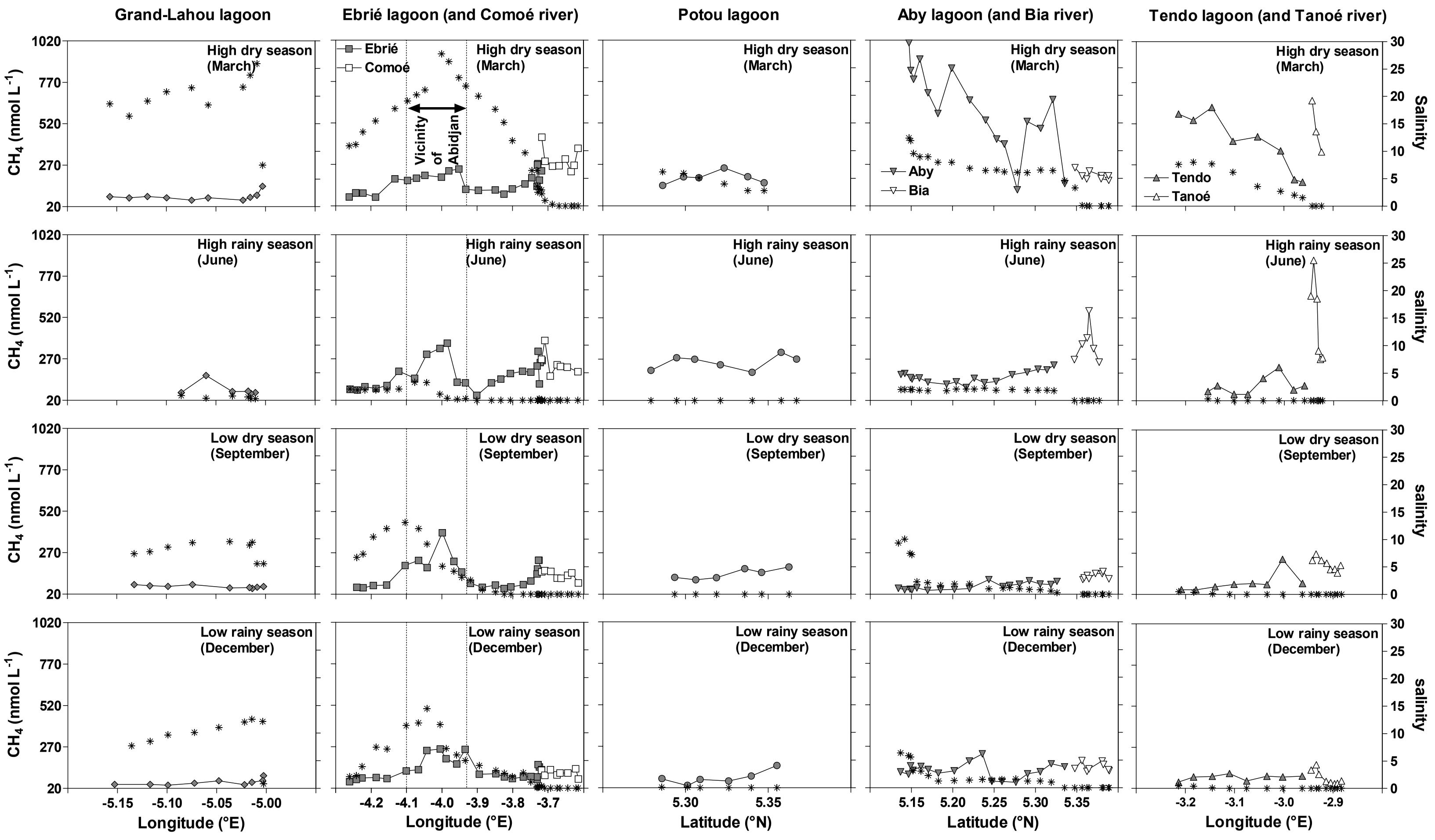

Figure 6.4: Seasonal and spatial variations of salinity (stars) and CH$_4$ concentration (other symbols, nmol L^{-1}) in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons and associated rivers (Comoé, Bia and Tanoé), during the high dry season (March), the high rainy season (June), the low dry season (September) and the low rainy season (December). In the Grand-Lahou, Ebrié and Tendo lagoons data are presented versus longitude, whereas in the Potou and Aby lagoons data are presented versus latitude.

Furthermore, the pCO_2, inorganic nutrient data and chlorophyll-a data obtained during our cruises are consistent with an enhancement of primary production during the high dry season (Koné et al. 2008). In stratified lagoons, CH_4 originates in majority from the decomposition of organic matter of phytoplanktonic origin, as the case in the Mariager Danish fjord (Fenchel et al. 1995). Part of the CH_4 produced using organic carbon exported from the surface to the anoxic bottom waters is oxidized mostly aerobically just above the pycnocline. Another part of it escapes oxidation and reaches the atmosphere. Higher CH_4 concentrations in surface waters of the Aby and Tendo lagoons reveal that CH_4 production exceeded oxidation in theses two stratified lagoons, in contrast to the well-mixed Grand-Lahou and Potou lagoons.

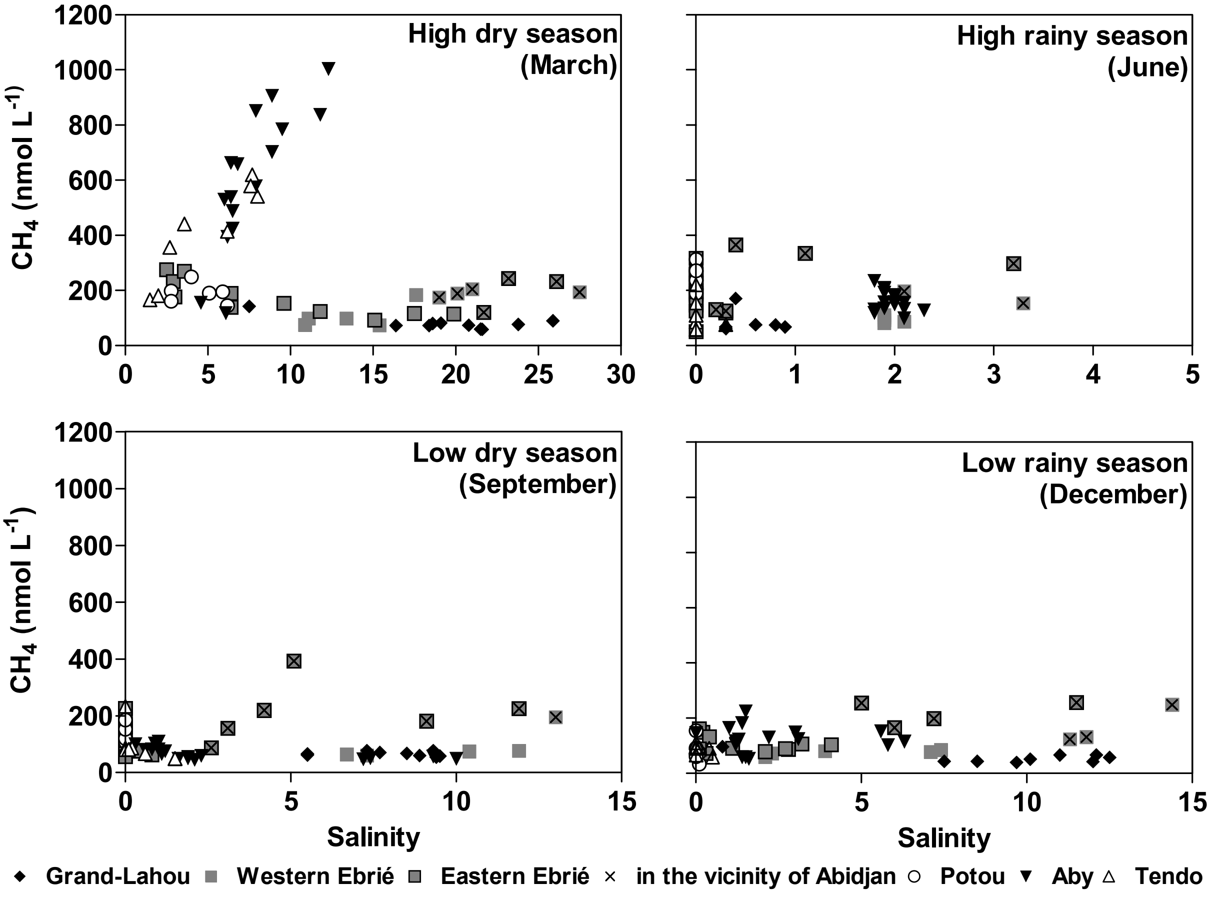

Figure 6.5: Seasonal of CH_4 concentration (nmol L^{-1}) as a function of salinity in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons and associated rivers (Comoé, Bia and Tanoé), during the high dry season (March), the high rainy season (June), the low dry season (September) and the low rainy season (December).

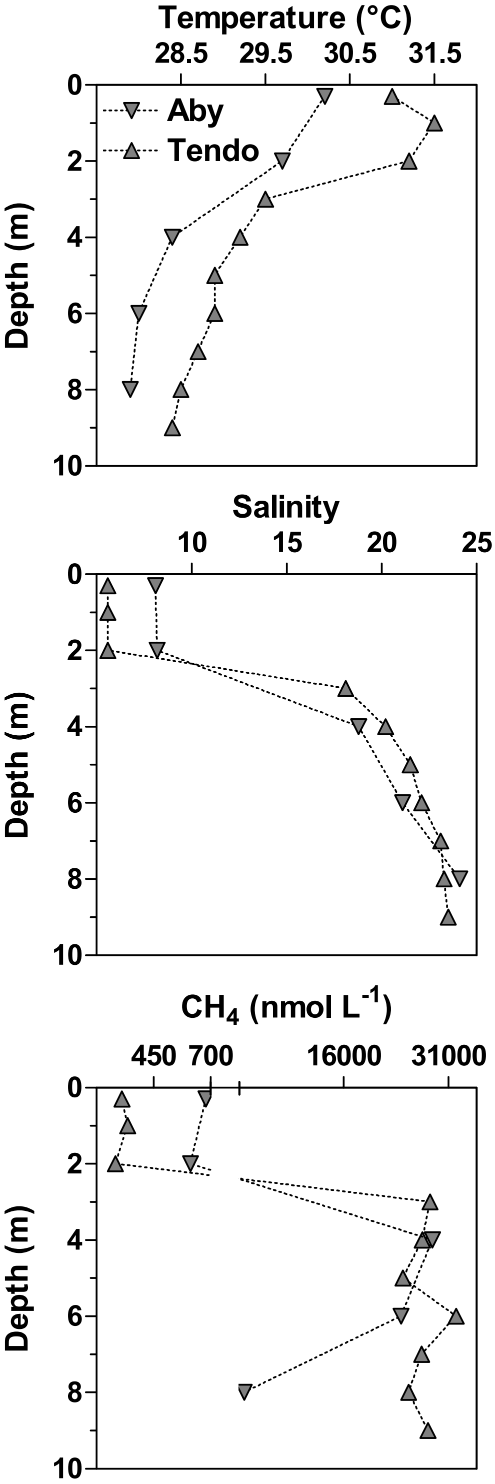

Figure 6.6: Vertical profiles of salinity, water temperature (°C) and CH_4 concentration (nmol L^{-1}) in the Aby (-3.231°E 5.228°N) and Tendo (-3.110°E 5.142°N) lagoons during the high dry season (March).

6.3.3 Diffusive air-water CH_4 fluxes in the rivers and lagoons

Table 6.2 shows the seasonal and annually integrated average of CH_4, %CH_4, wind speed (*u*) and diffusive air-water CH_4 fluxes (FCH_4) in the sampled rivers and lagoons. The Bia, Tanoé and Comoé rivers were always sources of CH_4 to the atmosphere and the diffusive air-water CH_4 flux values ranged seasonally from 21 to 1380 µmol m^{-2} d^{-1}, and annual integrated values ranged from 46 to 581 µmol m^{-2} d^{-1}. These values are within but in the lower end of the range of diffusive air-water CH_4 fluxes from temperate rivers (0 to 21562 µmol m^{-2} d^{-1}) (DeAngelis and Scranton 1993; Lilley et al. 1996; Jones and Mulholland 1998b;c; Hope et al. 2001; Abril and Iversen 2002). The emission of CH_4 from the 3 studied rivers was distinctly lower than the emission of CH_4 from the Amazon River (ranging from 4625 to 12562 µmol m^{-2} d^{-1}, Bartlett et al. 1990). This difference is due to the strong in-situ production of CH_4 in the floodplains of Amazon, while the dynamics of CH_4 in our 3 rivers seem to be mainly related to inputs from soil CH_4 and dilution (section 6.4.1).

The 5 lagoons were always a source of CH_4 to the atmosphere with diffusive air-water CH_4 fluxes ranging seasonally from 18 to 3428 µmol m^{-2} d^{-1}, the annual integrated values ranging from 50 to 1495 µmol m^{-2} d^{-1}, and an annual integrated area average for the 5 lagoons of 286 µmol m^{-2} d^{-1}. These values are within but in the higher end of the range of diffusive air-water CH_4 fluxes from tropical and temperate estuaries ranging from ~20 µmol m^{-2} d^{-1} to ~500 µmol m^{-2} d^{-1} (Bange et al. 1994; Upstill-Goddard et al. 2000; Middelburg et al. 2002; Abril and Borges 2004; Bange 2006; Shalini et al. 2006).

Figure 6.7 compares the annually integrated diffusive air-water CH_4 fluxes and the annually integrated air-water CO_2 fluxes in the 3 rivers and 5 lagoons. The diffusive air-water CH_4 fluxes are one order of magnitude lower than the air-water CO_2 fluxes. The 3 rivers were sources of CO_2 to the atmosphere, and the diffusive air-water CH_4 fluxes and air-water CO_2 fluxes are positively correlated. As discussed by Koné et al. (2008), CO_2 dynamics in the 3 rivers seem to be mainly related to inputs of soil CO_2 and dilution during the flooding period, hence the same processes that seem to control CH_4 dynamics in these rivers (section 6.4.1; **Figure 6.3**). In the 5 lagoons, the diffusive air-water CH_4 fluxes and air-water CO_2 fluxes are negatively correlated, and the Aby lagoon that is the strongest diffusive emitter of CH_4 to the atmosphere is a sink for atmospheric CO_2, unlike the other 4 lagoons that are sources of CO_2 to the atmosphere. The permanent stratification of the Aby and Tendo lagoons, enhances primary production and organic carbon export across the pycnocline leading to a low CO_2 emission to the atmosphere (Tendo lagoon) or a sink of atmospheric CO_2 (Aby lagoon), but at the same time this promotes anoxia in bottom waters that enhance methanogenesis and leads to stronger diffusive CH_4 emissions than the other lagoons that are not permanently stratified.

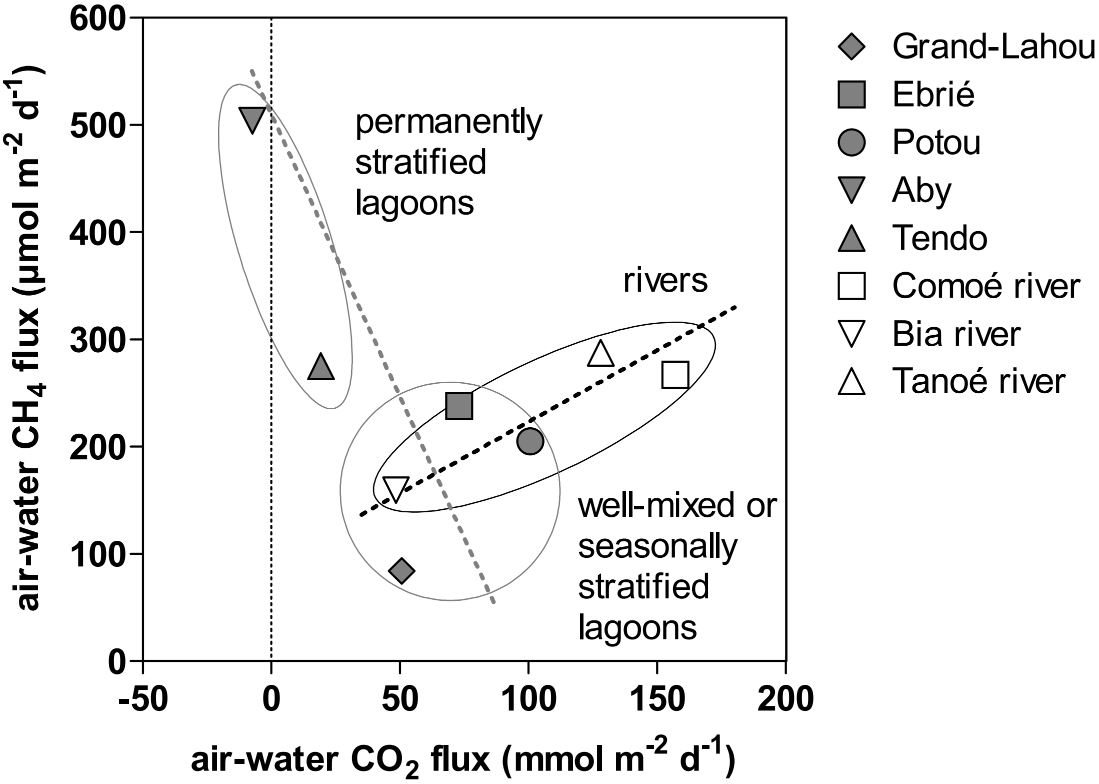

Figure 6.7: Annually integrated air-water CO_2 fluxes (mmol m^{-2} d^{-1}) versus annually integrated diffusive air-water CH_4 fluxes (µmol m^{-2} d^{-1}) in the in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons and associated rivers (Comoé, Bia and Tanoé). The air-water CO_2 fluxes were obtained at the same locations and same dates and computed using the same wind speed and k parameterization as the air-water CH_4 fluxes (for details methods refer to Koné et al. 2008). Linear regression for rivers (black dotted line) yields r^2=0.84 and P=0.2591 and for lagoons (grey dotted line) yields r^2=0.46 and P=0.2050.

6.4 Conclusions

Whatever the season, surface waters were over-saturated in CH_4 with respect to atmospheric equilibrium in the studied 3 rivers (2216% to 38619%) and the studied 5 lagoons (1574% to 51724%). The diffusive air-water CH_4 fluxes were consequently always directed to the atmosphere, ranging between 21 μmol m^{-2} d^{-1} and 1379 μmol m^{-2} d^{-1} in the rivers and between 18 μmol m^{-2} d^{-1} and 3428 μmol m^{-2} d^{-1} in the lagoons. The emission of CH_4 from the rivers and lagoons we report should be considered as minimal estimates for several reasons. The diffusive air-water CH_4 fluxes were computed with the Raymond and Cole (2001) k parameterization based on a compilation of tracer measurements that most probably provides conservative k values. In rivers and estuarine environments water currents strongly enhance water turbulence and k (Zappa et al. 2003; 2007; Borges et al. 2004), although it is probable that this not adequately quantified in k values derived from tracer methods that have a characteristic time scale (~1 d) that is incompatible with the water current characteristic time scale (~1 min). We did not quantify ebullition CH_4 fluxes, which in macrotidal systems can represent ~50% or more of the total emission of CH_4 to the atmosphere in estuarine environments (Kelley et al. 1990; Chanton et al. 1989; Shalini et al. 2006). Finally, direct emission of CH_4 from intertidal sediments to the atmosphere are strongly contribute in estuarine environments to the overall CH_4 emission at ecosystem scale ranging from ~7000 μmol m^{-2} d^{-1} in oligohaline regions to ~30 μmol m^{-2} d^{-1} in polyhaline regions (refer to review by Abril and Borges 2004). However, in the Ivory Coast lagoons, tidal flats and marches are not extended and changes in hydrostatic pressure in very shallow area is limited owing to the low tidal amplitude (< 1m; Brenon et al. 2004).

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7 Conclusions

The increase in the atmospheric concentrations of CO_2 and CH_4 is of concern since together these gases account for more than 90% of total anthropogenic greenhouse emissions to the atmosphere (respectively, 77% and 14%), and 81% of radiative climate forcing (respectively, 63% and 18%). In order to understand the causes responsible for the increase of atmospheric CO_2 and CH_4, all the sources and sinks of CO_2 and CH_4 need to be quantified and the underlying biogeochemical drivers understood.

Although tropical and subtropical coastal environments are expected to play a major role in the global budget of CO_2 and remain largely unknown for the global budget of CH_4, atmospheric CO_2 and CH_4 flux data at such latitudes are so far limited. There is also a lack of information on CO_2 and CH_4 fluxes in some coastal ecosystems, such as lagoons where the few studies of the carbon cycle have focussed solely on the ecosystem metabolism.

As outlined in chapter 1, we are still far from understanding energy flow and food web dynamics within mangrove environments and interactions with adjacent ecosystems. There are still fundamental gaps in our knowledge to fully constrain CO_2 emission from sediments and tidal DIC export. However, mineralization of mangrove-derived organic and its subsequent efflux as CO_2 to the atmosphere is expected to be significant.

Continental aquatic ecosystems (lakes and rivers) play a significant role in the global budget of CO_2 and CH_4 emissions to the atmosphere, but are currently neglected in predicting models for climate change. Atmospheric flux data in continental aquatic ecosystems are scare also at sub-tropical and tropical latitudes despite that they account for 60% of freshwater discharge from land to the oceans.

The aim of this thesis was to contribute to a better assessment of fluxes of CO_2 and CH_4 between tropical aquatic environments and the atmosphere, thereby focusing on rivers, lagoons, and waters surrounding forested mangroves. The research sites were 2 forested mangroves (Tam Giang and Kiên Vàng) in Vietnam, 3 rivers in Ivory Coast (Comoé, Bia and Tanoé) and 5 lagoons (Grand-Lahou, Ebrié, Potou, Aby and Tendo) in Ivory Coast (**Figure 7.1**). We specifically investigated: 1) the seasonal variability of CO_2 and CH_4 in these aquatic environments; 2) the assessment of the resulting gas fluxes with the atmosphere; and 3) the identification of processes controlling these emissions. The average CO_2 and CH_4 fluxes are summarised in **Table 7.1**. The main findings of this research are summarised below.

Figure 7.1: Map showing location of the study sites

7.1 Control of CO_2 dynamics in waters surrounding two mangrove forests in Vietnam

DIC and ancillary data were obtained during the dry and rainy seasons in the waters surrounding two 10 y old forested mangrove sites (Tam Giang and Kiên Vàng) located in the Nam Can and Ngoc Hien Districts (Ca Mau Province, South-West Vietnam). All parameters showed spatial heterogeneity and marked seasonal variations, but remained within the range of values previously reported for non-forested systems.

During both seasons, DIC, pCO_2, TAlk and $\%O_2$ were correlated with salinity in the mangrove creeks suggesting that a combination of lower water volume and longer residence time (leading to an increase in salinity due to evaporation) enhanced the enrichment in DIC, pCO_2 and TAlk, and an impoverishment in O_2. The low O_2 and high DIC and pCO_2 values suggest that heterotrophic processes in the water column and sediments controlled these variables. The latter processes were meaningful since the high DIC and TAlk values in the creek waters were related to some extent to the influx of pore waters. This was confirmed by the stochiometric relationship between TAlk and DIC that shows that anaerobic processes control these variables, although this approach did not allow identifying unambiguously the dominant diagenetic carbon degradation pathway.

Table 7.1: Annual air-water fluxes of CO_2 and CH_4 in the studied sites.

Sites		Campaigns		Air-water CO_2 fluxes (mmol C m^{-2} d^{-1})	Air-water CH_4 fluxes (µmol CH_4 m^{-2} d^{-1})
		Date	Number		
Mangrove creeks	Tam Giang	10-14/04/04	2	94	n.d.
		23-25/10/05			
	Kiên Vàng	10-14/04/04	2	135	n.d.
		23-25/10/05			
Lagoons	Grand-Lahou	08/06-07/07/06	4	51	84
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
	Ebrié	08/06-07/07/06	4	73	238
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
	Potou	08/06-07/07/06	4	101	205
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
	Aby	08/06-07/07/06	4	-7	505
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
	Tendo	08/06-07/07/06	4	19	276
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
Rivers	Comoé	08/06-07/07/06	4	170	267
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
	Bia	08/06-07/07/06	4	49	159
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			
	Tanoé	08/06-07/07/06	4	137	287
		06/09-22/09/06			
		24/11/-13/12/06			
		08-30/03/07			

n.d. No data

During the rainy season, dilution led to significant decreases of salinity, TAlk and DIC in both mangrove creeks and adjacent main channels. In the Kiên Vàng mangrove creeks a distinct increase of pCO_2 and decrease of $\%O_2$ were observed. The increase of TSM suggested enhanced inputs of organic matter probably from land surrounding the mangrove creeks, that could have led to higher benthic and water column heterotrophy. However, the flushing of water enriched in dissolved CO_2 originating from soil respiration and impoverished in O_2 could also have explained to some extent the patterns observed during the rainy season.

7.2 Control of CO_2 and CH_4 dynamics in 3 Ivory Coast rivers

pCO_2, CH_4 concentrations and ancillary data (salinity, chlorophyll-a, TSM and inorganic nutrients) were carried out in three rivers (Tanoé, Bia and Comoé) from Ivory Coast, during the four main seasons (high rainy season, low dry season, low rainy season, and high dry season respectively). The 3 studied rivers are the most important in Ivory Coast in terms of freshwater discharge (excepted for the Bandama).

The three rivers were oversaturated in CO_2 with respect to the atmosphere and the average pCO_2 values ranged from 1925 to 9595 ppm. The seasonal variability of pCO_2 in these rivers was due to dilution processes, as the maximal values were obtained during the low water and the minimal during high water. However, the seasonal cycle of pCO_2 was less marked in the Bia river than Comoé and Tanoé rivers, due to the presence of the Ayamé dam upstream of the sampling station in the Bia. The highest pCO_2 values obtained in the Tanoé river during the high dry season seem to be related of the presence of floating macrophytes (*Eichhornia crassipes*) due to root respiration and degradation of macrophytes organic matter.

The three rivers were also always over-saturated in CH_4 with respect to equilibrium with the atmosphere, with CH_4 concentrations ranging from 48 nmol L^{-1} (i.e., 2216% of saturation) to 870 nmol L^{-1} (i.e., 38619% of saturation). The amplitude of the seasonal variations of CH_4 in these rivers were high ~190 nmol L^{-1} , ~230 nmol L^{-1} and ~420 nmol L^{-1} in the Comoé, Bia and Tanoé rivers, respectively. An overall decrease of average CH_4 concentrations and a convergence of values were observed in the 3 rivers from the low water period to the flooding period, suggesting that dilution and/or an increasing of CH_4 outgassing due to freshwater discharge was a major driver of the seasonal cycle.

7.3 Controls of CO_2 and CH_4 dynamics in 5 Ivory Coast lagoons

pCO_2, CH_4 and ancillary data were obtained in Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons during the 4 characteristic seasons.

The Potou, Ebrié and Grand-Lahou lagoons were oversaturated in CO_2 with respect to atmospheric equilibrium during all seasons. These lagoons seemed to behave similarly to the oligohaline regions of macrotidal estuaries that typically are CO_2 sources to the atmosphere due to strong heterotrophic activity and inputs of riverine CO_2 enriched waters, with average ΔpCO_2 (ppm) ranging from 432 to 4756 ppm. In contrast, Aby and Tendo lagoons were under-saturated in CO_2 with respect to the atmosphere (except for the high rainy season in the Tendo due to strong freshwater inputs from Tanoé river) because of their strong permanent haline stratification (unlike the other lagoons) that seemed to lead to higher phytoplankton production based on observed higher chlorophyll-a concentrations and lower inorganic nutrient concentrations, and in agreement with previously published primary production measurements (Chantraine, 1980). The difference in carbon flows in the five lagoons appears to be related to their physical settings that depend on the depth of the inlet connecting to the sea (shallow in Aby lagoon versus deep in the Grand-Lahou and Ebrié lagoons).

Surface waters of the five lagoons were always over-saturated in CH_4 with respect to equilibrium with the atmosphere, with CH_4 concentrations ranging from 34 nmol L^{-1} (i.e., 1574% of saturation) to 1004 nmol L^{-1} (i.e., 51724% of saturation). Whatever the season, average CH_4 concentrations in the vicinity of the city of Abidjan were significantly to highly significantly higher than in western Ebrié lagoon and the adjacent eastern Ebrié lagoon (longitude < -3.8°E). This was related to local production of CH_4 fuelled by waste water inputs from the city of Abidjan (~3.8 million inhabitants). Seasonally, the largest CH_4 concentrations in the five lagoons were obtained in Aby and Tando lagoons during the high dry season (March). During this season, the decrease of freshwater inputs to the Aby and Tendo lagoons leads to a shallower mixed layer (~3 m) compared to the other seasons (~4 m to ~6 m), and also to a lesser degree of stratification due to the decrease of the vertical salinity gradient (Chantraine, 1980). This enhances the surface CH_4 concentrations since the shallower mixed layer will decrease the probability of the occurrence of CH_4 oxidation in the oxic layer, and also the diffusion of CH_4 across the pycnocline will be enhanced by the lesser stratification. These results suggest that, although permanently stratified systems are significant sinks of atmospheric CO_2 they could be significant sources of other greenhouse gases to the atmosphere.

7.4 Air-water CO_2 and CH_4 fluxes in the study sites

Average air-water CO_2 fluxes in the **Kiên Vàng mangrove** ranged from 32.2 to 154.7 mmol m^{-2} d^{-1} during the dry and rainy season, respectively, and in the **Tam Giang mangrove** from 141.5 and 128.5 mmol m^{-2} d^{-1} during the dry and rainy season, respectively. These flux estimates are within the range of air-water CO_2 fluxes in aquatics systems associated to other mangrove forests ranging between 13.8 and 56.7 mmol m^{-2} d^{-1} (Borges et al. 2003). Based on the air-water CO_2 fluxes computed for the Ca Mau mangrove creeks, we reevaluate the air-water CO_2 emission from mangroves to 72 mmolC m^{-2} d^{-1} that upward scaled to the most recent surface area of mangrove forests (146 10^3 km^2 in 2000; FAO, 2003) provides a CO_2 emission of 0.046 PgC yr^{-1}. This emission corresponds to about 7% of the overall emission from open oceanic waters at sub-tropical and tropical latitudes (30°N-30°S, 0.71 PgC yr^{-1}, based on Takahashi et al. (2002)) and to 24% of the overall emission of about 0.19 PgC yr^{-1} from coastal waters (including estuaries, marginal seas, coastal upwelling systems and coral reefs) at the same latitudes based on the compilation by Borges et al. (2005).

The unregulated **Tanoé and Comoé rivers** were characterized by higher annual air-water CO_2 fluxes (137 and 170 mmol C m^{-2} d^{-1}, respectively) than the **Bia river** (49 mmol C m^{-2} d^{-1}) where the freshwater discharge is regulated by the Ayamé dam. Annual air-water CO_2 fluxes in the Comoé, Bia and Tanoé rivers (ranging from 49 to 170 mmolC m^{-2} d^{-1}) are within the range reported by Cole and Caraco (2001) for worldwide rivers (20 to 1026 mmol C m^{-2} d^{-1}) and for tropical rivers (60 to 1026 mmol C m^{-2} d^{-1}). The diffusive air-water CH_4 flux values computed in these rivers ranged seasonally from 21 to 1380 µmol m^{-2} d^{-1}, and annual integrated values ranged from 46 to 581 µmol m^{-2} d^{-1}. The emission of CH_4 from our 3 rivers was distinctly lower than the emission of CH_4 from the Amazon River (ranging from 4625 to 12562 µmol m^{-2} d^{-1}, Bartlett et al. 1990). This difference is due to the strong in-situ production of CH_4 in the floodplains of Amazon, while the dynamics of CH_4 in our 3 rivers seems to be mainly related to inputs from soil CH_4 and dilution.

The **Ebrié, Potou and Grand-Lahou lagoons** were net sources of CO_2 to the atmosphere, since they were over-saturated in CO_2 throughout the year, and the annual F values (range from 51 to 101 mmol C m^{-2} d^{-1}) are consistent with those reported for macrotidal estuaries worldwide (range from 14 to 202 mmol C m^{-2} d^{-1}) and higher than those reported so far at sub-tropical and tropical latitudes (range from 14 to 39 mmol C m^{-2} d^{-1}) (Frankignoulle et al. 1998; Abril and Borges 2004; Borges 2005; Borges et al. 2005; 2006; Chen and Borges 2008). The **Aby lagoon** acted as a sink of atmospheric CO_2 (-7 mmol C m^{-2} d^{-1}) on an annual basis since under-saturation of CO_2 was observed throughout the year. However, the **Tendo lagoon** could be annually a source of CO_2 to the atmosphere, although the annual efflux of CO_2 (19 mmol C m^{-2} d^{-1}) is imposed by the large fluxes during the high rainy season (June) of 76 mmol C m^{-2} d^{-1}, while the rest of the year a sink of atmospheric CO_2 was computed ranging between -3 and -18 mmol C m^{-2} d^{-1}. The surface area weighted annual CO_2 flux in the 5 lagoons yields a net CO_2 emission to the atmosphere at a rate of 44 mmol C m^{-2} d^{-1}. This value is lower than the average values reported in other near-shore coastal ecosystems such as macro-tidal estuaries (118 mmol C m^{-2} d^{-1}), mangrove surrounding waters (51 mmol C m^{-2} d^{-1}) and salt marsh surrounding waters (64 mmol C m^{-2} d^{-1}) compiled by Borges (2005).

Air-water CH_4 fluxes computed in the 5 lagoons ranged seasonally from 18 to 3428 µmol m^{-2} d^{-1}. The annual integrated values ranging from 50 to 1495 µmol m^{-2} d^{-1}, and an annual integrated area average for the 5 lagoons of 286 µmol m^{-2} d^{-1}. These values are within but in the higher end of the range of diffusive air-water CH_4 fluxes from tropical and temperate estuaries ranging from ~20 µmol m^{-2} d^{-1} to ~500 µmol m^{-2} d^{-1} (Bange et al. 1994; Abril and Borges 2004; Bange 2006; Shalini et al. 2006).

7.5 Future work

The present thesis confirms that the waters surrounding mangrove forests are significant sources of CO_2 to the atmosphere but few data are available on dissolved inorganic carbon variability in the water column of mangrove ecosystems. Thus, more field data are needed to better constrain CO_2 fluxes in these ecosystems. Similarly, the role of organic carbon export from mangrove ecosystems to the adjacent marine systems is not fully understood. Coupling

DIC, DOC, POC measurements and isotopic analyses could help to fully understand the role of these ecosystems in the global carbon cycle.

Freshwater systems are significant sources of CO_2 and CH_4 to the atmosphere but, CO_2 and CH_4 flux estimates in these systems are scarce. Moreover, floating macrophytes that are a prominent component of tropical freshwater ecosystems can strongly modulate the air-water CO_2 fluxes. Floating macrophytes fix atmospheric CO_2, but root respiration and degradation of macrophyte organic matter lead to a net release of CO_2 in the water column. However, a large extent of these plants would physically block gas exchange across the air-water interface. Our data in the Tanoé river show that these macrophytes were important contributors to the over-saturation of CO_2 during the high dry season. Also, some of these floating macrophytes are transported to the adjacent lagoons and could play an important role in carbon dynamic in these coastal ecosystems.

The strong heterogeneity of air-water CO_2 fluxes we report in the Ivory Coast lagoons precludes us from concluding on the CO_2 sink or source of these ecosystems at global scale or regional scale. Lagoons we studied cover 25% of the total surface of lagoons in West Africa. Future work in other countries will help to full constrain CO_2 fluxes in these ecosystems. The local CH_4 emission to the atmosphere found in the vicinity of Abidjan due to waste water inputs shows the need to extend these measurements to other lagoons and bays that are impacted by human activities. Finally, we found that permanently stratified lagoons are sinks of atmospheric CO_2 but stronger diffusive CH_4 sources to the atmosphere. Further research on different stratified systems is required to verify these findings.

Our data shows that Ivory Coast rivers and lagoons display strong seasonal variability of pCO_2 and CH_4 concentrations that require a high resolution monitoring to provide unbiased air-waters fluxes estimates, that could be achieved by a bimonthly monitoring at a few select rivers and lagoons. Also numerous reservoirs (e.g., Ayamé, Kossou, Buyo, Taabo, Faé) of Ivory Coast remain unexplored in terms of C cycling and more specifically CO_2 and CH_4 dynamics.

8 References

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9 List of publications

Part of the manuscript

Koné Y.J.M. & A. V. Borges (2008). Dissolved inorganic carbon dynamics in the waters surrounding forested mangroves of the Ca Mau Province (Vietnam), Estuarine, coastal and shelf science, 77(3), 409-421. [1]

Koné Y.J.M., G. Abril, K. N. Kouadio, B. Delille & A.V. Borges (2008). Seasonal variability of carbon dioxide in the rivers and lagoons of Ivory Coast (West Africa), Estuaries and Coasts. In press. [2]

Koné Y.J.M., G. Abril, B. Delille & A.V. Borges (2008). Seasonal variability of methane in the rivers and lagoons of Ivory Coast (West Africa). Submitted. [3]

Related to this work

Kouadio K.N., D. Diomandé, A. Ouattara, **Y.J.M. Koné** & G. Gourène (2008). Taxonomic diversity and structure of benthic macroinvertebrates in Aby Lagoon (Ivory Coast, West Africa). Pakistan Journal of Biological Sciences. In press [4]

Inorganic carbon dynamics in the North Sea

Thomas, H., F. Prowe, S. van Heuven, Y. Bozec, H.J.W. de Baar, L.-S. Schiettecatte, K. Suykens, **M. Koné**, A.V. Borges, I.D. Lima & S.C. Doney (2007). Rapid decline of the CO_2 buffering capacity in the North Sea and implications for the North Atlantic Ocean. Global biogeochemical cycles, 21 (GB4001), doi:10.1029/2006GB002825. [5]

Thomas H., L.-S. Schiettecatte, K. Suykens, **Y.J.M. Koné**, E. H. Shadwick, A.E.F. Prowe, Y. Bozec, H.J.W. de Baar & A. V. Borges (2008). Enhanced ocean carbon storage from anaerobic alkalinity generation in coastal sediments. Submitted. [6]

Presentation at meetings

Borges A.V., **Y.M. Koné**, L.-S. Schiettecatte, B. Delille, M. Frankignoulle & S. Bouillon (2005). Preliminary results on the biogeochemistry in the Mekong estuary and delta (Vietnam). EGU General Assembly ,Vienna, Austria, 24-29 April. [7]

Thomas, H., F. Prowe, S. van Heuven, Y. Bozec, H.J.W. de Baar, L.-S. Schiettecatte, K. Suykens, **M. Koné**, A.V. Borges, I.D. Lima, S.C. Doney (2006). Rising CO_2 conditions and ocean acidification - a severe threat to high latitude coastal ecosystems. First IGBP–SCOR FTI Workshop on “Ocean Acidification - modern observations and past experiences”. Lamont-Doherty Earth Observatory of Columbia University, U.S.A, 28 - 30 September. [8]

Thomas H., H.J.W. de Baar, F. Prowe, S. van Heuven, Y. Bozec, L.-S. Schiettecatte, K.Suykens, **M. Koné**, A.V. Borges, I.D. Lima & S.C. Doney (2006). Temporal changes of the CO_2 system in the North Sea and the North Atlantic Ocean. Open science conference on the GHG Cycle in the Northern Hemisphere organised by CarboEurope-IP, CarboOcean and NitroEurope-IP, Sissi-Lassithi, Crete, Greece, 14-18 November. [9]

Koné Y.J.M. & A.V. Borges (2007). Dissolved inorganic carbon dynamics in the waters surrounding forested mangroves of the Ca Mau Province (Vietnam). EGU General Assembly, Vienna, Austria, 15-20 April. [10]

Koné Y.J.M., B. Delille & A.V. Borges (2007). Carbon dioxide dynamics in the tropical Ebrié lagoon (Ivory Coast). EGU General Assembly Vienna, Austria, 15-20 April. [11]

Thomas H., F. Prowe, S. van Heuven, Y. Bozec, H.J.W. de Baar, L.-S. Schiettecatte, K. Suykens, **M. Koné**, A.V. Borges, I.D. Lima & S.C. Doney (2007). Rising CO_2 conditions and ocean acidification - a severe threat to high latitude coastal ecosystems. EGU General Assembly, Vienna, Austria, 15-20 April. [12]

Thomas H., Prowe F., van Heuven S., Bozec Y., de Baar H.J.W, Schiettecatte L.-S., **Koné M.**, Suykens K. & A.V. Borges (2006). Why is pCO_2 in the North Sea rising faster than in the Atmosphere? EGU General Assembly, Vienna, Austria, 02–07 April. [13]

Koné Y. J. M., G. Gourene, G. Abril, B. Delille & A.V. Borges (2008). Seasonal variability of CO_2 fluxes in the tropical lagoons of Ivory Coast. EGU General Assembly, Vienna, Austria, 13 - 18 April. [14]

Thomas H., L.-S. Schiettecatte, K. Suykens, **Y.J. M. Koné**, F. Gazeau, Y. Bozec, H. de Baar & A.V. Borges (2008). Seasonal variability of total alkalinity in the North Sea, EGU General Assembly, Vienna, Austria, 13-18 April. [15]