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

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Abstract We report a data-set of dissolved methane (CH_4) in three rivers (Comoé, Bia and Tanoé) and five lagoons (Grand-Lahou, Ebrié, Potou, Aby and Tendo) 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 over-saturated in CH_4 with respect to atmospheric equilibrium (2221–38719%), 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 (DSi) confirm the dominance of a continental sources (from soils) for both CO_2 and CH_4 in these rivers. Diffusive air–water CH_4 fluxes ranged between 25 and 1187 μmol m^{-2} day^{-1}, and annual integrated values were 288 ± 107, 155 ± 38, and 241 ± 91 μmol m^{-2} day^{-1} in the Comoé, Bia and Tanoé rivers, respectively. In the five lagoons, surface waters were also over-saturated in CH_4 (ranging from 1496 to 51843%). Diffusive air–water CH_4 fluxes ranged between 20 and 2403 μmol m^{-2} day^{-1}, and annual integrated values were 78 ± 34, 338 ± 217, 227 ± 79, 330 ± 153 and 326 ± 181 μmol m^{-2} day^{-1} in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons, respectively. The largest CH_4 over-saturations were observed in the Tendo and Aby lagoons that are permanently stratified systems (unlike the other three 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 three well-mixed lagoons were strong sources of CO_2 to the atmosphere but less over-saturated in CH_4.

Keywords Methane · Lagoons · Rivers · Ivory Coast

Abbreviations

$\%CH_4$	Percent of CH_4 saturation
a	Coefficient of linear regression

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DSi	Dissolved silica
FCH_4	Diffusive air–water CH_4 flux
HDS	High dry season
HRS	High rainy season
k	Gas transfer velocity
k_{600}	Gas transfer velocity normalized to a Schmidt number of 600
Lat	Latitude
LDS	Low dry season
Long	Longitude
LRS	Low rainy season
n	number of measurements
NCEP	National Centers for Environmental Prediction
pCO_2	Partial pressure of CO_2
Sc	Schmidt number of CH_4
$TgCH_4$	Teragrams of CH_4
u	Wind speed
$\Delta[CH_4]$	Air–water gradient of CH_4
ΔpCO_2	Air–water gradient of pCO_2

Introduction

Methane (CH_4) is an atmospheric trace gas that contributes to ~18% of global mean radiative forcings of long-lived greenhouse gases (comprising carbon dioxide (CO_2), CH_4, nitrous oxide and halocarbons) (Forster et al. 2007). The CH_4 atmospheric concentration has steadily increased since the industrial revolution (~0.7 ppm) and 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 (Rigby et al. 2008).

Among the 500–580 $TgCH_4$ $year^{-1}$ emitted from the Earth surface to the atmosphere during the last three decades, nearly one half originated from wetlands, in majority from natural wetlands (145–230 $TgCH_4$ $year^{-1}$), but also from artificial wetlands like rice paddies (30–110 $TgCH_4$ $year^{-1}$), and hydroelectric reservoirs (70 $TgCH_4$ $year^{-1}$) (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 identified as a potentially significant additional source of CH_4 (8–48 $TgCH_4$ $year^{-1}$, Bastviken et al. 2004). The open ocean is a low source of CH_4 estimated at 4–15 $TgCH_4$ $year^{-1}$ (Houweling et al. 2000; Wuebbles and Hayhoe 2002). 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 $TgCH_4$ $year^{-1}$, among which 0.28 $TgCH_4$ $year^{-1}$ from continental shelves and 0.47 $TgCH_4$ $year^{-1}$ 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 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 sources, sinks and transport. In estuarine channels, net CH_4 inputs from the sediments to the water column and CH_4 production in the water column are generally low because oxic and suboxic respiration dominate (Abril and Borges 2004). Consequently, CH_4 in estuarine waters originates 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 vegetated 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). Majors 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; Middelburg et al. 2002), the emission to the atmosphere and the bacterial oxidation in the water column and sediment. The emission of CH_4 to the atmosphere usually dominates bacterial oxidation by a factor of 1–20 (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 salinity (Scranton and McShane 1991; De Angelis and Scranton 1993), but is enhanced by high turbidity (Abril et al. 2007). Hence, CH_4 oxidation is generally confined to the upper reaches of estuaries, where salinity is low and turbidity is 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 1980). At the interface between terrestrial and marine environments, lagoons are subject to both continental and marine influences (Castel et al. 1996). The continental inputs into lagoons are mainly from rivers, rain and ground water. This leads to the input of large amounts of particulate material in the form of clay particles and organic detritus but also of dissolved organic carbon and nutrients of natural origin or arising from human activity in the vicinity of the lagoons (fertilizers, domestic and industrial effluents, …). Most of organic carbon inputs are deposited in the lagoons (Castel et al. 1996) where they fuel intense mineralization (Sorokin et al. 1996) leading to the efflux of CO_2 to the atmosphere (Koné et al. 2009). A few studies have addressed the CH_4 efflux to the atmosphere from shallow or/and intertidal lagoon sediments (Purvaya and Ramesh 2000; 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 diffusive 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 (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 river (Table 1). The five studied lagoons differ by a wide range of riparian population density, of freshwater inputs (Table 1), and of physical settings (permanent or seasonal or no stratification). Hence, these lagoons provide a large spectrum of biogeochemical settings to investigate CH_4 dynamics, and are representative of most of the kinds of lagoons encountered in West Africa, and at tropical latitudes.

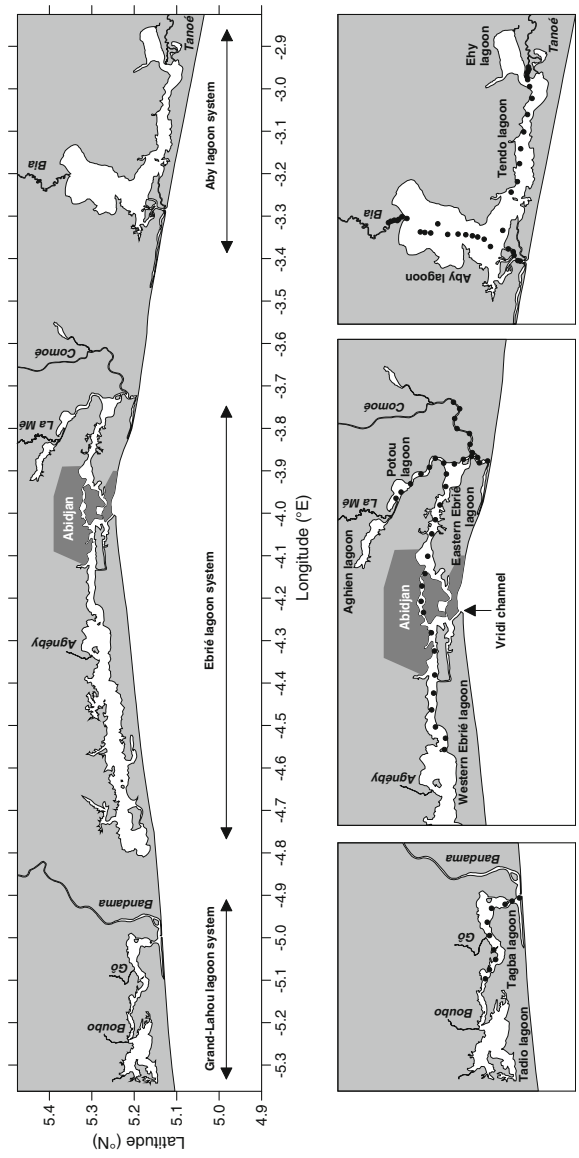

Fig. 1 Map showing the location of lagoons and rivers in Ivory Coast, and the sampling stations (*lower panels*)

Materials and methods

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

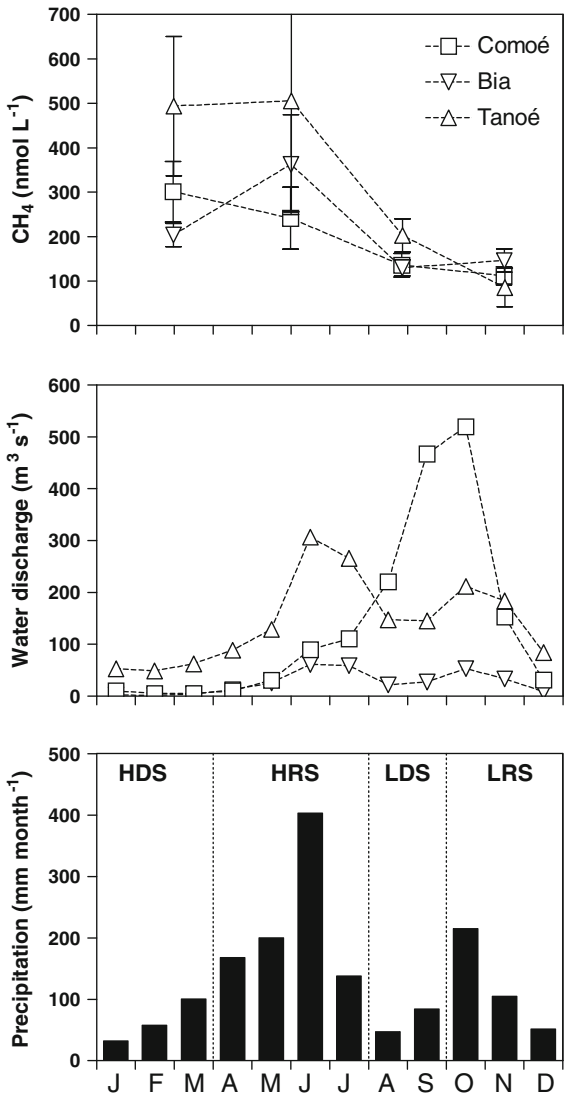

Fig. 2 Seasonal variations of CH_4 concentration (nmol l^{-1}) in the Bia ($n = 8$), the Tanoé ($n = 8$) and the Comoé ($n = 8$) rivers, average monthly freshwater discharge ($m^3\ s^{-1}$) and average monthly precipitation (mm $month^{-1}$), during the high dry season (HDS, March), the high rainy season (HRS, June), the low dry season (LDS, September) and the low rainy season (LRS, December). *Error bars* correspond to standard deviation on the mean

season from August to September, and the low rainy season from October to December (Fig. 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 in 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 (Fig. 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 the Ehy lagoon, and receives freshwater from the Bia and Tanoé rivers. Inter-tidal areas in these lagoons are occupied by mud-flats and mangroves and correspond to 45, 37 and 24% of the open water surface area in the Aby, Ebrié and Grand-Lahou lagoon systems, respectively (Hughes and Hughes 1992). The main physical characteristics of the Ivory Coast lagoons and rivers are given in Table 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 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

Table 1 Main physical characteristics of the lagoons and rivers flowing into these lagoons in Ivory Coast, 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[a]	200	8900	27
Potou	22	0.03	2.7	0–6	La Mé[a]	140	4300	47
Grand-Lahou	190	0.5	2.0	0–26	Bandama[a]	1050	97000	298

[a] Not sampled

in deeper areas. Tidal amplitude in the Ebrié lagoon system is <1 m (Brenon et al. 2004), and should be similar in the Grand-Lahou lagoon system but lower in the Aby lagoon system (data unavailable for the latter two lagoon systems).

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).

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 (Grand-Lahou, Ebrié, Potou, Aby and Tendo) and three rivers (Comoé, Bia and Tanoé). 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, 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, 23 samples in the Ebrié lagoon, 6 samples in the Potou lagoon, 16 samples in the Aby lagoon and 8 samples in the Tendo lagoon (Fig. 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. Water was sampled in serum bottles of 40 ml taking care to avoid formation of bubbles, poisoned with $HgCl_2$ and sealed. Concentrations of CH_4 were determined by gas chromatography with flame ionization detection, after creating a 12 ml headspace with N_2, as described by Abril and Iversen (2002). Certified CH_4:N_2 mixtures (Air Liquide) of 10 and 500 ppm CH_4 were used as standards. At all stations, CH_4 samples were obtained in duplicate and the overall reproducibility of CH_4 concentration measurements was better than ±5%. Dissolved CH_4 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 (u) was measured at each sampling station with a hand-held anemometer for a period of about 5 min.

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

$$FCH_4 = k\,\Delta[CH_4]$$

where k is the gas transfer velocity of CH_4 and $\Delta[CH_4]$ is the air–water gradient of CH_4 computed from CH_4 concentration in the water and a constant atmospheric CH_4 concentration of 1.8 ppm.

k was computed from k normalized to a Schmidt number of 600 (k_{600}) according to:

$$k = k_{600}\sqrt{\frac{600}{Sc}}$$

where Sc is the Schmidt number of CH_4 computed from water temperature with the formulations for salinity 0 and 35 given by Wanninkhof (1992), and to a given salinity assuming that Sc varies linearly with salinity.

k_{600} was computed from u using the "non-dome data" parameterization given by Raymond and Cole (2001):

$$k_{600} = 1.58\, e^{0.3u}$$

This parameterization is based on 14 k_{600} data points derived for the mass balance of naturally occurring tracers (^{222}Rn and chlorofluorocarbons) and purposeful tracers (^{3}He and SF_6) gathered from five rivers and estuaries. This parameterization assumes by its formulation that wind speed is the main driver of water turbulence and k.

The u values from field measurements at about 2 m height were referenced to 10 m height using the formulation given by Johnson (1999). In order to take into account site specific wind sheltering by environmental windbreaks, for each study site a relationship was derived between the daily averages of measured u values and the daily u values from the National Centers for Environmental Prediction (NCEP) reanalysis daily averages surface flux (http://www.cdc.noaa.gov/), averaged at four stations covering the sampled region (−10.63°E 6.67°N; −8.75°E 6.67°N; −10.63°E 4.76°N; −8.75°E 4.76°N) (Table 2). These relationships are site specific due to variable damping effect of wind speed, related for instance to forest cover in the rivers. The correlation between daily averages of u field measurements and the NCEP daily u values was overall good, and statistical significance of the correlations increased with increasing range of u values and increasing number of data points (Table 2). The coefficient (a) of the linear regressions forced through zero was below unit in the narrower and more sheltered rivers (Bia and Tanoé) and was highest in the Ebrié lagoon, the most extensive and less sheltered of the lagoons. Hereafter, u refers to the NCEP values adjusted with the a values given in Table 2. FCH_4 was computed with the adjusted daily NCEP u values for a time period of 1 month centred on the date of the middle of each field cruise. Such an approach allows to account for the day-to-day variability of u in each of the study sites, and to provide FCH_4 values that are seasonally representative.

Table 2 Coefficient (a) of the linear regressions forced through zero between daily wind speeds from the NCEP (averaged at four stations covering the sampled region (−10.63°E 6.67°N; −8.75°E 6.67°N; −10.63°E 4.76°N; −8.75°E 4.76°N)) and daily averages of wind speeds measured in field merged from all cruises, number of data points (n) and range of daily averages of wind speeds measured in field in the Comoé, Bia and Tanoé rivers, and the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons

	a	n	r^2	Range (m s^{-1})
Rivers				
Comoé	1.46	4	0.86	0.9–5.1
Bia	0.55	4	0.70	1.2–2.0
Tanoé	0.59	4	0.24	0.8–1.9
Lagoons				
Grand-Lahou	1.45	4	0.27	2.4–5.8
Ebrié	2.07	7	0.69	1.5–7.5
Potou	1.38	4	0.82	1.7–4.4
Aby	1.34	7	0.63	1.0–6.7
Tendo	1.75	4	0.34	2.1–6.2

Average monthly rainfall was obtained during 2000–2006 at Adiaké station (−3.3°E 5.28°N) close to Aby lagoon, provided by the Direction Météorologique d'Adiaké. Average monthly freshwater discharge values during 2000–2005 were measured at Bianou and Yakassé stations for the Bia and the Comoé rivers, respectively (data from the Direction de l'Eau d'Abidjan). Average monthly freshwater discharge values in the Tanoé river were only available for 1978, at Alanda station (from the University of New Hampshire Global Runoff Data Centre, available at http://www.grdc.sr.unh.edu/). Hence, freshwater discharge and precipitation data in Fig. 2 are climatological 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 were 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.

Results and discussion

Dynamics of CH_4 in the three rivers

Figure 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., 2221% of saturation) to 870 nmol l^{-1} (i.e., 38719% of saturation). These CH_4 over-saturations are within the range reported for temperate and tropical rivers ranging between ~260 and 128420% (e.g., literature 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, 230 and 420 nmol l^{-1} in the Comoé, Bia and Tanoé rivers, respectively. An overall decrease of CH_4 concentrations occurred in the three 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. Similar seasonal patterns with a CH_4 maximum during summer (low water period) and a CH_4 minimum during winter (flooding period) have been observed in lowland temperate European rivers (Middelburg et al. 2002; Abril et al. 2007). This pattern might be due on the one hand to large dilution and high degassing rates during the flooding period (Hope et al. 2001) and, on the other hand, to limitation of in-stream CH_4 production at high discharge (De Angelis and Scranton 1993). In addition, during the flooding period, rivers receive preferentially waters from surface runoff, that are poor in CH_4, and contribution of CH_4 inputs from ground waters becomes minor. Conversely, during the low water period, deep pathways of ground waters enriched in CH_4 dominate, which leads to higher CH_4 concentrations in river waters (Jones and Mulholland 1998a, b).

Koné et al. (2009) reported the seasonal pattern of pCO_2 and dissolved silicate (DSi) in the same three Ivory Coast rivers, and these authors concluded that pCO_2 was mainly derived from drained soil CO_2, and that DSi was derived from rock weathering. The seasonal cycles of these two quantities were strongly controlled by dilution during the flooding period. The positive relationship between the seasonal average CH_4 concentrations and seasonal average pCO_2 and DSi (Fig. 3) suggests that drainage of soil CH_4 and dilution during the flooding period are the major drivers of CH_4 in these three rivers, as previously reported in several temperate rivers (e.g., Upstill-Goddard et al. 2000; Hope et al. 2001; Middelburg et al. 2002).

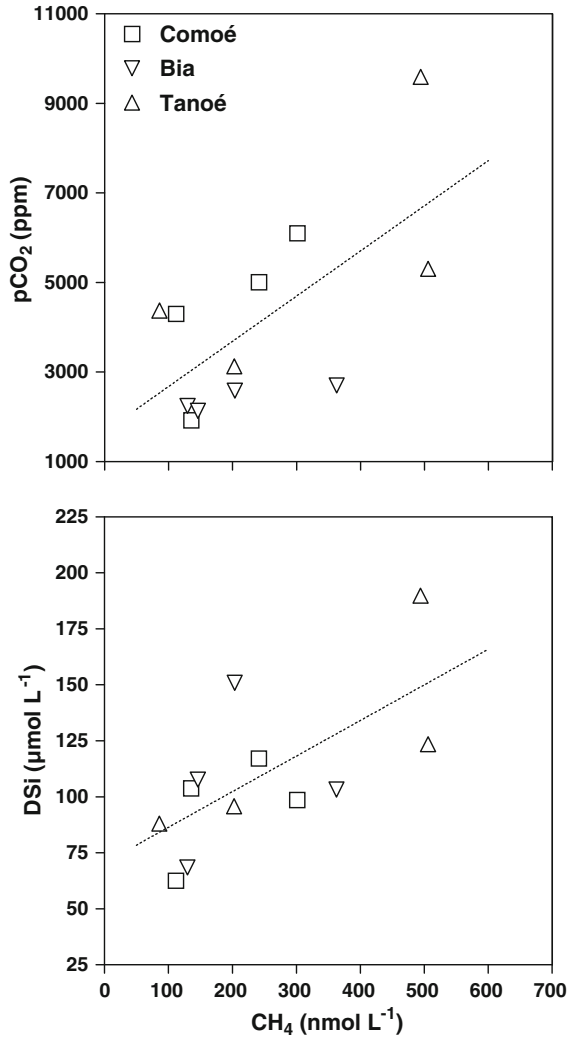

Fig. 3 Comparison of seasonal averages of CH_4 concentrations (nmol l^{-1}) and partial pressure of CO_2 (pCO_2 in ppm) and dissolved silicate (DSi in µmol l^{-1}) in the Bia ($n = 8$), the Tanoé ($n = 8$) and the Comoé ($n = 8$) rivers. The pCO_2 and DSi data were obtained at the same locations and same dates as the CH_4 data (Koné et al. 2009). 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 $P = 0.0188$

Jones and Mulholland (1998a) investigated in detail the spatial variations of riverine CH_4 concentrations in several temperate rivers in the U.S.A. along gradients of stream size, elevation and soil organic carbon content. These authors reported a CH_4

maximum in small headwater streams at highest elevation and organic soil content, that they attributed to large CH_4 groundwater inputs from soils. In contrast, in lowland rivers, summer CH_4 concentrations increased with river size and moving downstream, due to higher in-stream CH_4 production. 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 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 Ivory Coast rivers we sampled, during the high dry season (March) and the high rainy season (June), the average CH_4 concentrations (Table 3) were significantly to highly significantly higher in the smaller Bia river than in the larger Comoé river, (Table 1), confirming the dominance of a terrestrial CH_4 source (from soils).

The average CH_4 concentrations in the three studied rivers (Table 3) are quite high compared to other small tropical rivers such as Kaneohe river (Hawaii, 33 nmol l^{-1}, Sansone et al. 1999), Sepik river (Papua New Guinea, 80–130 nmol l^{-1}, Wilkinson et al. 1978), or large river mainstems as the Orinoco river (Venezuela, 160–190 nmol l^{-1}, Smith et al. 2000), the Amazon river (Brazil, 44–62 nmol l^{-1}, Richey et al. 1988; 150–210 nmol l^{-1}, Bartlett et al. 1990), and the Yangtze river (China, 112–190 nmol l^{-1}, Zhang et al. 2004). However, the CH_4 concentrations in our three 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; Bartlett et al. 1990) due to strong local CH_4 production fuelled by organic carbon inputs from macrophytes and flooded forest. Based on the extent of inundation reported by Hughes and Hughes (1992) we estimate that the surface area of floodplains corresponds between $\sim$5 and 10 times the surface area of the Comoé river mainstem. This could explain the higher CH_4 concentrations in the Ivory Coast rivers than in the small tropical rivers (Kaneohe and Sepik rivers). However, the ratio between the water volume of the mainstem to the lateral inputs of CH_4 from the floodplains should also modulate the CH_4 content of the mainstem (for an equal lateral flux of CH_4 from the floodplains, the increase of CH_4 in the mainstem will be higher if the volume of the mainstem is lower). This could explain why CH_4 concentrations in the Amazon mainstem are lower than in the Ivory Coast rivers, while the inundated floodplain surface area corresponds to $\sim$34 times the surface area of the mainstem during high water (Richey et al. 2002).

Dynamics of CH_4 in the five lagoons

Figure 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 (Long) for the Grand-Lahou, Ebrié and Tendo lagoons and as a function of latitude (Lat) 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., 1496% of saturation) to 1004 nmol l^{-1} (i.e., 51843% of saturation). These CH_4 over-saturations are within the range reported for temperate and tropical estuarine environments ranging between $\sim$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, outgassing to the atmosphere, and production and oxidation in waters and sediments of the lagoon. A 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 (Fig. 4). During the low rainy season (December), 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 (Fig. 2). Finally, during the high dry season (March), the CH_4 concentrations were significantly higher in

Table 3 Average (±standard deviation) of CH_4 concentration (nmol l^{-1}), CH_4 percent of saturation (%CH_4 in %), diffusive air–water CH_4 fluxes (μmol m^{-2} day^{-1}), the gas transfer velocity (k_{600} in cm h^{-1}) and wind speed (u in m s^{-1}) in the Comoé, Bia and Tanoé 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)

	Rivers			Lagoons				
	Comoé	Bia	Tanoé	Grand-Lahou	Ebrié	Potou	Aby	Tendo
High dry season (March)								
CH_4 (nmol l^{-1})	301 ± 64	204 ± 24	494 ± 129	81 ± 23	164 ± 60	189 ± 33	602 ± 244	412 ± 161
%CH_4 (%)	14393 ± 3070	9688 ± 1208	23152 ± 5909	4330 ± 1022	8462 ± 3030	9335 ± 1616	30191 ± 12550	20289 ± 8024
FCH_4 (μmol m^{-2} day^{-1})	488 ± 188	151 ± 26	374 ± 107	127 ± 54	437 ± 263	286 ± 101	877 ± 452	847 ± 471
k_{600} (cm h^{-1})	5.3 ± 1.7	2.5 ± 0.3	2.5 ± 0.3	5.3 ± 1.7	9.0 ± 4.0	4.9 ± 1.5	4.8 ± 1.4	6.8 ± 2.6
u (m s^{-1})	3.9 ± 1.1	1.4 ± 0.4	1.6 ± 0.4	3.8 ± 1.1	5.5 ± 1.5	3.6 ± 1.0	3.6 ± 1.0	4.6 ± 1.3
High rainy season (June)								
CH_4 (nmol l^{-1})	241 ± 64	362 ± 103	506 ± 229	86 ± 38	180 ± 87	252 ± 41	162 ± 35	109 ± 52
%CH_4 (%)	10950 ± 2877	16577 ± 4696	22586 ± 10232	2117 ± 933	8335 ± 3973	11503 ± 1879	7662 ± 1630	5065 ± 2361
FCH_4 (μmol m^{-2} day^{-1})	312 ± 118	241 ± 73	337 ± 158	51 ± 28	376 ± 238	308 ± 93	200 ± 65	180 ± 105
k_{600} (cm h^{-1})	4.6 ± 1.2	2.3 ± 0.2	2.4 ± 0.3	4.6 ± 1.2	7.3 ± 2.7	4.3 ± 1.1	4.2 ± 1.0	5.7 ± 1.8
u (m s^{-1})	3.5 ± 0.9	1.3 ± 0.3	1.4 ± 0.4	3.4 ± 0.9	4.9 ± 1.2	3.2 ± 0.8	3.2 ± 0.8	4.1 ± 1.0
Low dry season (September)								
CH_4 (nmol l^{-1})	136 ± 25	130 ± 17	203 ± 35	66 ± 8	141 ± 83	144 ± 29	68 ± 21	91 ± 56
%CH_4 (%)	6241 ± 1117	5815 ± 746	8926 ± 1532	3155 ± 774	6507 ± 3839	6573 ± 1350	3081 ± 910	4113 ± 2491
FCH_4 (μmol m^{-2} day^{-1})	186 ± 67	84 ± 14	134 ± 28	87 ± 29	303 ± 239	183 ± 66	80 ± 35	151 ± 114
k_{600} (cm h^{-1})	4.8 ± 1.5	2.4 ± 0.3	2.5 ± 0.3	4.8 ± 1.5	7.8 ± 3.5	4.5 ± 1.3	4.4 ± 1.2	6.1 ± 2.2
u (m s^{-1})	3.6 ± 1.0	1.3 ± 0.4	1.4 ± 0.4	3.6 ± 1.0	5.0 ± 1.4	3.4 ± 0.9	3.3 ± 0.9	4.3 ± 1.2
Low rainy season (December)								
CH_4 (nmol l^{-1})	112 ± 19	146 ± 24	86 ± 40	56 ± 17	127 ± 60	81 ± 37	124 ± 43	87 ± 16
%CH_4 (%)	5262 ± 893	6767 ± 1157	3898 ± 1819	2763 ± 774	6154 ± 3024	3824 ± 1769	5939 ± 2024	4188 ± 757
FCH_4 (μmol m^{-2} day^{-1})	130 ± 39	93 ± 18	54 ± 26	62 ± 25	216 ± 131	89 ± 48	134 ± 56	126 ± 44
k_{600} (cm h^{-1})	3.9 ± 1.0	2.2 ± 0.2	2.3 ± 0.2	3.9 ± 0.9	5.8 ± 2.0	3.7 ± 0.9	3.6 ± 0.8	4.7 ± 1.4
u (m s^{-1})	2.9 ± 0.8	1.1 ± 0.3	1.2 ± 0.3	2.9 ± 0.8	4.2 ± 1.2	2.8 ± 0.8	2.7 ± 0.8	3.5 ± 1.0
Annually integrated								
CH_4 (nmol l^{-1})	206 ± 46	238 ± 49	345 ± 124	74 ± 24	156 ± 73	175 ± 36	245 ± 86	175 ± 70
%CH_4 (%)	9578 ± 2131	10607 ± 2284	15732 ± 5592	2999 ± 825	7511 ± 3479	8209 ± 1698	12017 ± 4301	8439 ± 3375
FCH_4 (μmol m^{-2} day^{-1})	288 ± 107	155 ± 38	241 ± 91	78 ± 34	338 ± 217	227 ± 79	330 ± 153	326 ± 181
k_{600} (cm h^{-1})	4.6 ± 1.3	2.3 ± 0.2	2.4 ± 0.3	4.6 ± 1.3	7.4 ± 3.0	4.3 ± 1.2	4.2 ± 1.1	5.8 ± 2.0
u (m s^{-1})	3.4 ± 0.9	1.3 ± 0.3	1.4 ± 0.4	3.4 ± 0.9	4.9 ± 1.3	3.2 ± 0.9	3.2 ± 0.9	4.1 ± 1.1

Annually integrated values were computed using 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)

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 also observed at the river—estuary transition (zero salinity region) of several 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 dominance of CH_4 outgassing and/or CH_4 oxidation over CH_4 production in these areas. The ratio between CH_4 oxidation and CH_4 outgassing is affected by several environmental conditions such as increasing depth and turbidity that favour CH_4 oxidation, increasing salinity that inhibits CH_4 oxidation, and increasing wind and tidal currents that enhance CH_4 outgassing (De Angelis and Scranton 1993; Abril and Iversen 2002; Abril et al. 2007). In some cases, an intermediate CH_4 maximum also occurs at the river—estuary transition where 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 entrance 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 3), enhancing the efflux of riverine CH_4 to the atmosphere at the entrance of the lagoons. Also, in the central Ebrié lagoon, tidal current speeds can reach $\sim$0.9 m s^{-1}, higher than near the mouth of the Comoé river $\sim$0.1 m s^{-1} (Brenon et al. 2004), and thus increasing k (e.g. Zappa et al. 2003; Borges et al. 2004a, b), potentially further enhancing CH_4 outgassing. The enhancement of bacterial CH_4 oxidation by suspended matter (Abril et al. 2007) is probably limited in the studied river–lagoon transitions, where the concentration of suspended matter never exceeds 20 mg l^{-1} (Koné et al. 2009).

The CH_4 distribution in the 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 $\sim$70 and 110 nmol l^{-1}, respectively (Fig. 4). Such homogeneity in CH_4 distributions suggest stable conditions, with low CH_4 production and oxidation rates in these two well mixed lagoons.

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 eastern Ebrié lagoon (Long <-3.8°E). This CH_4 maximum occurred at high salinity during the high dry season (March), at intermediate salinities during the low dry season (September) and the low rainy season (December) and at low salinities during the high rainy season (March) (Fig. 4). Despite strong seasonal salinity variations, no significant seasonal differences were observed in average CH_4 concentrations in the vicinity of the city of Abidjan (Fig. 4). This CH_4 maximum is most probably related to local production of CH_4 fuelled by untreated wastewater inputs from the city of Abidjan ($\sim$3.8 million inhabitants).

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 ("Dynamics of CH_4 in the three rivers"), average CH_4 concentrations in the Bia river and the Aby lagoon were not significantly different. 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 three other lagoons and than during the other three seasons in both the Aby and Tendo lagoons. During the high dry season (March), CH_4 was positively correlated with salinity (Fig. 5) in surface waters of the Aby ($r^2 = 0.66$, $P = 0.0001$, $n = 16$) and the Tendo ($r^2 = 0.84$, $P = 0.0013$, $n = 8$) lagoons, confirming a local production of CH_4.

Vertical profiles in the water column of the Aby and Tendo lagoons in March (Fig. 6) reveal very high CH_4 concentrations below the pycnocline, where anoxia prevails (Chantraine 1980). Anoxia favours the degradation of organic matter by methanogenesis 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 oxycline and intense CH_4 oxidation in the surface layers (Ward et al. 1987; Fenchel et al.

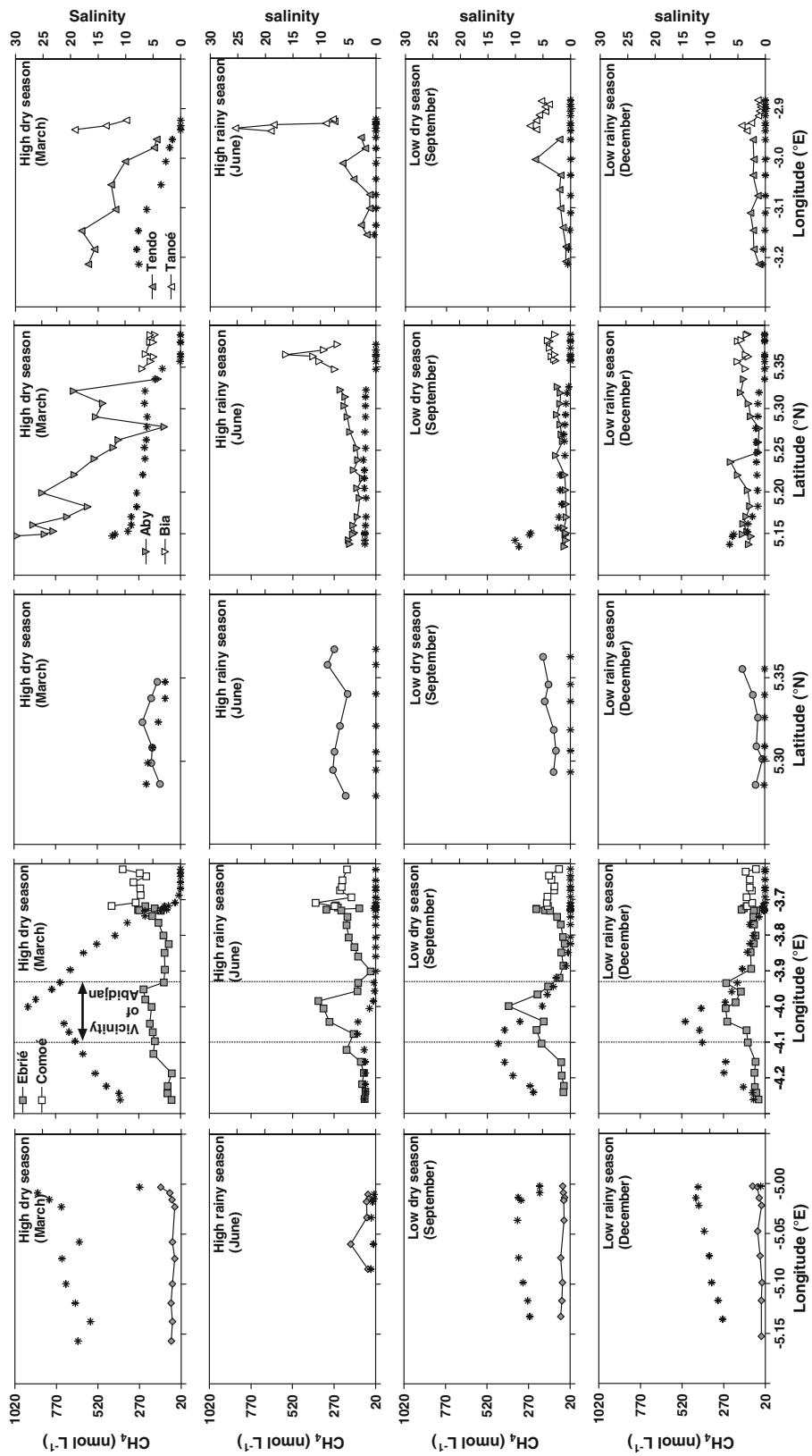

Fig. 4 Seasonal and spatial variations of salinity (*stars*) and CH_4 concentration (*other symbols*, nmol l^{-1}) in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons and associated rivers (Comoé, Bia and Tanoé), during the high dry season (March), the high rainy season (June), the low dry season (September) and the low rainy season (December). In the Grand-Lahou, Ebrié and Tendo lagoons data are presented versus longitude (°E), whereas in the Potou and Aby lagoons data are presented versus latitude (°N)

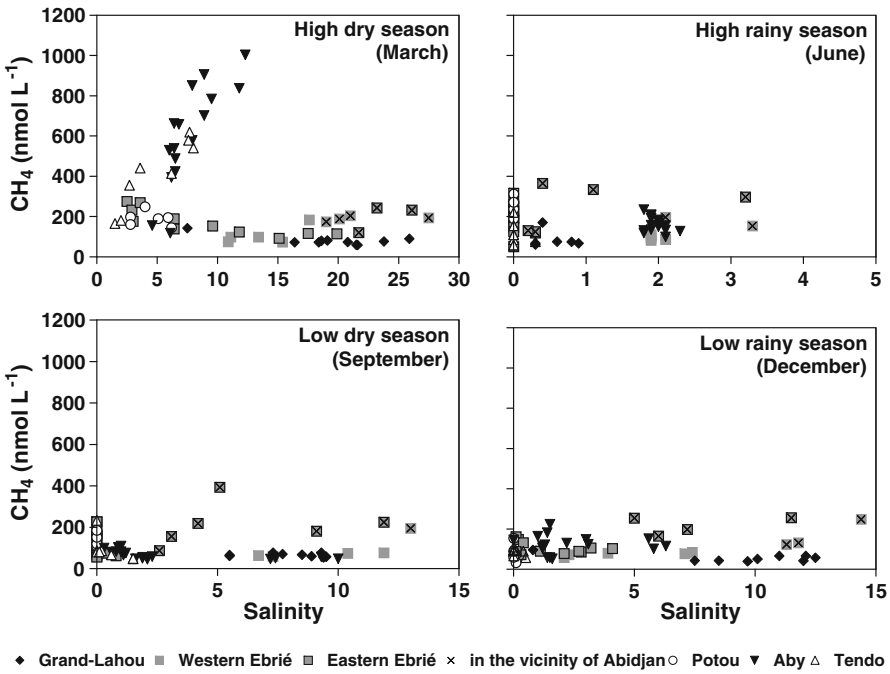

Fig. 5 Seasonal variations of CH_4 concentration (nmol l^{-1}) as a function of salinity in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons during the high dry season (March), the high rainy season (June), the low dry season (September) and the low rainy season (December)

1995). During the high dry season (March), the decrease of freshwater inputs to the Aby and Tendo lagoons leads to a shallower mixed layer (~3 m) compared to the other seasons (~4–6 m), and also to a lesser degree of stratification due to the decrease of the vertical salinity gradient (Chantraine 1980). This leads to higher surface CH_4 concentrations since the diffusion of CH_4 across the pycnocline is enhanced by the lesser stratification. Moreover, the increase of salinity during the high dry season (March) (Figs. 5, 6) might inhibit the activity of methanotrophic bacteria in surface waters (De Angelis and Scranton 1993). Further, the shallower aerobic mixed layer during the high dry season reduces the probability of CH_4 oxidation compared to the other seasons when the mixed layer is deeper. 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 owing to lower stratification. Indeed, measurements of primary production reported by Chantraine (1980) were higher during the high dry season in the Aby (9.0 g O_2 m^{-2} day^{-1} in February 1979) and Tendo lagoons (5.4 g O_2 m^{-2} day^{-1} in February 1979) than the other seasons (5.4 g O_2 m^{-2} day^{-1} in July 1979 and 3.1 g O_2 m^{-2} day^{-1} in October 1979 in the Aby lagoon; 3.1 g O_2 m^{-2} day^{-1} in July 1979 and 2.2 g O_2 m^{-2} day^{-1} in October 1979 in the Tendo lagoon). The seasonal patterns of pCO_2, inorganic nutrients and chlorophyll-*a* obtained during our cruises were consistent with an enhancement of primary production during the high dry season (Koné et al. 2009). In stratified marine and brackish systems, CH_4 originates in majority from the decomposition of organic matter of phytoplankton origin, as for instance in Mariager fjord (Fenchel et al. 1995). Part of the CH_4 produced from organic carbon exported from the surface to the anoxic bottom waters is oxidized mostly aerobically just above the pycnocline. The part of CH_4 that escapes oxidation can be released to 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 with the well-mixed Grand-Lahou and Potou lagoons.

Diffusive air–water CH_4 fluxes in the rivers and lagoons

Table 3 shows the seasonal and annually integrated averages of CH_4, $\%CH_4$, FCH_4, k_{600} and u in the

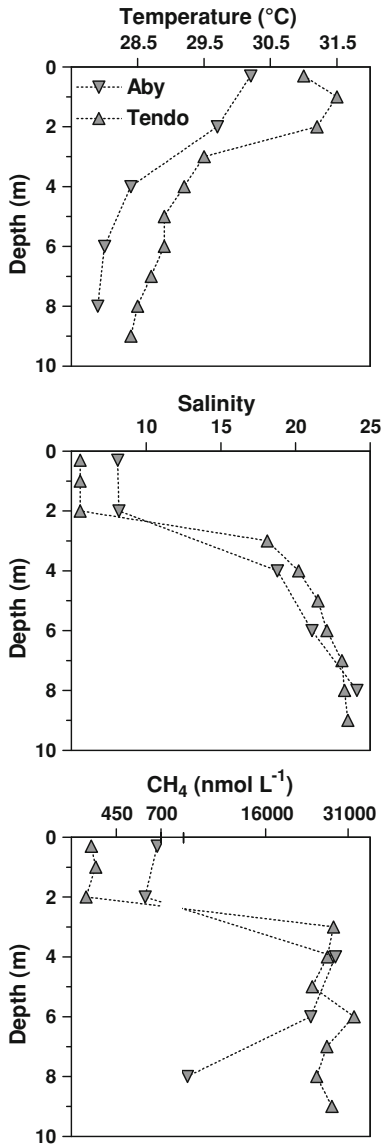

Fig. 6 Vertical profiles of salinity, water temperature (°C) and CH_4 concentration (nmol l^{-1}) in the Aby (−3.231°E 5.228°N) and Tendo (−3.110°E 5.142°N) lagoons during the high dry season (March)

sampled rivers and lagoons. The computed k_{600} values were higher in the Comoé river than in the two other rivers due to stronger wind speeds related to a lesser wind damping effect by surrounding forests in the wider Comoé river. The monthly averages of k_{600} values in the three rivers ranged between 2.2 ± 0.2 and 5.3 ± 1.7 cm h^{-1} and bracket the average k_{600} value of 3.3 cm h^{-1} assumed characteristic of large rivers by Cole and Caraco (2001). The computed monthly k_{600} values in the lagoons ranged between 3.6 ± 0.8 and 9.0 ± 4.0 cm h^{-1} and were higher than in the rivers owing to stronger wind speeds. The computed monthly k_{600} values were higher in the Ebrié lagoons than in the other lagoons due to higher wind speeds. The seasonal variability of k_{600} in estuaries has been seldom investigated. In the Scheldt estuary, monthly k_{600} values range between 12.0 and 24.0 cm h^{-1} (Borges et al. 2004a). The higher k_{600} values in the Scheldt estuary than in the Ivory Coast lagoons are related to higher wind speeds ranging seasonally from 2.6 to 7.5 m s^{-1} but also to a strong contribution of tidal currents to k values. The Scheldt estuary is a strongly macro-tidal estuary with tidal amplitudes up to 5 m and tidal currents up to 1.5 m s^{-1}. The restricted lagoons in Ivory Coast are micro-tidal such as the Ebrié lagoon where maximal tidal amplitude is lower than 0.6 m, and where in most parts tidal currents are below 0.1 m s^{-1} with maximal tidal currents of 0.9 m s^{-1} in the Vridi channel (Brenon et al. 2004). Based on the relationship of O'Connor and Dobbins (1958), the upper most value of the contribution of tidal currents to k_{600} can be evaluated to 4.2 cm h^{-1} using the maximal tidal current 0.9 m s^{-1} and a depth of 15 m at the Vridi channel. However, in most of the Ebrié lagoon tidal currents are low (0.1 m s^{-1}) leading to a low contribution of tidal currents to k_{600} evaluated with the O'Connor and Dobbins (1958) relationship ranging from 1.4 to 2.4 cm h^{-1}, for depths ranging between 15 and 5 m, respectively. While information is not available on tidal currents of other lagoons, they are expected to be similar than in the Ebrié lagoon for other restricted lagoons (Grand-Lahou) and lower in the chocked lagoons (Aby and Tendo).

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 25 to 1187 µmol m^{-2} day^{-1}, and annual integrated values ranged from 155 to 288 µmol m^{-2} day^{-1}. These values are within but in the lower end of the range of diffusive air–water CH_4 fluxes from temperate rivers (0–21562 µmol m^{-2} day^{-1}) (De Angelis and Scranton 1993; Lilley et al. 1996; Jones and Mulholland 1998a, b; Hope et al. 2001; Abril and Iversen 2002). The emission of CH_4 from the three studied rivers was distinctly lower than the emission of CH_4 from the Amazon River (ranging from 4625 to 12562 µmol m^{-2} day^{-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 three rivers seem to be mainly related to inputs from soil CH_4 and dilution ("Dynamics of CH_4 in the three rivers").

The five lagoons were always a source of CH_4 to the atmosphere with diffusive air–water CH_4 fluxes ranging seasonally from 20 to 2403 μmol m^{-2} day^{-1}, the annual integrated values ranging from 78 to 338 μmol m^{-2} day^{-1}, and an annual integrated area average for the five lagoons of 367 ± 163 μmol m^{-2} day^{-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 to 500 μmol m^{-2} day^{-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 7 compares the annual averages of %CH_4 and the annual averages of the air-gradient of pCO_2 (ΔpCO_2) in the three rivers and five lagoons. The three rivers were over-saturated in CO_2 with respect to the atmosphere, and %CH_4 was positively correlated to ΔpCO_2. As discussed by Koné et al. (2009), CO_2 dynamics in the three rivers seemed to be mainly related to inputs of soil CO_2 and dilution during the flooding period, hence, the same processes that seemed to control CH_4 dynamics in these rivers

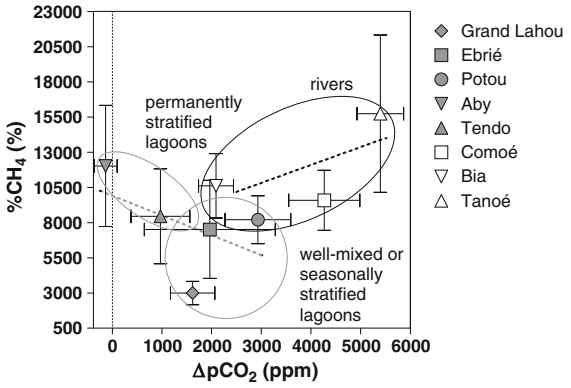

Fig. 7 Annual averages of the CH_4 percent of saturation (%CH_4 in %) versus annual averages of the air-water gradient of pCO_2 (ΔpCO_2 in ppm) in the in the Grand-Lahou, Ebrié, Potou, Aby and Tendo lagoons, and in the Comoé, Bia and Tanoé rivers. The ΔpCO_2 data were obtained at the same locations and same time as the CH_4 data (Koné et al. 2009). Linear regression for rivers (*black dotted line*) yields $r^2 = 0.42$ and $P = 0.549$ and for lagoons (*grey dotted line*) yields $r^2 = 0.25$ and $P = 0.393$. *Error bars* correspond to standard deviation on the mean

("Dynamics of CH_4 in the three rivers"; Fig. 3). In the five lagoons, %CH_4 was negatively correlated to ΔpCO_2, and the Aby lagoon that was the most over-saturated in CH_4 was under-saturated in CO_2, unlike the other four lagoons that were over-saturated in CO_2. 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 over-saturation (Tendo lagoon) or a CO_2 under-saturation (Aby lagoon), but at the same time this promotes anoxia in bottom waters that enhance methanogenesis and leads to stronger CH_4 over-saturation than the other lagoons that are not permanently stratified.

Conclusions

Whatever the season, surface waters were over-saturated in CH_4 with respect to atmospheric equilibrium in the three studied rivers (2221–38719%) and the five studied lagoons (1496–51843%). The diffusive air–water CH_4 fluxes were consequently always directed to the atmosphere, ranging between 25 and 1187 μmol m^{-2} day^{-1} in the rivers and between 20 and 2403 μmol m^{-2} day^{-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 in rivers and estuaries 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. 2004a, b), although it is probable that this not adequately quantified in k values derived from tracer methods that have a characteristic time scale (~1 day) that is incompatible with the water current characteristic time scale (~1 min). We did not quantify ebullition CH_4 fluxes, which in macrotidal estuarine systems can represent ~50% or more of the total emission of CH_4 to the atmosphere (Chanton et al. 1989; Kelley et al. 1990; Shalini et al. 2006). Finally, direct emission of CH_4 from intertidal sediments to the atmosphere strongly contribute in estuarine environments to the overall CH_4 emission at ecosystem scale ranging from ~7000 μmol m^{-2} day^{-1} in oligohaline regions to

~ 30 μmol m^{-2} day^{-1} in polyhaline regions (refer to review by Abril and Borges 2004).

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