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Estimates and Variability of the Air-Sea CO_2 Fluxes in the Gulf of Guinea during the 2005-2007 Period

Urbain Koffi[1,2*], Georges Kouadio[1,2], Yves K. Kouadio[2]

[1]Ecole Normale Supérieure d'Abidjan, Laboratoire des Sciences Physiques, Fondamentales et Appliquées, Abidjan, Côte d'Ivoire
[2]Université Felix Houphouët-Boigny de Cocody, Abidjan, Côte d'Ivoire
Email: *urbain_koffi@yahoo.fr

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Abstract

Measurements of CO_2 parameters (*i.e.* Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC)) were made from June 2005 to September 2007 in six EGEE ("Etude de la circulation océanique et de savariabilitédans le Golfe de GuinEE") cruises to better assess air-sea CO_2 fluxes in the Gulf of Guinea (6˚N - 10˚S, 10˚E - 10˚W). Two empirical relationships TA-Salinity and DIC-Salinity-Temperature were established. These relationships were then used to estimate the monthly fugacity of CO_2 (fCO_2) and air-sea CO_2 fluxes. The monthly mean flux of CO_2 reaches 1.76 ± 0.82 mmol·m^{-2}·d^{-1} (resp. 2.90 ± 1.45 mmol·m^{-2}·d^{-1}) at the north of the Equator (resp. at the South). The north-south gradient observed as the patterns of the air-sea CO_2 fluxes was mainly driven by the oceanic fCO_2. This gradient was due to the low values of the CO_2 parameters flowing by the Guinea Current (6˚N - 0˚) from the west to the east while the air-sea CO_2 fluxes increased in the south (10˚S - 0). In the north, the climatology of Takahashi underestimated the CO_2 fluxes in the Gulf of Guinea when comparing to the estimated fluxes. This was due to the north-south gradient, which did not well reproduce by the climatology of Takahashi.

Keywords

CO_2 Fluxes, Total Alkalinity, Dissolved Inorganic Carbon, Gulf of Guinea

1. Introduction

During the 1980-2000 period, the fugacity of CO_2 (fCO_2) measurements has been carried out to follow the evo-

*Corresponding author.

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lution of oceanic CO_2 in the eastern equatorial Atlantic [1]-[3]. This monitoring has allowed 1) understanding the ocean behavior associated to the increase of atmospheric CO_2 and 2) determining the impact of ocean acidification on the marine ecosystem [4]. However, measurements are often fragmented in time and space. So, the seasonal cycle of CO_2 is still not well understood over large parts of the ocean. And the limited understanding of the air-sea CO_2 transfer rate introduces large errors in the fluxes estimates [5]. Moreover, the air-sea CO_2 fluxes were not directly recorded, but it is derived and associated with large uncertainty [6]. These aspects probably make the global estimate of the air-sea CO_2 fluxes changes difficult to construct from the synthesis of regional studies.

Different methods have been used to assess these air-sea CO_2 fluxes [6] [7]. Some were based on diagnostic and prognostic models of fCO_2 or DIC as "diagnostic models that use empirical interpolation schemes applied to fCO_2, and biogeochemical prognostic ocean model", and others are based on a synthesized climatology surface dataset of fCO_2. In the tropical oceans, the air-sea CO_2 fluxes were estimated using both oceanic and atmospheric inversion methods. These methods converge to a mean CO_2 outgassing [8] despite the existing discrepancy between models and observations. Many authors [9] used a global carbon model to find a mean air-sea CO_2 fluxes of about 0.31 $mmol \cdot m^{-2} \cdot d^{-1}$ for the 1990s and the early 2000 over the tropical Atlantic belt (14˚N - 14˚S). Similar results have been also obtained by [10] using inversion methods over the 1991-2000 period. Such value (~0.31 $mmol \cdot m^{-2} \cdot d^{-1}$) was different from the air-sea CO_2 fluxes (~0.20 $mmol \cdot m^{-2} \cdot d^{-1}$) estimates by models.

The region of the tropical Atlantic belt represented also a source of CO_2 with a low seasonal variability [11]. Moreover, the uncertainties that were underlined above are not often provided in most of the results. So, our work addresses this problem in the Gulf of Guinea (GG) during different periods of measurements, and where $ffCO_2$ trends could be estimated with regard to existing observations. The purpose of this paper is to assess the best annual air-sea CO_2 fluxes estimates and quantify its seasonal and interannual variability in the eastern tropical Atlantic. The datasets and method are presented in Section 2. In Section 3, the characteristics of the study area are given, while a comparative analysis of the seasonal and interannual variability of the CO_2 fluxes is made and discussed in Section 4. Finally, a conclusion and perspectives are provided in the last section.

2. Data and Methods

2.1. Data

Six oceanographic cruises (**Figure 1**) named "Etude de la circulation océanique et de savariabilitédans le Golfe de GuinEE" (EGEE) project [12] was conducted (2 cruises/year, see **Table 1**) from June 2005 to September 2007 in the eastern equatorial Atlantic. This project was the oceanic component of the African Monsoon Multidisciplinary Analyses (AMMA) program. The yearly cruises have consisted of two legs starting and ending in Cotonou (Benin, West Africa) during June and September [13].

A total of 195 samples surface seawater was collected for Dissolved Inorganic Carbon (DIC) and TA Total Alkalinity (TA) analyses. Samples were poisoned with a saturated $HgCl_2$ solution to stop biological activities. DIC and TA were measured using potentiometric titration that derived from the method developed by Edmond [14] with a closed cell. The equivalent points were estimated using a non–linear regression method [15] while Certified Reference Materials (CRMs) provided by Prof. A. Dickson (Scripps Institution of Oceanography, San Diego, USA) was used for calibration [16]. The accuracy of DIC and TA in this work reaches ±2 $\mu mol \cdot kg^{-1}$.

Table 1. Dates of EGEE cruises in the eastern equatorial Atlantic from June 2005 to September 2007.

Cruises	Dates
EGEE 1	7th June - 6th July 2005
EGEE 2	29th August - 30th September 2005
EGEE 3	27th May - 7th July 2006
EGEE 4	19th November - 1st December 2006
EGEE 5	6th June - 3rd July 2007
EGEE 6	1st - 30th September 2007

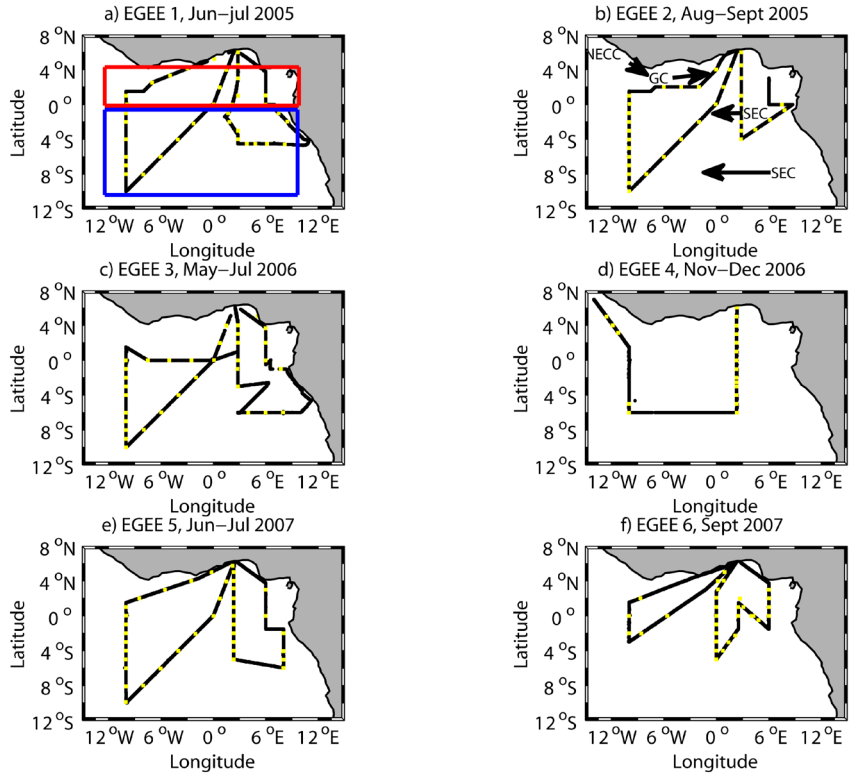

Figure 1. Location of TA and DIC sampled (yellow dots) and track (black line) during the EGEE cruises. The northern (red) and southern (blue) regions are indicated by boxes; Arrows show the oceanic circulation in the Gulf of Guinea.

The fCO_2 measured during EGEE 3 was used to determine the best set of dissociation constants for the calculation of fCO_2 at stations where DIC and TA were recorded. It was also used to validate fCO_2 derived from our extrapolated DIC and TA along the EGEE 3 cruise track. Then, EGEE data were supplemented by data from FOCAL 4, 6 and 8, CITHER 1, and EQUALANT 99 cruises provided by several authors [1]-[3] [17]. These oceanographic cruises were carried out from the 1980s to the 2000s in the eastern equatorial Atlantic (**Table 2**).

The precipitation dataset was extracted from the Global Precipitation Climatology Project (GPCP) [18] on a 1˚ × 1˚ regular grid over the Tropical Atlantic Ocean for the period 2005-2007. The GPCP dataset was composed by a combination of *in situ* observations with satellite microwave and infrared measurements.

2.2. Maintaining the Integrity of the Specifications

The air-sea CO_2 fluxes (F) is calculated using Equation (1):

$$F = ks\Delta fCO_2, \tag{1}$$

Whereas

$k = 0.27\left(U_{10}\right)^2\left(660/Sc\right)^{1/2}$ (in $cm \cdot h^{-1}$) is the CO_2 gas transfer velocity, ΔfCO_2 is the difference between seawater fCO_2 and atmospheric fCO_2, and s is the solubility of CO_2 in seawater (in $mol \cdot L^{-1} \cdot atm^{-1}$) with regard to Sea Surface Salinity (SSS) and Sea Surface Temperature (SST) [19]; the weekly mean CO_2 exchange coefficient $K\left(K = k \cdot s\right)$ in the 6˚N - 10˚S and 10˚E - 10˚W is derived from QuikSCAT wind speeds [20] using the quadratic relationship of [21] at a spatial resolution of 1˚ × 1˚. $U_{10}\left(m \cdot s^{-1}\right)$ represents the wind speed at 10 m above sea surface and Sc is the Schmidt number [21] [22]. The atmospheric fCO_2 was calculated from the monthly CO_2 molar fraction recorded at the Ascension Island at 7.92˚S - 14.42˚W from 2005 to 2007 [23] with a mean value of about 373.2 ± 0.75 µatm.

In addition, the fluorescence was measured using the CTD sensor during the EGEE cruises while chlorophyll ***a*** was sampled only during EGEE 3 cruise and analyzed according to the HPLC standard technique [24]. However,

Table 2. Summary cruises conducted in the eastern equatorial Atlantic from 1980s to the 2000s.

Cruises	FOCAL (4, 6, 8)	CITHER 1	EQUALANT 99
Dates	July - August 1983 (F4) January - February 1984 (F6) July - August 1984 (F8)	January - March 1993	July - August 1999

fluorescence data will be used in this study instead of chlorophyll ***a*** since it is available in all cruises.

The following paragraphs outline the chemistry of carbon dioxide in the ocean. When it is dissolved in the seawater, the carbonate system can be described by the Equations (2), (3), (4) and (5).

$$CO_2 + H_2O \underset{}{\overset{K_1}{\rightleftharpoons}} HCO_3^- + H^+ \text{ with } K_1 = \frac{\left[HCO_3^-\right]\left[H^+\right]}{\left[CO_2\right]} \quad (2)$$

$$HCO_3^- \overset{K_2}{\rightleftharpoons} CO_3^{2-} + H^+ \text{ with } K_2 = \frac{\left[CO_3^{2-}\right]\left[H^+\right]}{\left[HCO_3^-\right]} \quad (3)$$

where, K_1 and K_2 represent stoichiometric equilibrium constants for the description of the carbonate system in the seawater. The different sums of the dissolved forms (*i.e.* CO_2, HCO_3^-, and CO_3^{2-}) give the DIC and the carbonate alkalinity (CA) following Equations (4) and (5):

$$DIC = \left[CO_2\right] + \left[CO_3^{2-}\right] + \left[HCO_3^-\right] \quad (4)$$

$$CA = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] \quad (5)$$

In Equation (5), the carbonate ion CO_3^{2-} is counted twice because it has a double negative charges. The CA is the part of the TA, which includes boron compounds and more:

$$TA = 2\left[CO_3^{2-}\right] + \left[HCO_3^-\right] + \left[B(OH)_4^-\right] + \left[\text{minor basis}\right] + OH^- + \left[H^+\right] \quad (6)$$

Unfortunately, the concentrations of the individual species of the carbon dioxide system in solution cannot be measured directly. The Equations (2), (3), (4) and (5) have six unknown variables (*i.e.* CO_2, HCO_3^-, $\left[CO_3^{2-}\right]$, $[H^+]$, [DIC] and [CA]) and only four variables (*i.e.* $[CO_2]$, $[H^+]$, [DIC] and [TA]) can be measured directly. The system is determined when two variables at least are known and all the parameters can then be calculated with ancillary information. That allows to get a complete description of the carbon dioxide system in seawater [15] [25].

Moreover, oceanic fCO_2 was estimated from TA and DIC using the different dissociation constants. In order to choose the best dissociation constants, measured fCO_2 [26] are compared with the values calculated from TA and DIC during the EGEE 3 cruise. The dissociation constants of [27] refitted by [28], present small values of the root mean square error (~7 µatm) and mean bias error (~ +4 µatm). Thereafter, they will be used to calculate the oceanic fCO_2.

For each year, the relationships established by [13] were used to estimate fCO_2 of FOCAL 6, CITHER 1 and EQUALANT 99 cruises (**Table 3**). These authors found that fCO_2 ranged between 330 µatm and 420 µatm in the GG even if it could exist extreme values associated to the equatorial upwelling [29]. The fugacity of CO_2 was estimated during three cruises carried out in boreal winter (January-February 1984 and January-March 1993) and in boreal summer (July-August 1999) using these relationships. Although measured fCO_2 data were few, the values of the fugacity of CO_2 were well reproduced [13] and the mean estimated fCO_2 was very close to the mean measured fCO_2 during these three cruises.

The annual and monthly fluxes of CO_2 in GG (6˚N - 10˚S; 10˚E - 10˚W) derived from the [13] relationships were calculated at a 1˚ × 1˚ spatial resolution using the SST data of the TMI (Tropical Rainfall Measuring Mission Microwave Imager). The climatological and others mean air-sea CO_2 fluxes were calculated using the CO_2 gas transfer velocity relationship of [21]. The gridded mean air-sea CO_2 fluxes ($mmol \cdot m^{-2} \cdot d^{-1}$) for each day was computed by multiplying daily mean values of K and ΔfCO_2. The daily mean value of K was obtained

Table 3. Mean fCO_2 computed by using the relationship of [13] during three cruises.

	Cruises		
fCO_2 (µatm)	**FOCAL 6 (January - February 84)**	**CITHER 1 (January - March 93)**	**EQUALANT 99 (July - August 99)**
Measured	373 ± 23	370 ± 30	398 ± 30
Calculated	377 ± 8	373 ± 5	403 ± 11

by dividing its weekly (resp. monthly) mean value by seven (resp. by 30 days). [11] noted a low seasonal variability of the mean values of K in the tropical Atlantic belt (14˚N - 14˚S). The mean zonal flux was computed by multiplying the gridded air-sea CO_2 fluxes by the surface representing each grid. Furthermore, the spatial mean air-sea CO_2 fluxes (in Pg-C y^{-1}) was the sum of the air-sea CO_2 fluxes of each grid.

3. Characteristics of the Study Area

The study area (6˚N - 10˚S; 10˚E - 10˚W) was divided in two regions (see **Figure 1(a)**) according to the ocean circulation (**Figure 1(b)**). The first region from 6˚N to the Equator (0˚) was characterized by low concentrations of TA, DIC and fCO_2 [2] [13]. During EGEE cruises periods (**Figure 2**), the high GPCP precipitations (black bars) due to the position of the Intertropical Convergence Zone on the tropical Atlantic Ocean could affect the concentration of the CO_2 parameters in the north-west. Then, these low concentrations were transported eastwards in the ocean basin by the Guinea Current (GC), which is the prolongation of the North Equatorial Counter Current (NECC) [30]. In the second region (0˚ - 10˚S), where low GPCP precipitations (green bars) were observed during EGEE cruises, equatorial upwelling occurs slightly at the south of the Equator and extends zonally throughout the Atlantic. The mechanisms that explain the upwelling are local wind forcing and remote forcing west of the gulf of Guinea [29] [30]. The equatorial upwelling appears between April and May when there is an intensification of the winds at the south of the Equator [31] [32]. This intensification is important in boreal summer during which the cold tongue appears from June to the beginning of October [33] [34]. The upwelling brings cold water rich in CO_2 to the surface and then, this water mass is advected westwards by the South Equatorial Current (SEC) [1].

According to [35], high chlorophyll ***a*** values (5 - 10 $mg \cdot m^{-3}$) were observed in the Congo River delta (at the eastern tropical Atlantic) during the year. The Congo plume reached its maximum extent and the chlorophyll ***a*** concentration coincided with the development of the maximum offshore of chlorophyll ***a*** from May to September. The distribution of fluorescence recorded in the ocean basin is shown in **Figure 3**. These values were quite similar to those obtained by [35], with maximum values higher in June than in September in EGEE 3 (**Figure 3(c)**). During all cruises, the fluorescence values were still lower around 0.2 $mg \cdot m^{-3}$. The maximum (~0.87 $mg \cdot m^{-3}$) was detected westward at 1˚N; 10˚W far from the Congo River mouth in June 2005 (**Figure 1(c)**). The value (~0.58 $mg \cdot m^{-3}$) recorded at 5.35˚S; 10.65˚E in June 2006 could be associated to the signature of the Congo River during EGEE 3 cruise which reached this River delta. However, the biological activity in the eastern tropical Atlantic was quite low due to the fact that the Typical Tropical Structure that characterizes this area has a low chlorophyll ***a*** and anutrient-depleted upper mixed [36]. **Figure 4** shows a case of vertical profiles of the fluorescence and nitrates during the upwelling season at 1˚S and along the transect 10˚W. In this upwelling season, the samples of seawater were done during all the cruises. The fluorescence reached 0.1 $mg \cdot m^{-3}$ (resp. 0.35 $mg \cdot m^{-3}$) at the surface in June 2006 (resp. in June 2005 and 2007). The values were high at the subsurface for the three years. The profiles of nitrates were similar to those of the fluorescence, but high fluorescence was associated to a decrease of the nitrate. Moreover, nitrates were mostly consumed at the depth of the subsurface chlorophyll maximum and very low surface values were measured. This induces a weak impact of the biological activity on the oceanic CO_2 variability.

4. Variability of the Air-Sea CO_2 Fluxes

Before computing TA and DIC, it is useful to remind and understand the processes, which impact the distribution of these carbon components in the ocean. Air-sea exchange of CO_2 changes the content of the inorganic carbon species in seawater but leaves TA unaltered. TA is the equivalent of all bases that can accept a proton to the

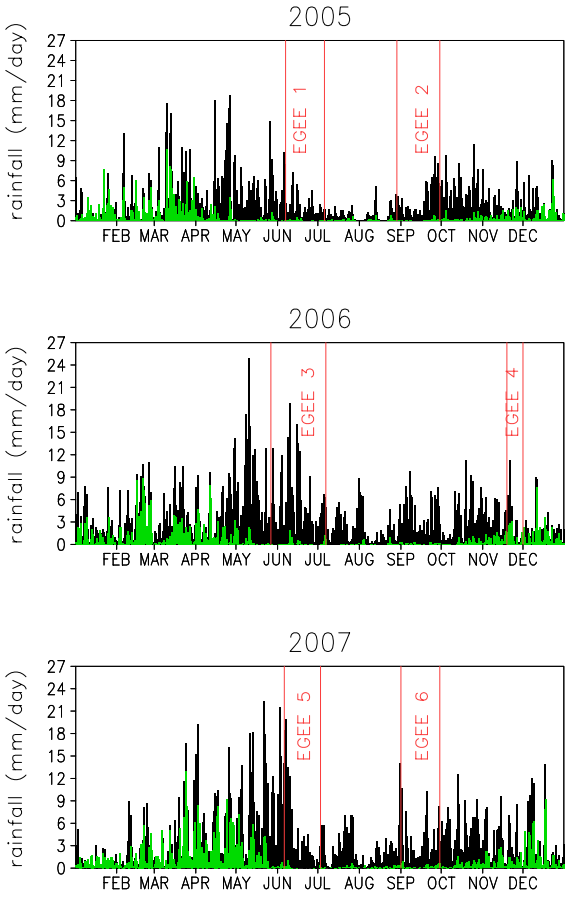

Figure 2. GPCP rainfall averaged over 10˚W - 10˚E; 6˚N - 0˚ (black) and over 10˚W - 10˚E; 0˚ - 10˚S (green) during (top) 2005, (middle) 2006 and (bottom) 2007.

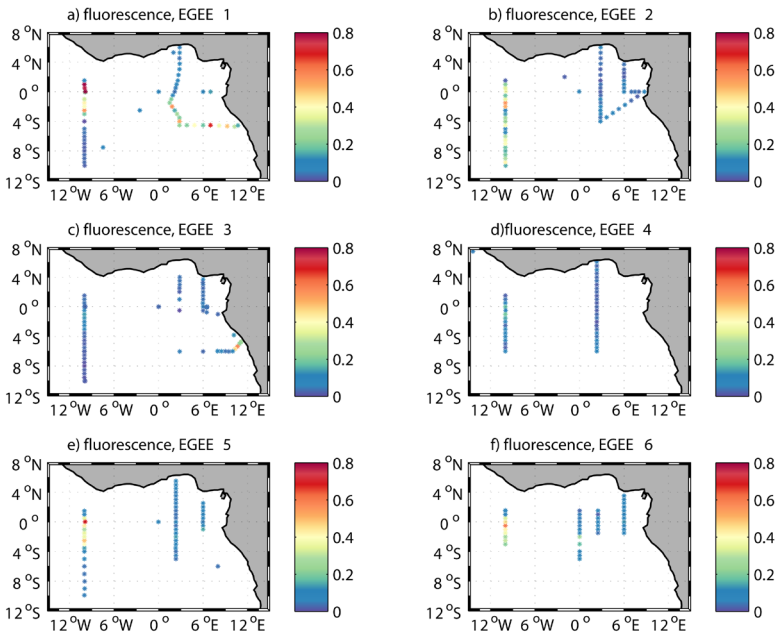

Figure 3. Distribution of the fluorescence (mg·m^{-3}) at the surface during the EGEE cruises.

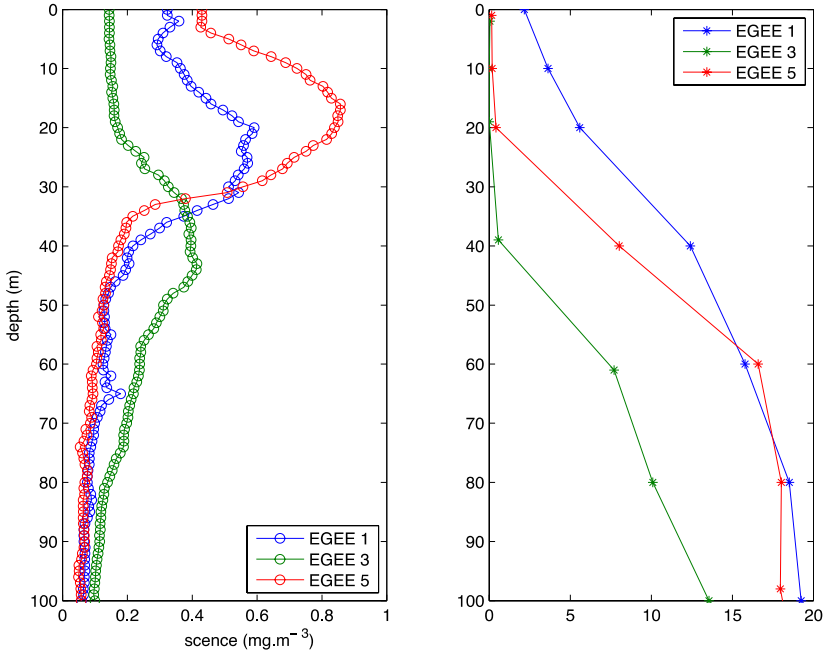

Figure 4. Vertical profiles of (left panel) the fluorescence and (right panel) the nitrates during the upwelling season at 1˚S; 10˚W in 2005, 2006 and 2007.

carbonic acid endpoint. Bicarbonate and carbonate are roughly 98% of TA at pH = 8.1 [15] [35] [37]. Around 1% of CO_2, 0.002% of carbonic acid (H_2CO_3), 9% of carbonate (CO_3^{2-}) and 90% of bicarbonate (HCO_3^-) make up the DIC [15]. TA and DIC were calculated in the eastern equatorial Atlantic with regression relationships DIC-SSS-SST and TA-SSS [13] using climatological SSS field from the World Ocean Atlas [38], and monthly SST from TRMM over the 2005-2007 period. The standard errors reached respectively ±7.2 µmol·kg^{-1} and ±16.6 µmol·kg^{-1} on the predicted TA and DIC.

4.1. Seasonal and Interannual Variability

Figure 5 shows the seasonal cycle of the air-sea CO_2 fluxes in both regions (6˚N - 0˚ and 0˚ - 10˚S) in 2006, since the patterns were quite similar in 2005 and 2007 (not shown). Low values (resp. high values) were noted in January - May (resp. July - October). In the 6˚N - 0˚ area (resp. 0˚ - 10˚S area), the mean air-sea CO_2 fluxes ranges between −0.16 ± 0.66 mmol·m^{-2}·d^{-1} (resp. 0.78 ± 0.89 mmol·m^{-2}·d^{-1}) in March to 3.76 ± 1.12 mmol·m^{-2}·d^{-1} (resp. 4.76 ± 1.90 mmol·m^{-2}·d^{-1}) in August. When looking at the two areas, a north-south gradient was observed in the distribution of the air-sea CO_2 fluxes in the Gulf of Guinea. Not surprisingly the ocean CO_2 source was higher in south of the Equator than in the north. This gradient was due to the GC, which allowed transporting eastward−unsalted waters due to precipitations, and contributed to the dilution and the decrease of CO_2 in the northern region. Furthermore, at the south of the Equator, upwelled waters that made the air-sea CO_2 fluxes mainly driven by the oceanic fCO_2 supply the CO_2.

The **Table 4** shows the air-sea CO_2 fluxes during the EGEE cruises. Each year has been divided into two semesters to take into account the non-upwelling (January - June) and the upwelling (included in July - December) periods in the GG. The air-sea CO_2 fluxes was higher (~2.5 times) in July - December in January - June for all the three years (2005, 2006 and 2007). The upwelled water was responsible for the high CO_2 out gassing from July to September, which increased the air-sea CO_2 fluxes. Low year-to-year variability of CO_2 fluxes was also observed for each semester. However, a slight drop appeared in 2006 compared to 2005 and 2007. This could be explained by the relative high SST in 2006, which was due to the time shift in the development of the cold tongue and the intensity of the upwelling [39]. Moreover, [26] found that the low concentration of CO_2 in 2006 could be caused by the transport of water, which was in contact with the atmosphere long time enough to come close to equilibrium.

To remove the seasonal and interannual variability, the anomalies of the air-sea CO_2 fluxes were computed

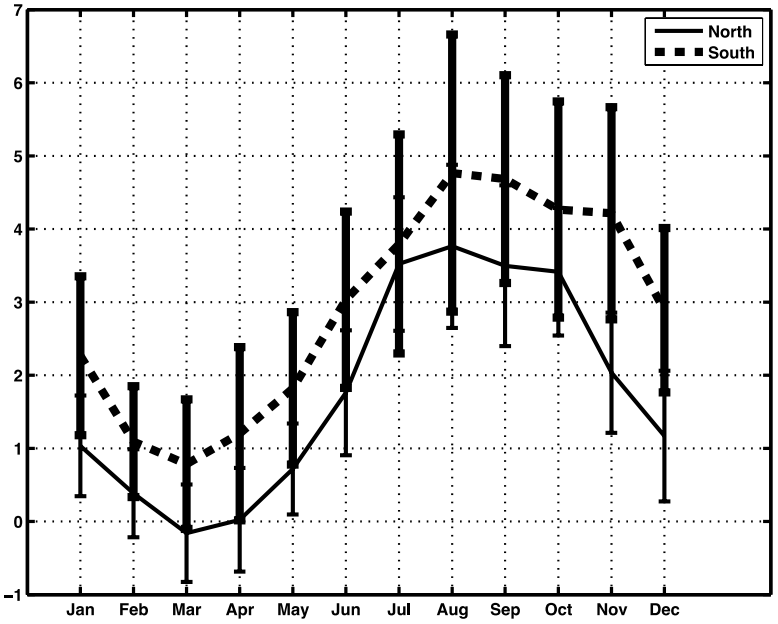

Figure 5. Monthly air-sea CO_2 fluxes (mmol·m^{-2}·d^{-1}) estimated in the eastern equatorial Atlantic (east of 10˚W) in the north (6˚N-Equator, black line) and in the south (Equator/10˚S, dashed line). Positive (resp. negative) values represent ocean carbon source (resp. sink). Standard deviations (±1σ) are indicated by vertical bars.

Table 4. The mean seasonal CO_2 fluxes (mmol·m^{-2}·d^{-1}) for three years in the EGEE cruises.

	CO_2 fluxes (mmol·m^{-2}·d^{-1})	
Year	January - June	July - December
2005	1.58 ± 1.16	4.08 ± 1.61
2006	1.39 ± 1.06	3.75 ± 1.47
2007	1.52 ± 1.17	4.01 ± 1.54

and standardized for 2005, 2006 and 2007. During these periods, no relationship was found between ENSO index and the air-sea CO_2 fluxes (not shown). The Hovmöller diagram (**Figure 6**) shows a slight variation of the CO_2 fluxes in the south of the Equator. At 5˚S, the ocean behavior was not homogenous because of the local drop of the SST (~26˚C), which could create a sink of the CO_2 fluxes. At the northern part of the Equator, a significant year-to-year variability of the costal upwelling appeared during the monsoon period. The coldest months were observed in 2005 and consequently imply a high value (>2 mmo·m^{-2}·d^{-1}) of the air-sea CO_2 fluxes.

4.2. Comparison with Other Data Fluxes Estimations

This sub-section highlights the differences between the CO_2 fluxes estimated during EGEE 3 in 2006, the climatology of [40], and the FOCAL 4 (F4, see **Table 2**) and FOCAL 8 (F8, see **Table 2**) cruises. EGEE 3 is chosen because it is the cruise during which fCO_2 were measured underway (see **Figure 1(c)**). The climatology of [40] was referenced to the year 2000 and has been built by averaging the CO_2 fluxes in our study area previously defined. The mean climatological fluxes in the northern (resp. in the southern) region reached 0.56 ± 0.24 mmol·m^{-2}·d^{-1} (resp. 0.74 ± 0.33 mmol·m^{-2}·d^{-1}). The weak difference between the northern and the southern fluxes (~0.18 mmol·m^{-2}·d^{-1}) implied that the north-south gradient was not well reproduced by the climatology of [40]. This could be due to the coarse resolution (4˚ latitude × 5˚ longitude) used in the climatology, which

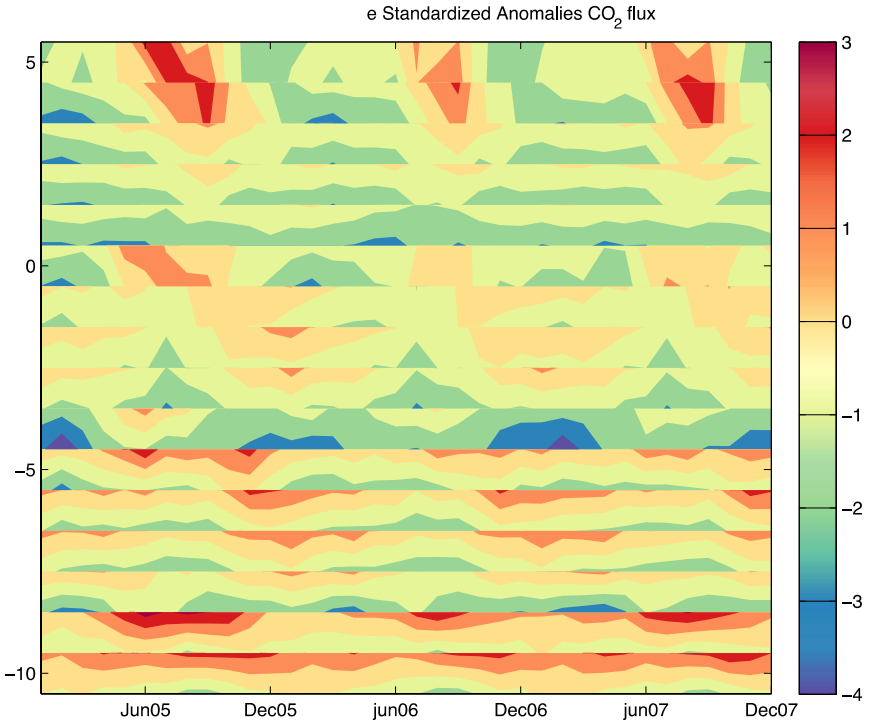

Figure 6. Hovmoller diagram for the standardized anomalies CO_2 fluxes.

tended to smooth the difference between northern and southern waters. In the case of F4 and F8, the comparison is made by averaging the CO_2 fluxes between 5˚N - 5˚S and along 4˚W where data were available.

From June to December, the climatology of [40] (**Figure 7**), F4 and F8 mean fluxes reached 0.95 ± 0.5 mmol·m^{-2}·d^{-1}, 0.56 ± 1.33 mmol·m^{-2}·d^{-1} and 0.82 ± 1.96 mmol·m^{-2}·d^{-1} respectively. Our estimated fluxes by using EGEE 3 (see **Figure 7**) were 2.30 ± 1.55 mmol·m^{-2}·d^{-1}. It was two times higher than that of the climatology of Takahashi *et al.* [40] and four times higher than that of the F4 cruise and finally, three times higher than that of F8. This difference of fluxes values could be explained by the local phenomena that were not taken into account by the coarse horizontal resolution of the climatology of [40]. During January - May, the mean fluxes from the climatology of [40] were almost constant and remained on average around 0.5 mmol·m^{-2}·d^{-1}. From June to December, the climatological mean fluxes had the same value (~1 mmol·m^{-2}·d^{-1}), then falls to 0.5 mmol·m^{-2}·d^{-1}. Over the same period, our estimated fluxes were higher than 1 mmol·m^{-2}·d^{-1}.

During F4 and F8 cruises, the fluxes reached −0.25 ± 0.79 mmol·m^{-2}·d^{-1} and −0.16 ± 1.27 mmol·m^{-2}·d^{-1} (resp. 1.28 ± 1.32 mmol·m^{-2}·d^{-1} and 1.71 ± 2.09 mmol·m^{-2}·d^{-1}) in the north (resp. in the south). The weak values in the north implied an equilibrium state with the atmosphere, while the high values in the south indicated that the region was a source. The climatology of [40] and the EGEE 3 estimated fluxes during the same months as F4 and F8, showed positive values indicating that both regions were sources. The evolution of the northern region from an equilibrium state (FOCAL, in 1983-1984) to a source area (EGEE 3 cruises, in 2006) is in agreement with the works of [41]. This author showed the increase of oceanic fCO_2 faster than the atmospheric CO_2 in the southern ocean. This fact implied the decrease of the oceanic CO_2 sink.

5. Conclusions

The purpose of this paper is to 1) assess the best annual air-sea CO_2 fluxes estimates and 2) quantify its seasonal and interannual variability in the Gulf of Guinea. EGEE data from June 2005 to September 2007 were used to realize this work.

The relationships established by [13] were validated over the year in comparison of measured and calculated fCO_2 from FOCAL 6, CITHER 1 and EQUALANT 99 cruises. These relationships were used to map monthly fields of TA and DIC on a 1˚ × 1˚ grid [42] from which, fCO_2 and monthly air-sea CO_2 fluxes were calculated

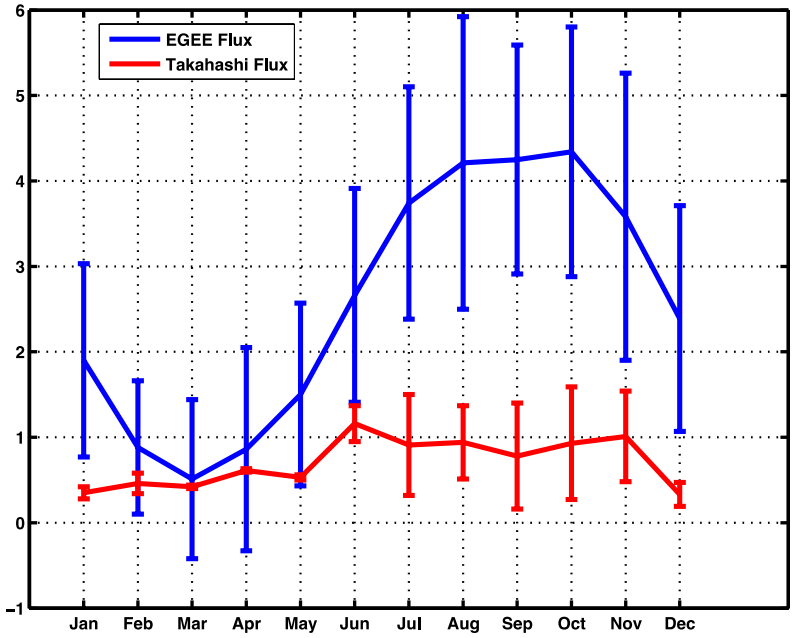

Figure 7. Evolution of climatological mean air-sea CO_2 fluxes (red line) and EGEE fluxes in 2006 (blue line) between 6˚N - 10˚S, 10˚W - 10˚E.

since the biological activity had a weak impact on the variability of the oceanic CO_2.

The ocean CO_2 source was higher in the south of the Equator than in the north. This was due to the upwelling system that transports DIC rich water at the surface. A north-south gradient was also observed in the distribution of the air-sea CO_2 fluxes in the Gulf of Guinea. The Guinea Current that allowed transporting eastward-unsalted waters due to precipitations and contributed to the dilution and the decrease of CO_2 in the north induces this gradient. In both regions, the air-sea CO_2 fluxes presented a clear seasonality with low values in January - May and high values in July - October. When using the same gas transfer coefficient [21], the climatology of [40] underestimated the CO_2 fluxes in comparison to our estimated fluxes. The differences were explained by the north-south gradient that was not well reproduced by the climatology of [40]. The coarse resolution of this climatology tended to smooth the difference between northern and southern waters. On an annual basis, the Gulf of Guinea was found to be a CO_2 source of the atmosphere. Although fCO_2 was calculated in this work, it could be interested to 1) include these complementary observations in fCO_2 data synthesis to better estimate the air-sea CO_2 fluxes in the tropical Atlantic and 2) study the temporal evolution of fCO_2.

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References

[1] Andrié, C., Oudot, C., Genthon, C. and Merlivat, L. (1986) CO_2 Fluxes in the Tropical Atlantic during FOCAL Cruises. *Journal of Geophysical Research*: *Oceans* (1978-2012), **91**, 11741-11755. http://dx.doi.org/10.1029/JC091iC10p11741

[2] Oudot, C., Ternon, J.-F. and Lecomte, J. (1995) Measurements of Atmospheric and Oceanic CO_2 in the Tropical Atlantic: 10 Years after the 1982-1984 FOCAL Cruises. *Tellus B*, **47**, 70-85. http://dx.doi.org/10.1034/j.1600-0889.47.issue1.8.x

[3] Bakker, D.C., Baar, H.J. de and Jong, E. de (1999) The Dependence on Temperature and Salinity of Dissolved Inor-

ganic Carbon in East Atlantic Surface Waters. *Marine Chemistry*, **65**, 263-280. http://dx.doi.org/10.1016/S0304-4203(99)00017-1

[4] Feely, R.A., Sabine, C.L., Lee, K., Berelson, W., Kleypas, J., Fabry, V.J., *et al*. (2004) Impact of Anthropogenic CO_2 on the $CaCO_3$ System in the Oceans. *Science*, **305**, 362-366. http://dx.doi.org/10.1126/science.1097329

[5] Le Quéré, C., Takahashi, T., Buitenhuis, E.T., Rödenbeck, C. and Sutherland, S.C. (2010) Impact of Climate Change and Variability on the Global Oceanic Sink of CO_2. *Global Biogeochemical Cycles*, **24**. http://dx.doi.org/10.1029/2009gb003599

[6] Ishii, M., Feely, R.A., Rodgers, K.B., Park, G.-H., Wanninkhof, R., Sasano, D., *et al*. (2014) Air-Sea CO_2 Flux in the Pacific Ocean for the Period 1990-2009. *Biogeosciences*, **11**, 709-734. http://dx.doi.org/10.5194/bg-11-709-2014

[7] Lenton, A., Tilbrook, B., Law, R., Bakker, D., Doney, S.C., Gruber, N., *et al*. (2013) Sea-Air CO_2 Fluxes in the Southern Ocean for the Period 1990-2009. *Biogeosciences*, **10**, 4037-4054. http://dx.doi.org/10.5194/bg-10-4037-2013

[8] Denman, K.L., *et al*. (2007) Couplings between Changes in the Climate System and Biogeochemistry. Climate Change 2007: The Physical Science Basis. In: Solomon, S., *et al*., Eds., *Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, 500-587.

[9] Gruber, N., Gloor, M., Mikaloff Fletcher, S.E., Doney, S.C., Dutkiewicz, S., Follows, M.J., *et al*. (2009) Oceanic Sources, Sinks, and Transport of Atmospheric CO_2. *Global Biogeochemical Cycles*, **23**. http://dx.doi.org/10.1029/2008gb003349

[10] Baker, D.F., Law, R.M., Gurney, K.R., Rayner, P., Peylin, P., Denning, A.S., *et al*. (2006) Trans Com 3 Inversion Intercomparison: Impact of Transport Model Errors on the Interannual Variability of Regional CO_2 Fluxes, 1988-2003. *Global Biogeochemical Cycles*, **20**.

[11] Takahashi, T., Sutherland, S.C. and Kozyr, A. (2009) Global Ocean Surface Water Partial Pressure of CO_2 Database: Measurements Performed during 1968-2008 (Version 2008). ORNL/CDIAC-152, NDP-088r, Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, US Department of Energy, Oak Ridge. http://cdiac.esd.ornl.gov/oceans/ndp_088/index.html

[12] Redelsperger, J.-L., Thorncroft, C.D., Diedhiou, A., Lebel, T., Parker, D.J. and Polcher, J. (2006) African Monsoon Multidisciplinary Analysis: An International Research Project and Field Campaign. *Bulletin of the American Meteorological Society*, **87**, 1739-1746. http://journals.ametsoc.org/doi/abs/10.1175/BAMS-87-12-1739 http://dx.doi.org/10.1175/bams-87-12-1739

[13] Koffi, U., Lefèvre, N., Kouadio, G. and Boutin, J. (2010) Surface CO_2 Parameters and Air-Sea CO_2 Flux Distribution in the Eastern Equatorial Atlantic Ocean. *Journal of Marine Systems*, **82**, 135-144. http://dx.doi.org/10.1016/j.jmarsys.2010.04.010

[14] Edmond, J.M. and Gieskes, J. (1970) On the Calculation of the Degree of Saturation of Sea Water with Respect to Calcium Carbonate under *in Situ* Conditions. *Geochimica et Cosmochimica Acta*, **34**, 1261-1291. http://dx.doi.org/10.1016/0016-7037(70)90041-4

[15] Dickson, A.G. and Goyet, C. (1994) Handbook of Methods for the Analysis of the Various Parameters of the Carbon Dioxide System in Sea Water. Version 2, Oak Ridge National Laboratory, Oak Ridge. http://dx.doi.org/10.2172/10107773

[16] Dickson, A.G. (1981) An Exact Definition of Total Alkalinity and a Procedure for the Estimation of Alkalinity and Total Inorganic Carbon from Titration Data. *Deep Sea Research Part A. Oceanographic Research Papers*, **28**, 609-623. http://dx.doi.org/10.1016/0198-0149(81)90121-7

[17] Parard, G., Lefèvre, N. and Boutin, J. (2010) Sea Water Fugacity of CO_2 at the PIRATA Mooring at 6˚S, 10˚W. *Tellus B*, **62**, 636-648. http://dx.doi.org/10.1111/j.1600-0889.2010.00503.x

[18] Huffman, G.J., Adler, R.F., Arkin, P., Chang, A., Ferraro, R., Gruber, A., *et al*. (1997) The Global Precipitation Climatology Project (GPCP) Combined Precipitation Dataset. *Bulletin of the American Meteorological Society*, **78**, 5-20. http://dx.doi.org/10.1175/1520-0477(1997)078<0005:TGPCPG>2.0.CO;2

[19] Weiss, R. (1974) Carbon Dioxide in Water and Seawater: The Solubility of a Non-Ideal Gas. *Marine Chemistry*, **2**, 203-215. http://dx.doi.org/10.1016/0304-4203(74)90015-2

[20] Boutin, J., Quilfen, Y., Merlivat, L. and Piolle, J.-F. (2009) Global Average of Air-Sea CO_2 Transfer Velocity from QuikSCAT Scatterometer Wind Speeds. *Journal of Geophysical Research Oceans*, **114**, C04007.

[21] Sweeney, C., Gloor, E., Jacobson, A.R., Key, R.M., McKinley, G., Sarmiento, J.L., *et al*. (2007) Constraining Global Air-Sea Gas Exchange for CO_2 with Recent Bomb ^{14}C Measurements. *Global Biogeochemical Cycles*, **21**, GB2015. http://dx.doi.org/10.1029/2006GB002784

[22] Naegler, T., Ciais, P., Rodgers, K. and Levin, I. (2006) Excess Radiocarbon Constraints on Air-Sea Gas Exchange and the Uptake of CO_2 by the Oceans. *Geophysical Research Letters*, **33**, L11802.

http://dx.doi.org/10.1029/2005GL025408

[23] Tsutsumi, Y., Mori, K., Hirahara, T., Ikegami, M. and Conway, T.J. (2009) Technical Report of Global Analysis Method for Major Greenhouse Gases by the World Data Center for Greenhouse Gases. WMO/TD-No. 1473.

[24] Foster, R.A., Subramaniam, A. and Zehr, J.P. (2009) Distribution and Activity of Diazotrophs in the Eastern Equatorial Atlantic. *Environmental Microbiology*, **11**, 741-750. http://dx.doi.org/10.1111/j.1462-2920.2008.01796.x

[25] Zeebe, R.E. and Wolf-Gladrow, D.A. (2001) CO_2 in Seawater: Equilibrium, Kinetics, Isotopes. Gulf Professional Publishing. http://store.elsevier.com/product.jsp?isbn=9780444509468

[26] Lefèvre, N. (2009) Low CO_2 Concentrations in the Gulf of Guinea during the Upwelling Season in 2006. *Marine Chemistry*, **113**, 93-101. http://dx.doi.org/10.1016/j.marchem.2009.01.001

[27] Mehrbach, C., Culberson, C.H., Hawley, J.E. and Pytkowicx, R.M. (1973) Measurement of the Apparent Dissociation Constants of Carbonic Acid in Seawater at Atmospheric Pressure. *Limnology and Oceanography*, **18**, 897-907. http://dx.doi.org/10.4319/lo.1973.18.6.0897

[28] Dickson, A.G. and Millero, F.J. (1987) A Comparison of the Equilibrium Constants for the Dissociation of Carbonic Acid in Seawater Media. *Deep Sea Research Part A. Oceanographic Research Papers*, **34**, 1733-1743. http://dx.doi.org/10.1016/0198-0149(87)90021-5

[29] Copin-Montégut, C. and Raimbault, P. (1994) The Peruvian Upwelling near 15 S in August 1986. Results of Continuous Measurements of Physical and Chemical Properties between 0 and 200 m Depth. *Deep Sea Research Part I*: *Oceanographic Research Papers*, **41**, 439-467. http://dx.doi.org/10.1016/0967-0637(94)90090-6

[30] Stramma, L. and Schott, F. (1999) The Mean Flow Field of the Tropical Atlantic Ocean. *Deep Sea Research Part II*: *Topical Studies in Oceanography*, **46**, 279-303. http://dx.doi.org/10.1016/S0967-0645(98)00109-X

[31] Picaut, J. (1983) Propagation of the Seasonal Upwelling in the Eastern Equatorial Atlantic. *Journal of Physical Oceanography*, **13**, 18-37. http://dx.doi.org/10.1175/1520-0485(1983)013<0018:POTSUI>2.0.CO;2

[32] Verstraete, J.-M. (1992) The Seasonal Upwellings in the Gulf of Guinea. *Progress in Oceanography*, **29**, 1-60. http://dx.doi.org/10.1016/0079-6611(92)90002-H

[33] Voituriez, B. (1981) Les sous-courants équatoriaux nord et sud et la formation des dômes thermiques tropicaux. *Oceanologica Acta*, **4**, 497-506.

[34] Wauthy, B. (1983) Introduction à la climatologie du Golfe de Guinée. *Océanographie Tropicale*, **18**, 103-138.

[35] Pérez, V., Fernández, E., Marañón, E., Serret, P. and García-Soto, C. (2005) Seasonal and Interannual Variability of Chlorophyll *a* and Primary Production in the Equatorial Atlantic: *In Situ* and Remote Sensing Observations. *Journal of Plankton Research*, **27**, 189-197. http://dx.doi.org/10.1093/plankt/fbh159

[36] Herbland, A. and Voituriez, B. (1979) Hydrological Structure Analysis for Estimating the Primary Production in the Tropical Atlantic Ocean. *Journal of Marine Research*, **37**, 87-101.

[37] Sverdrup, H.U., Johnson, M.W. and Fleming, R.H. (1942) The Oceans, Their Physics, Chemistry, and General Biology. Prentice-Hall, New York. http://ark.cdlib.org/ark:/13030/kt167nb66r/

[38] Antonov, J.I., Locarnini, R.A., Boyer, R.A., Mishonov, A.V. and Garcia, H.E. (2006) World Ocean Atlas 2005, Vol. 2: Salinity. US Government Printing Office, Washington DC.

[39] Marin, F., Caniaux, G., Giordani, H., Bourlès, B., Gouriou, Y. and Key, E. (2009) Why Were Sea Surface Temperatures So Different in the Eastern Equatorial Atlantic in June 2005 and 2006? *Journal of Physical Oceanography*, **39,** 1416-1431. http://dx.doi.org/10.1175/2008JPO4030.1

[40] Takahashi, T., Sutherland, S.C., Wanninkhof, R., Sweeney, C., Feely, R.A., Chipman, D.W., *et al*. (2009) Climatological Mean and Decadal Change in Surface Ocean pCO_2, and Net Sea-Air CO_2 Flux over the Global Oceans *Deep Sea Research Part I*: *Oceanographic Research Papers*, **56**, 2075-2076. http://dx.doi.org/10.1016/j.dsr.2009.07.007

[41] Metzl, N. (2009) Decadal Increase of Oceanic Carbon Dioxide in Southern Indian Ocean Surface Waters (1991-2007). *Deep Sea Research Part II*: *Topical Studies in Oceanography*, **56**, 607-619. http://dx.doi.org/10.1016/j.dsr2.2008.12.007

[42] McNeil, B.I., Metzl, N., Key, R.M., Matear, R.J. and Corbiere, A. (2007) An Empirical Estimate of the Southern Ocean Air-Sea CO_2 Flux. *Global Biogeochemical Cycles*, **21**, GB3011. http://dx.doi.org/10.1029/2007GB002991