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Estimates of the Fugacity of CO_2 in the Vridi Channel (Côte d'Ivoire)

Kouakou Urbain Koffi [a*], Marcel Konan Yao [b], Raoul Pêlèmayo Touré [c,d] and Koffi Sebastien Ouffoué [b]

[a] *Département des Sciences et Technologies, École Normale Supérieure, Abidjan, Côte d'Ivoire.*
[b] *Reaction and Constitution of Matter Laboratory, UFR SSMT, Université Felix Houphouet-Boigny, Côte d'Ivoire.*
[c] *Département des Sciences et Techniques, Université Alassane Ouattara, Bouaké, Côte d'Ivoire.*
[d] *Laboratory of Matter, Environmental and Solar Energy Sciences, Université Felix Houphouet-Boigny, Côte d'Ivoire.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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ABSTRACT

From July to November 2023 and in April 2024, surface waters were collected at three separate sampling sites within the Vridi channel, to measure physical and chemical parameters such as salinity, temperature, pH, Dissolved Inorganic Carbon (DIC). The fCO_2 and Total Alkalinity were calculated from pH and DIC. These surface waters were sampling during 4 seasons to study the variability of the carbonate system parameters. Low salinity and low temperature were observed in July -August because this period corresponded to high precipitation inducing salinity dilution and the appearance of coastal upwelling. High salinity and temperature were observed in a great dry season. In the whole, salinity and temperature have same trends of variability. Whatever the

**Corresponding author: E-mail: urban.koffi@gmail.com;*

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season, surface waters were oversaturated in fCO_2 with respect to atmospheric equilibrium in the Vridi channel except in dry season. On average the fCO_2 decreased from the great cold season to the hot season following marine season. Indeed, the high coastal upwelling appeared in July and disappeared in October. The variability of the channel fCO_2 followed the upwelling events along the coastal areas. Moreover, parameters such as Total Alkalinity (TA), Dissolved Inorganic Carbon and pH undergone the influence of coastal upwelling as fCO_2 in the Vridi channel.

Keywords: Atlantic Ocean; fugacity of CO_2; Total Alkalinity; Vridi channel; Ebrié system; lagoon.

1. INTRODUCTION

Inner estuaries and other near-shore ecosystems act as sources of CO_2 to the atmosphere due to their heterotrophic ecosystem metabolic status [1–4]. Lagoons are among the most common near-shore coastal environments occupying 13% of the World's coastline [5,6]. At the interface between terrestrial and marine environments, lagoons are subject to both continental and marine influences. Rivers, rain and ground water are the mainly continental inputs into the lagoons. These waters did 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 dissolved organic matter and nutrients arising from human activity in the vicinity of the lagoons. Coastal lagoon ecosystems are directly related to many processes *i.e*. coastal lagoons are dynamic, open systems where functions are dominated and controlled by the physical and chemical environment [7].

In coastal lagoons, Dissolved Inorganic Carbon (DIC), and particularly partial pressures of CO_2 (pCO_2) are driven by several thermodynamic and biotic factors, induced by river water inputs, tidal exchanges, mixing of water masses, photosynthesis and aerobic/anaerobic degradation of organic matter, precipitation/ dissolution of calcium carbonate, benthic/pelagic couplings, and air–water exchanges [8–10]. Seasonal measurements of the carbonate system parameters have been performed for instance across salinity gradient transects or strategically located stations along lagoon channels or estuaries [11–14].

In Côte d'Ivoire, [14] found that three lagoons (Potou, Ebrié, and Grand-Lahou) were oversaturated in CO_2 during all seasons. They behaved as CO_2 sources to the atmosphere due to net ecosystem heterotrophy and inputs of riverine CO_2 rich waters. While two lagoons (Aby and Tendo) were CO_2 sinks because they were undersaturated in CO_2 with respect to the atmosphere. Indeed, there was higher biological activities in these lagoons due too much phytoplankton concentration. Yet, very few systematic scientific works have been carried out in coastal lagoons in comparison to estuaries.

In this work, we describe the variability of CO_2 system parameters such as Dissolved Inorganic Carbon (DIC), pH, Total Alkalinity (TA) and fugacity of CO_2 (fCO_2) during four seasons in Vridi channel. This study characterizes the extent of seasonal variability in fCO_2 over an annual cycle, then to compare it with fCO_2 impacted by environmental factors in tidal waters.

2. MATERIALS AND METHODS

2.1 The Study Area and its Hydrography

Lagoons are the most prominent coastal ecosystems of Côte d'Ivoire covering an area of 1,200 km^2, corresponding to one of large fractions of the surface area of lagoons in West Africa [16].

The Vridi channel is situated in southern Côte d'Ivoire (Fig. 1). It is precisely located at longitude 4°0'50" W, latitude 5°15'23" N. This artificial estuary is achieved by the breakthrough of the spit near Jacqueville dam when performing the autonomous harbor of Abidjan in 1933. It runs from southwest (west jetty; channel entrance) to northeast (east jetty; channel exit). The Vridi channel is 2,700 m long, with an average width of 370 m and an average depth of around 18 m. Its eastern jetty, oriented towards the lagoon environment, has an average width of 370 m, an arm's length slope of 7.5 m and an average depth of -23.6 m. Its ocean-facing jetty has an average width of 350 m, a 6.5 m shoreline and an average depth of 29.5 m. Its draught is around 16 m, with an air draught of around 15 m.

Fig. 1. Three sampling sites location in Vridi channel during the study period (adapted from [15])

The water seasons of the Vridi channel have five seasons as follow: a hot season (HS) from February to April; a rainy season (RS) from May to July; a great cold season (GSC) from August to September; a flood season (FS) from October to November and; a short cold season (SCS) from December to January [17,18].

The rivers in Côte d'Ivoire have two different hydrological regimes [19]. 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 [14,20].

The watershed of this estuary is invaluable because of the presence of the Atlantic Ocean. On the continent, its watershed is related to that of Ebrié system [15]. Indeed, the aquatic ecosystem is an important autonomous Harbor of Abidjan, which is the one of the largest ports in West Africa. This port is home to the great industrial area of Côte d'Ivoire [21,22].

2.2 Data

This study was carried out over the period from July to November 2023 and in April 2024. During these periods, surface waters were collected at three separate sampling sites within the Vridi channel (Fig. 1)., to ensure optimum measurement accuracy of physical and chemical parameters. These samples were collected for a period of nine hours, with the aim of estimating the variability of carbonate system. Sampling was carried out as follows: the first sample was collected on July 2023 and the last on April 2024. Each measurement is assigned a number and a date with a 30-minute interval. On average, there were 18 measurements per day. 72 water samples were taken from a maximum depth of 2 m below the surface of the channel in polyethylene bottles. Once collected, the pH, salinity and temperature of these samples were measured in situ using a WTW 3630 IDS multiparameter with a precision of ±0.01, ±0.01 psu and ±0.1°C respectively. Next, the water samples were poisoned with a saturated $HgCl_2$ solution, to reduce the pH of the samples to below 2 m in order to inhibit the potential actions of the microorganisms. The samples were then hermetically sealed and stored in a cooler containing a significant quantity of ice. Sample processing and in situ storage were carried out in compliance with ISO 5667-3. Once in the laboratory, the Dissolved Inorganic Carbon (DIC) was determined using an automatic potentiometric titrimeter (titrando Metrohm) with 0.1 M HCl as titrant. TA and fCO_2 were computed from pH and DIC with based on the "CO2SYS" program configured by [23]. The estimated precision of fCO_2 and TA were estimated accuracy of ±4 µatm and ±4 µmol kg^{-1} respectively [24,25].

3. RESULTS AND DISCUSSION

3.1 Physical Features

In the Vridi channel, the measured salinity and temperature ranged from 4.62 psu to 31.65 psu, and from 24.9°C to 32.7°C respectively. On average, measured salinity and temperature in 2023 were still lower than those recorded in 2024 (Table 1). It is noticed that the maximum salinity as maximum temperature was observed in April 2024 and their weak values were reported in July-August 2023 (Fig. 2). Indeed, March is the end of great dry season along the coast [14,18,21,26,27]. During this period, there is no water from the rivers to dilute salinity in the Ebrié lagoon because of low precipitations on the coast and the temperature is high (> 30 °C). As salinity and temperature were collected early in April so they were impacted by a long dry season. Also, low salinity and low temperature were observed in July -August because in this period (Long Rainy Season) the precipitation is still high, salinity is diluted. Vridi channel is connected to the Atlantic Ocean then the coastal upwelling water with low temperature seemed to be recorded in our sampling sites. In the whole, salinity and temperature have same trends which are different when these two parameters were measured in the seawater. In coastal or open ocean and marginal sea, salinity and temperature exhibited contrasting variations [28–30].

Our measured salinity values are significantly higher than those obtained by [31] and [32]. Indeed, these authors carried out salinity measurements in the Adjin and Potou [31] and Aby [32] lagoons. Their measurements are below 1 psu, often close to zero despite a season. However, [14] carried out salinity measurements in four lagoons (Aby, Ebrié, Tendo, Potou and Tagba) whose values (15-20 psu) seem close to our own. Also, they highlighted that salinity in Ebrié lagoon presented strong longitudinal gradients with the highest salinities at the vridi channel but decreasing eastward and westward due to the freshwater inputs from some rivers.

Taking in account the season, if we compare our temperature values (Table 1) with those obtained by certain authors [14,31–33], they are slightly lower. Indeed, [33] found that the seasonal variation in temperature for Potou lagoon was 25.19-33.50 °C while for a recent period it averaged slightly high (29.21±0.43 °C) according to [31]. In situ temperatures for the Aby lagoon [32] have a range of values (27.72-30.73 °C) slightly exceeding those observed in our campaigns. Similar results were provided by [14] for study carried out on 4 lagoons, as in the case of salinity. Nevertheless, [31] found an average temperature for Adjin lagoon (26.72±0.09°C) quite close to our measurements (Table 1) following the season in April particularly.

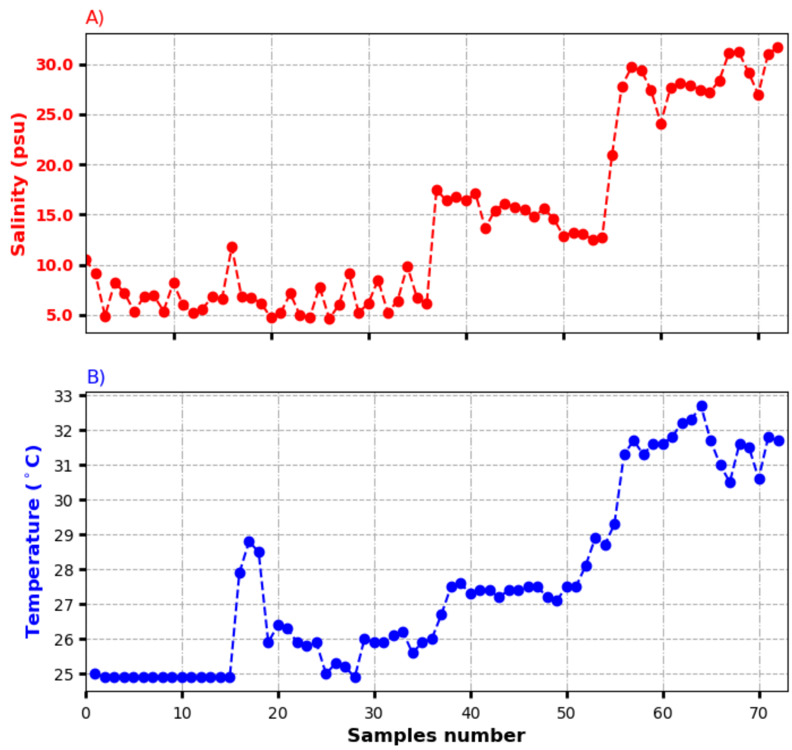

Fig. 2. Distribution of salinity (red: top panel) and temperature (blue: bottom panel) during the sampling period in Vridi channel

Table 1. Mean of physical and chemical parameters in Vridi channel

Date	Salinity (psu)	pH	Temperature (°C)	DIC (µmol/kg)	TA (µmol/kg)	fCO_2 (µatm)
16/07/2023	7.12±1.86	7.36±0.13	25.49±1.35	345.24±18.27	672.98±121.25	972.38±297.73
26/08/2023	6.38±1.57	7.09±0.21	25.79±0.43	349.30±5.78	482.02±147.50	1517.39±937.48
26/11/2023	15.01±1.62	7.41±0.16	27.55±0.53	494.18±244,32	496.80±242.50	562,40±329.85
06/04/2024	28.16±2.62	7.65±0.12	31.46±0.76	142.11±64.03	189.75±64.58	84.03±55.19

Mean ± 1σ: standard deviation (± 1σ)

3.2 Distribution of the CO_2 System Parameters (pH, DIC, TA and fCO_2)

3.2.1 Distribution of pH

On the sampling sites, the measurements of pH ranged between 6.75 and 7.85 (Fig. 3). The measured pH shows that in two different periods, the water in the Vridi canal was on average neutral. But in high rainy season and little dry season, pH values were slightly lower than those in November and April. This result is corroborated by [15] showing that from October 2018 to September 2019, highest pH was found in February to April period and its lowest value between October and November. Indeed, during the dry season the channel waters were fed essentially by the warm waters from the Atlantic Ocean. During the low rainy season, the warm Sudanese waters of the Comoé River settle completely in this channel.

According to the authors or the periods, the pH values obtained are slightly acidic, then neutral or slightly basic. For Potou lagoon, [33] found a range of values fairly close to acidity and basicity (5.20-7.90). The range of variation in pH remains fairly wide. Authors such as [31] and [14] provided pH values of 6.26-7.02 and 6.52-7.22 respectively in the neutral range, whose amplitudes are low. While [32] showed that Aby lagoon was almost basic (7.12-7.87). Only the latter result differs slightly from our measurements. Again, [15] mentioned that the superficial sediments were exposed to slightly neutral to basic water due the range of measured pH during all season.

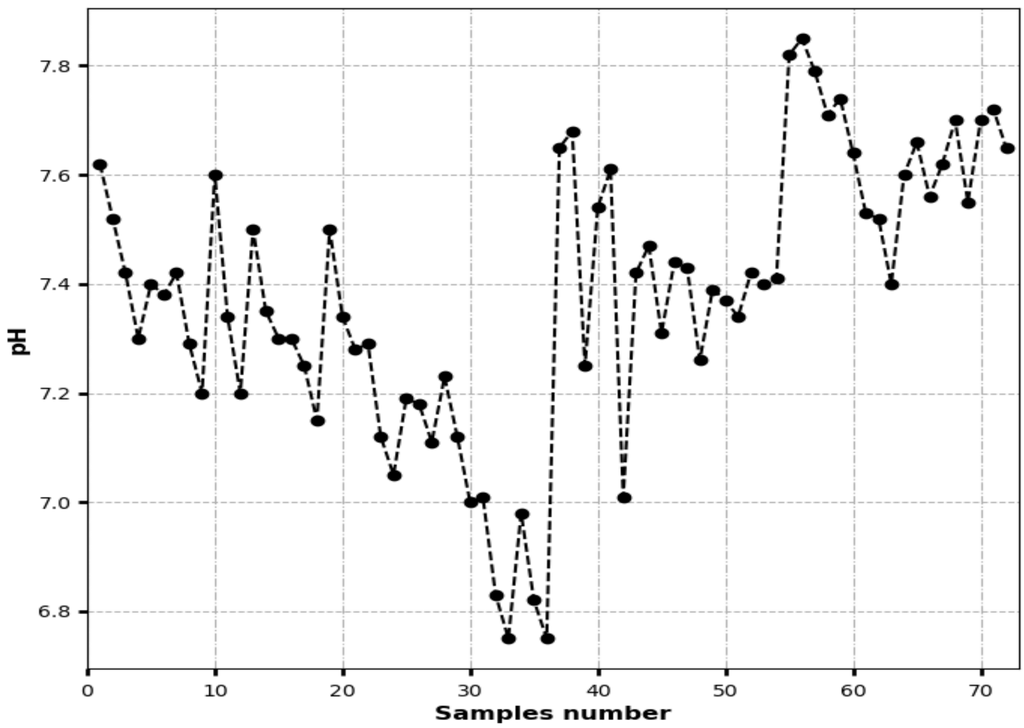

Fig. 3. Measurements of pH in Vridi channel during our study periods

3.2.2 Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) dynamics

TA as DIC values ranged from 102 to 1014 µmol/kg, and from 69 to 1016 µmol/kg respectively. On average TA and DIC were high in rainy season in comparison to the dry season. During the great cold period, the coastal upwelling water from the Atlantic Ocean moved to the Vridi channel. The upwelled water rich in CO_2 impacted the concentrations of TA and DIC. [14] found good relationships between TA and salinity according to the season and the sides of the Ebrié lagoon. Indeed, TA variability is due to the influence of many rivers such as Mé, Comoé and Agneby in eastern and western sides respectively. This paradox between the presence of these waters and the upwelling waters is explained by the exceptionally abundant rainfall experienced by Côte d'Ivoire during the long rainy season with on average 954 mm [34].

In addition, this channel is the transit point for many industries pollutant carried by the coastal rivers inputs from the continent particularly, and by the Atlantic Ocean [18,21,27]. This pollution is due to human activities such as the intensification of agriculture with the intensive use of chemical fertilizers in watersheds.

Using the whole dataset, we determined relationships between TA and salinity, DIC and salinity. The equations of the fit are given as follow:

$$TA= -16.66(\pm 2.35) * Sal + 696.48(\pm 39.5) \quad r^2 = 0.42 \quad (1)$$

$$DIC= -8.31(\pm 2.12) * Sal + 450.5(\pm 39.5) \quad r^2 = 0.18. \quad (2)$$

The standard error on the predicted TA and on the predicted DIC is ±179 µmol/kg, ±161 µmol/kg respectively. The standard errors were higher than those (TA: ±7.2 µmol/kg; DIC: ±16.6 µmol/kg) found during the EGEE cruises [28] showing clear discrepancy between measured and calculated TA and DIC respectively.

In the context of our study, an examination of the all of the channel data revealed a linear regression between TA and salinity with an r^2 value of 0.42 ($p = 9.1949E-10$). This means that only 42% of the variation in TA can be explained by the changes in salinity. It is important to notice that the correlation is relatively weak despite this correlation is significant. The weak correlation underlines that certain factors (not well captured in this study) other than salinity could significantly influence TA. Inaddition, the carbon cycle and marine ecosystems are influenced by terrestrial inputs, such as river outflow and upwelling dynamics in coastal areas [35,36]. As TA, relationship between DIC and salinity was established with an r^2 value (0.18) very weak ($p=0.0002$) but it is also significant. Consequently, the classic empirical relationships could not reproduce the concentrations of DIC in coastal waters, as it does not reflect the entire coastal lagoon dynamics that impact DIC spatio-temporal variability [37].

3.2.3 Distribution of CO_2 fugacity (fCO_2) in Vridi channel

In the channel, the highest fCO_2 (>3000 µatm) appeared in August 2023 and the lowest value (35 µatm) in April 2024 (Fig. 4). The peak-to-peak value is too much (~3000 µatm). This variability is related to the seasons as defined previously. Indeed, in July-August the channel undergoes the intrusion of the Atlantic Ocean. During this period, there are upwellings (equatorial and coastal) in the Atlantic Ocean which are responsible for the large CO_2 outgassing from the deep to the surface water [28,38].

As presented in Table 1, on average the fCO_2 decreased from the great cold season to the hot season. In fact, the high coastal upwelling appeared in July and disappeared in October, and the minor coastal upwelling was observed between February to March [39]. During dry season, water circulation is very weak in the lagoon except in its central part under tidal forcing [40]. So, the variability of the channel fCO_2 followed the upwelling events along the coastal areas.

In 2009, [14] showed up the range of fCO_2 variability in three rivers close to the Vridi channel. The mean of fCO_2 for these three rivers (Comoé, Tanoé and Bia rivers) was higher than the atmospheric equilibrium. These values of fCO_2 ranged between1925 µatm and 9595 µatm. These highest fCO_2 were due to the lowest biological activities or higher freshwater discharge. In addition, during rainy season, the Comoé freshwater discharge induces a strong circulation in the eastern part of the lagoon [40]. Thus, the precipitation recorded during the rainy periods have considerable impact on the coastal water characteristics at this location. By superimposing pH and fCO_2, it is noticed that

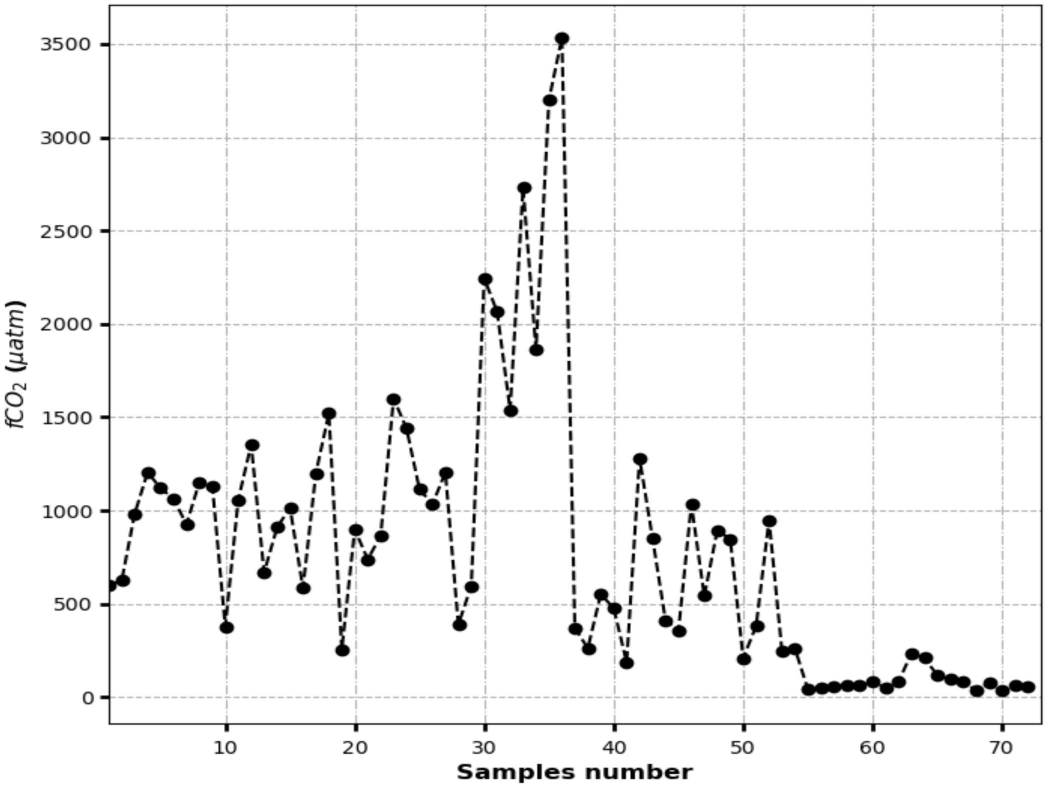

Fig. 4. Calculated fugacity of CO_2 (fCO_2) in Vridi channel

water became slightly acidic when there was an increase in fCO_2 at the surface water. The peak-to-peak value fCO_2 is about twice of our fCO_2 gap value.

During ROAM cruises from October 2018 to December 2020 in Jacqueville (Côte d'Ivoire) [29] close to the coast, calculated fCO_2 values often exceeded 1000 µatm in the July-August period because in this period, coastal upwelling was intense. Outside this period, mean fCO_2 values ranged from 500 µatm to 600 µatm. These show that coastal areas remain a source of CO_2 for the atmosphere, like the Vridi channel, even if fCO_2 values did not reach those of the Vridi Channel.

In the temperate coastal lagoon (France), some authors [41] found that fCO_2 values showed weak seasonal variations increasing from April 2008 (474±14 µatm) to September 2008 (515±36 µatm) before decreasing towards November 2008 (463 µatm). Indeed, they provided the impact of tide and biological activities on fCO_2 variability on a daytime or a year. Despite surface waters of the Arcachon lagoon were oversaturated in CO_2 with respect to the atmosphere fCO_2 (390 µatm), they are still lower in comparison of our results.

Also, in a tidal creek in the Duplin River salt marsh-estuary coastal ecosystem (Georgia, USA), strong seasonal and tidal/diurnal variations in fCO_2 were measured by [42] with values ranging from 500 µatm at high tide to 4,000 µatm at low tide and from 1,600 µatm at high tide to 12,000 µatm at low tide during the coldest and warmest months, respectively. Horizontal advection with the intrusion of river water into the creek at high tide can explain the lower measured values. These surface waters seemed oversaturated in CO_2 because this lagoon is still a source CO_2 all the season.

4. CONCLUSION

From July to November 2023 and in April 2024, surface waters were collected at three separate sampling sites within the Vridi channel, to ensure optimum measurement accuracy of physical and chemical parameters such as salinity, temperature, pH, Dissolved Inorganic Carbon (DIC), pH. The fCO_2 and Total Alkalinity were calculated from pH and DIC.

Low salinity and low temperature were observed in July -August because in this period because this period corresponded to high precipitation (salinity dilution) and the appearance of coastal upwelling (low temperature). High salinity and temperature were observed in a long dry season. In the whole, salinity and temperature have same trends of variability. Whatever the season, surface waters were oversaturated in fCO_2 with respect to atmospheric equilibrium in the Vridi channel except in dry season. On average the fCO_2 decreased from the great cold season to the hot season. Indeed, the high coastal upwelling appeared in July and disappeared in October. The variability of the channel fCO_2 followed the upwelling events along the coastal areas. Moreover, parameters such Total Alkalinity (TA), Dissolved Inorganic Carbon and pH undergone the influence the coastal upwelling as fCO_2 in the Vridi channel. In the temperate coastal lagoon (France), fCO_2 values showed weak seasonal variations increasing from April 2008 to September 2008 before decreasing towards November 2008. Despite the fCO_2 values were oversaturated in CO_2 with respect to the atmosphere fCO_2, they are still weaker in comparison of our results. Nevertheless, some lagoon areas have high fCO_2 values with values reaching 9500 µatm often. Also, others studies have shown the impact of tides inducing fCO_2 values of over 10000 µatm.

During ROAM cruises in Jacqueville (Côte d'Ivoire) close to the coast, fCO_2 values often exceeded 1000 µatm in the July-August period because in this period, coastal upwelling was intense. Despite these high fCO_2 values, the study area released on average less CO_2 to the atmosphere in comparison to the Vridi channel.

This study is limited on a seasonal variability of chemical and physical parameters because the measurements did not take account the impact of the tides on these parameters. In addition, it will be useful to have a time-series to better estimate the fCO_2 with uncertainty in the Vridi channel. Also, time-series data could help to study the impact of the pH on the plankton in the channel.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc) and text-to-image generators have been used during writing or editing of manuscripts.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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