Atmospheric CO_2 flux from mangrove surrounding waters

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[1] The partial pressure of CO_2 (pCO_2) was measured at daily and weekly time scales in the waters surrounding mangrove forests in Papua New Guinea, the Bahamas and India. The pCO_2 values range from 380 to 4800 μatm. These data, together with previously published data, suggest that overall oversaturation of CO_2 with respect to atmospheric equilibrium in surface waters is a general feature of mangrove forests, though the entire ecosystems (sediment, water and vegetation) are probably sinks for atmospheric CO_2. The computed CO_2 fluxes converge to about $+50$ mmolC m^{-2} day^{-1}. If this conservative value is extrapolated for worldwide mangrove ecosystems, the global emission of CO_2 to the atmosphere is about 50×10^6 tC year^{-1}. Based on this tentative estimate, mangrove waters appear to be regionally a significant source of CO_2 to the atmosphere and should be more thoroughly investigated, especially at seasonal time scale. INDEX TERMS: 4806 Oceanography: Biological and Chemical: Carbon cycling; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4820 Oceanography: Biological and Chemical: Gases; 4231 Oceanography: General: Equatorial oceanography; 4235 Oceanography: General: Estuarine processes. Citation: Borges, A. V., S. Djenidi, G. Lacroix, J. Théate, B. Delille, and M. Frankignoulle, Atmospheric CO_2 flux from mangrove surrounding waters, Geophys. Res. Lett., 30(11), 1558, doi:10.1029/2003GL017143, 2003.

1. Introduction

[2] Mangroves are among the most productive coastal intertidal ecosystems in the world, confined to the tropics and subtropics, that dominate approximately 75% of the world's coastline between 25°N and 25°S, and are estimated to cover between 0.17 and 0.20×10^6 km^2. The mangrove ecosystem as a whole (aquatic, below- and above-ground compartments) is net autotrophic, but the water column and the sediment are largely net heterotrophic, due to three processes: (1) aquatic primary production is limited by high turbidity, canopy shadow and large changes in salinity; (2) water column and sediments receive important quantities of leaf and wood litter from the overlying canopy; (3) export of labile organic carbon from mangroves to adjacent aquatic systems, although variable from one site to another, can be low [see *Jennerjahn and Ittekkot*, 2002]. Consequently, the mangrove surrounding waters should act as a net source of CO_2 to the atmosphere, although no attempt has been made so far to estimate its magnitude.

2. Sites and Methods

[3] Nagada Creek (5°09′S 145°48′E) is a small tidal creek (3 km long, 400 m wide) in the northern Papua New Guinea coast, that opens to Nagada Lagoon. The latter is a wide lagoon (maximum width 5 km) separated from the Pacific Ocean by a continuously submerged barrier reef. Nagada Creek is fringed by well developed mangroves while seagrass beds and submerged reefs are mainly present at the mouth of the creek. Gaderu Creek (16°50′N 82°19′E) is the main tidal creek connecting the Godavari estuary (Anhra Pradesh, east coast of India) to the semi-enclosed shallow Kakinada Bay. It has a total length of 11 km (about 30 m wide and 4 m deep) and consists of intertidal mudflats, most of which are covered by mangrove forest and no seagrass beds or coral reefs are found nearby. Norman's Pond Cay (23°46′N 76°07′W) is one of the many Exuma Cays islands (Bahamas archipelago) which form the boundary between the shallow Great Bahama Bank and the deep Exuma Sound. Norman's Pond (about 500 m long and wide, 2 m deep), is a brackish to hypersaline pond where a dense mangrove is present. It is located in the southern part of the Norman's Pond Cay and connected to the leeward shore of the island by a tidal channel.

[4] In Papua New Guinea (July–August 2000), pH, Total Alkalinity (TAlk), salinity and water temperature were sampled every second day around 10:00 (local time), during 2 weeks, in a small (400 m long, 100 m wide) and shallow (3 m deep) cove surrounded by dense mangrove in the upper part of Nagada Creek (5°9′N 145°47′E). About 1 h later, a second station (5°9′N 145°48′E) located in Nagada Lagoon, near the mouth of Nagada Creek, was sampled. In the Bahamas (December 2000), we used a floating equilibrator system (FES) to carry out three 24 h cycles of pCO_2, water temperature and wind speed measurements, with an one minute sampling interval. Two daily cycles were carried out in Norman's Pond (23°46′N 76°07′W) and one at Block Rock (23°49′N 76°10′W) in Bock Cay. The FES consists of an equilibrator mounted on a buoy, including batteries, a solar panel, air and water temperature probes, an anemometer and a data logger. A non-dispersive infrared gas analyser (Li-Cor, Li-6262) was used to measure pCO_2 by equilibration, with an estimated accuracy of ±5 μatm. In India (June 2001), we carried out a 24 h cycle in Gaderu Creek (16°47′N 82°18′E) with measurements of pH, TAlk, salinity, temperature and dissolved oxygen sampled every hour. The same variables were also sampled during a survey of Kakinada Bay (28 May 2001) and along a transect in the Godavari estuary (1 June 2001). In Papua New Guinea and India, wind speed measurements were made with a hand-held anemometer and all dissolved variables, except TAlk, were measured on site with portable instruments. For a detailed description of the pH and TAlk measurement methods, the computations of pCO_2 and DIC (Dissolved Inorganic Carbon) from pH and TAlk and the calibration procedure of the Li-6262 refer to *Frankignoulle and Borges* [2001].
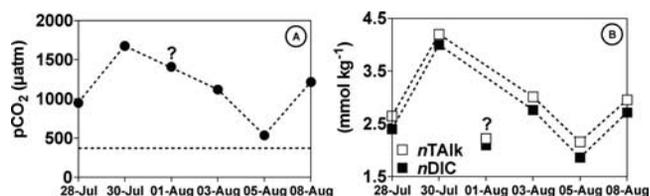
Figure 1. Variations of pCO$_2$ (full circles), nTAlk (open squares) and nDIC (full squares) in July–August 2000, in Nagada Creek (Papua New Guinea). Horizontal dotted line corresponds to atmospheric equilibrium.

3. Results and Discussion

3.1. pCO$_2$, DIC and TAlk Dynamics

[5] In Nagada Creek (Papua New Guinea), pCO$_2$ values vary from 540 to 1680 μatm, during the 12 days sampling period (Figure 1A). Normalized TAlk (nTAlk) and normalized DIC (nDIC) follow closely the pCO$_2$ evolution, except for the sample from August 1 (Figure 1B). This strongly suggests that the same process increases the three variables. Furthermore, this process is specific to the mangrove because the average pCO$_2$, nTAlk and nDIC values are significantly higher than those in the adjacent Nagada Lagoon (Table 1). In Gaderu Creek (India), the pCO$_2$ variations are striking during the 24 h cycle, with values ranging between 1380 and 4770 μatm (Figure 2A). As in Nagada Creek, nTAlk and nDIC follow the trend of pCO$_2$ (Figure 2B). Also, the average pCO$_2$, nTAlk and nDIC values are much higher than those in the adjacent Godavari estuary and those in Kakinada Bay (Table 1). On first analysis, pCO$_2$, nDIC and Oxygen saturation level (%O$_2$) exhibit the patterns expected from the daily cycle of primary production and respiration (decrease of pCO$_2$ and nDIC until sunset, increase of pCO$_2$ and nDIC during the night until dawn, and %O$_2$ showing the inverse trend). However, there are two inconsistencies with this interpretation. First, pCO$_2$ and nDIC strongly decrease (and %O$_2$ increases) one hour before sunrise. Second, pCO$_2$ and nDIC values remain almost constant from 22:00 to 05:00, instead of increasing regularly throughout the night as expected from respiration (%O$_2$ evolution shows the same trend). A closer look at Figure 2 reveals that the lowest pCO$_2$, nTAlk and nDIC values correspond to high tide and the highest values are observed at low tide (%O$_2$ shows the inverse trend), and, coincidently high tide occurred at dusk.

[6] To explain the daily variations of various chemical parameters during three 24 h cycles in the creek waters of a

Table 1. Average ± Standard Deviation of pCO$_2$ (μatm), nDIC (mmol kg^{-1}) and nTAlk (mmol kg^{-1}) at the Different Sites in Papua New Guinea (top half of table) and India (bottom half of table)

	pCO$_2$	nDIC	nTAlk
Nagada Creek (6)	1180 ± 360	2.6 ± 0.79	2.9 ± 0.7
Nagada Lagoon (6)	585 ± 200	1.8 ± 0.1	2.1 ± 0.1
Gaderu Creek (25)	2565 ± 868	2.5 ± 0.1	2.6 ± 0.1
Godavari estuary (2)[a]	465 ± 20	1.9 ± 0.2	2.2 ± 0.2
Kakinada Bay (9)	500 ± 125	1.7 ± 0.1	2.0 ± 0.1

DIC and TAlk were normalized to a constant salinity close to the mean of the sampled values: 34 in Papua New Guinea and 30 in Gaderu Creek. Numbers in brackets are the number of samples.

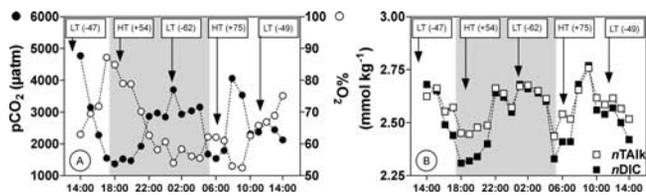[a]For the same salinity range (28.4–31.6) as the one sampled at Gaderu Creek.

Figure 2. Variations of pCO$_2$ (full circles), %O$_2$ (open circles), nTAlk (open squares) and nDIC (full squares) during a 24 h cycle in Gaderu Creek (India, 4–5 June 2001). High tide (HT) and low tide (LT) are given in cm, relative to mean sea level, based on tide tables for Kakinada harbour. The shaded area corresponds to night-time. %O$_2$ is computed from observed O$_2$ concentration (O$_{2observed}$) and O$_2$ concentration at saturation (O$_{2saturation}$) according to: %O$_2$ = O$_{2observed}$/O$_{2saturation}$.

Brazilian mangrove, *Ovalle et al.* [1990] suggested the following mechanism: during the ebb and at low tide, there is a strong influx of porewater that mixes with the creek water, substantially affecting the chemical properties of the latter. During the flow, the migration of porewater towards the creek strongly decreases until it stops when the sediment surface is inundated at high tide. The time course of nTAlk and nDIC in Gaderu Creek fits well with this hypothesis, as it is a well established fact that mangrove porewaters have a high TAlk and DIC content [e.g. *Ovalle et al.*, 1990; *Middelburg et al.*, 1996; *Alongi et al.*, 2001; *Kristensen et al.*, 2000]. *Ovalle et al.* [1990] explain the high porewater TAlk by sulfate reduction that along with aerobic respiration, account for almost all the diagenetic carbon degradation in mangroves. Generally, sulfate reduction is the major diagenetic pathway in mangroves [e.g. *Alongi et al.*, 1998], but in some cases aerobic degradation predominates [*Alongi et al.*, 2001], and in one Thai mangrove, iron reduction was reported as the dominant process [*Kristensen et al.*, 2000].

[7] The relative variation of TAlk and DIC follows a well established stochiometry that is specific to the biogeochemical process controlling these variables. In Nagada Creek, nTAlk and nDIC are well correlated and the slope of the
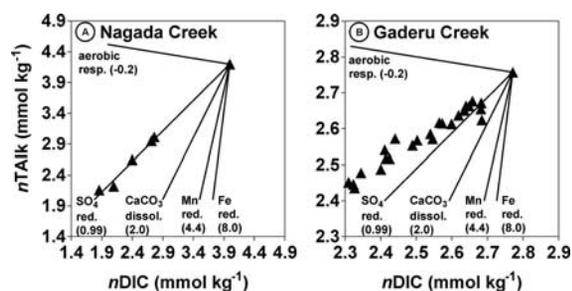

Figure 3. nTAlk *versus* nDIC in Nagada Creek (Papua New Guinea) and Gaderu Creek (India). Solid lines correspond to the theoretical evolution to attain the highest nTAlk and nDIC values for the potential biogeochemical processes that can control these variables: areobic respiration (areobic resp.), sulfate reduction (SO$_4$ red.), calcium carbonate dissolution (CaCO$_3$ dissol.), manganese reduction (Mn red.) and iron reduction (Fe red.). Numbers in brackets correspond to the theoretical slope of the relative variation of nTAlk and nDIC for each of the biogeochemical processes.
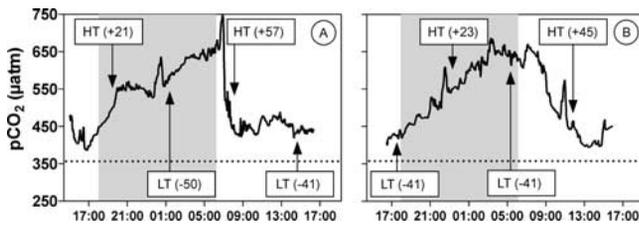
Figure 4. pCO$_2$ variations during two 24 h cycles in Norman's Pond (Bahamas) carried out on 10–11 December 2000 (A) and 14–15 December 2000 (B). Horizontal dotted line corresponds to atmospheric equilibrium. Measurements of high tide (HT) and low tide (LT) are given in cm, relative to mean sea level and were obtained nearby but outside the pond. The shaded area corresponds to night-time.

regression line (0.99 ± 0.04, r^2 = 0.994, N = 6) is very close to the one predicted if sulfate reduction was the main biogeochemical process controlling these variables, and assuming a net accumulation of FeS in the sediments (Figure 3A). In Gaderu Creek, the slope of the regression line of nTAlk and nDIC is also highly significant (0.61 ± 0.03, r^2 = 0.945, N = 25) but lower than the one predicted assuming that sulfate reduction is the only biogeochemical process controlling these variables (Figure 3B). This suggests that in this system areobic respiration also strongly contributes to the TAlk and DIC dynamics. Another mechanism that could explain such a pattern is the oxidation in the water column of H$_2$S released for the sediments. This would decrease nTAlk but leave nDIC unaffected.

[8] The input to the creek of porewater with a high DIC and TAlk content can explain the weekly variability of pCO$_2$, nDIC and nTAlk in Nagada Creek (Figure 1). Indeed, the highest values were observed either at low tide or during the ebb, and the lowest values (August 5) were obtained at high tide. The corresponding values of pCO$_2$, nTAlk and nDIC, respectively, 538 μatm, 2.16 and 1.86 mmol kg^{-1}, are close to the average values of Nagada Lagoon waters (Table 1).

[9] In Norman's Pond, the range of pCO$_2$ variations was 385–750 μatm during the first 24 h cycle and 395–690 μatm during the second one (Figure 4). The daily change of pCO$_2$ during both 24 h cycles follows the general pattern expected from the diel alternation between photosynthesis and respiration. No significant pCO$_2$ signature is associated to low or high tides. This could be due to the fact that, in this semi-enclosed system, the tidal amplitude is smaller than outside the pond and the input of porewater is therefore

less marked and less dependent on tidal inundation as described for Nagada Creek and Gaderu Creek. The average pCO$_2$ values during both 24 h cycles in Norman's Pond (516 ± 83 (sd, standard deviation, N = 1521) μatm and 531 ± 89 (sd, N = 1403) μatm) are significantly higher than the average pCO$_2$ value obtained during the 24 h cycle carried out at Block Rock, close to Bock Cay, (396 ± 7 (sd, N = 1461) μatm). Furthermore, the range of daily variations is one order of magnitude lower at Block Rock, as indicated by the standard deviation values. These differences are most probably related to the absence of mangrove forest on Bock Cay and the fact that this cycle was carried out in the open waters of the Bahamas Bank.

3.2. Air-Water CO$_2$ Fluxes

[10] The air-water CO$_2$ fluxes (F) were computed according to the equation F = α.k.ΔpCO$_2$, where α is the solubility coefficient of CO$_2$, k is the gas transfer velocity of CO$_2$ and ΔpCO$_2$ is the air-water gradient of pCO$_2$. We used the relationship of k as a function of wind speed given by *Carini et al.* [1996], based on a SF$_6$ release experiment in the Parker River estuary. This formulation was preferred to those used for open oceanic waters because mangrove systems are relatively similar to estuary ones from a physical point of view (shallow and relatively sheltered). Note that the *Carini et al.* [1996] relationship gives lower k values when compared to other relationships developed for estuaries [see *Raymond and Cole*, 2001], probably because of strong fetch-limitation and low tidal currents in the Parker River estuary, so the fluxes we computed are minimal estimates. The strongest atmospheric CO$_2$ fluxes were computed for Gaderu Creek and the lowest for Norman's Pond, in accordance with the ΔpCO$_2$, in spite of relatively different wind speed values at each site (Table 2). The error on the flux computations taking into account the estimated uncertainty on ΔpCO$_2$ of ±5 μatm yields ±4% for Norman's Pond, ±1% for Nagada Creek, ±0.3% for Gaderu Creek, increasing with decreasing values of ΔpCO$_2$. If an uncertainty of ±5% on the wind speed measurements is added, then the error on the flux computations becomes, on average, ±10% for Norman's Pond, ±5% for Nagada Creek, ±2% for Gaderu Creek. A further bias in the CO$_2$ flux computations could arise from the representativeness of the immediate wind measurements for each site. However, it is not possible to evaluate this source of uncertainty because of the absence of meteorological stations at the studied sites. Finally, the fluxes computed with the *Carini et al.* [1996] relationship are on average, for the three sites, 25% lower than those computed with the *Raymond and Cole* [2001]

Table 2. Average ± Standard Deviation of Wind Speed (m s^{-1}), CO$_2$ Gas Transfer Velocity (k in cm h^{-1}) as Formulated by *Carini et al.* [1996], the pCO$_2$ Air-Water Gradient (ΔpCO$_2$ in μatm) and the Atmospheric CO$_2$ Flux (mmolC m^{-2} day^{-1}), for the Three Study Sites Plus Published Data in Four Other Sites

Site	wind speed	k	ΔpCO$_2$	Atmospheric CO$_2$ flux	refs
Nagada Creek (Papua New Guinea ∼ 5°S 146′E)	3.0 ± 2.1	8 ± 6	799 ± 357	43.6 ± 33.2	1
Gaderu Creek (India ∼ 17°N 82°E)	1.4 ± 1.9	4 ± 5	2215 ± 864	56.0 ± 100.9	1
Norman's Pond (Bahamas ∼ 23°N 76°W)	5.5 ± 1.3	13 ± 3	165 ± 86	13.8 ± 8.3	1
Saptamukhi Creek (India ∼ 22°N 89°E)	nd	4[a]	2210 ± 1460	56.7 ± 37.4	2
Mooringanga Creek (India ∼ 22°N 89°E)	nd	4[a]	830 ± 363	23.2 ± 10.1	2
Itacuraçá Creek (Brazil ∼ 23°S 44°W)	nd	4[a]	3845 ± 3520	113.5 ± 104.4	3
Florida Bay (U.S.A. ∼ 25°N 81°W)	nd	4[a]	170 ± 200	4.6 ± 5.4	4

[a]Taken as constant (see text). nd. no data. 1. This study. 2. *Ghosh et al.* [1987]. 3. Based on the pH and TAlk data from *Ovalle et al.* [1990] and computed using the thermodynamic constants described by *Frankignoulle and Borges* [2001]. 4. *Millero et al.* [2001].

relationship, that is based on a compilation of k values from various estuaries and using different methodologies.

[11] All the pCO$_2$ data available, to our best knowledge, in literature for the waters surrounding mangrove forests are summarised in Table 2. As for our three study sites, CO$_2$ oversaturation is observed in other mangrove waters, although highly variable from one site to another. Since wind speed is not reported in these publications, the corresponding air-water CO$_2$ fluxes were computed using a constant k value of 4 cm h^{-1}, that is in the lower range of the k values from our study sites (Table 2). The choice of this low value is based on the fact that the study sites are, except Florida Bay, narrow creeks that seem relatively well sheltered as Gaderu Creek. The range of the CO$_2$ fluxes is high but in agreement with the one computed for our three study sites.

4. Synthesis

[12] Based on the above CO$_2$ data, we can speculate that oversaturation of CO$_2$ with respect to atmospheric equilibrium is the general feature in the waters surrounding mangrove forests. Although information on the seasonal variability of CO$_2$ fluxes in mangrove waters is missing, we feel that CO$_2$ flux data in 7 mangrove ecosystems, covering both subtropical and tropical latitudes, allow us to attempt a preliminary extrapolation and global integration. The computed air-water CO$_2$ fluxes converge to a value of about 50 mmolC m^{-2} day^{-1}, although the range of variability encompasses one order of magnitude. If we extrapolate this conservative value to the surface area of worldwide mangrove ecosystems ($\sim$0.2 10^6 km^2) the global emission of CO$_2$ to the atmosphere would be about 50 10^6 tC year^{-1}. This emission is comparable to the global estimation of leaf litter remineralized within mangroves (23 10^6 tC year^{-1}), according to a recent review of literature [*Jennerjahn and Ittekkot*, 2002]. It should be noted that the CO$_2$ flux integration was made over the surface area of the mangrove forests per se but that the surface area of the waters directly influenced by mangroves, although unknown, is probably higher. This CO$_2$ emission can be considered modest at a global scale since the net open oceanic CO$_2$ sink is globally of about 2.2 GtC year^{-1}. On a regional scale, the subtropical and tropical open oceanic waters behave as a net source of CO$_2$ of about 0.43 GtC year^{-1} [between 32°N and 32°S, based on *Takahashi et al.*, 1997, extracted from the internet at http://ingrid.ldeo.columbia.edu/SOURCES/ .LDEO/.Takahashi/]. Thus, mangrove surrounding waters would be an additional CO$_2$ source of about 12% to the one of open oceanic waters, in tropical and subtropical latitudes, with a surface area about one thousand times smaller.

[13] Further research is needed to better evaluate the role of mangrove ecosystems in the global carbon cycle. The sediments of human impacted mangroves are known to be more acidic than natural ones [*Middelburg et al.*, 1996], while, the dominant diagenetic organic carbon degradation pathway of recently reclaimed mangroves is different than in natural (old) ones [*Alongi et al.*, 1998]. The impact of these processes on DIC dynamics of the adjacent waters and related CO$_2$ fluxes has not yet been investigated. Also, about 20% of the global production and about 30% of the global accumulation of CaCO$_3$ occur in tropical latitudes, but the role of mangrove ecosystems as a sink of CaCO$_3$ still remains to be determined [*Middelburg et al.*, 1996]. Finally, the open continental shelf areas adjacent to mangrove forests influenced by their organic carbon and nutrient inputs should also investigated from the point of view of atmospheric CO$_2$ fluxes.

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