Carbon Dioxide Daily Variations and Atmospheric Fluxes Over the Open Waters of the Great Bahama Bank and Norman's Pond Using a Novel Autonomous Measuring System

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ABSTRACT.—A novel autonomous measuring device that acquires the partial pressure of CO_2 (pCO_2) by equilibration and several other parameters is described. This device, the Floating Equilibrator System (FES) was tested in field conditions for the first time in the Great Bahama Bank, in December 2000. We successfully carried out two 24 h cycles in Norman's Pond, one in front of the Caribbean Marine Research Centre (CMRC) and another one near Bock Cay. Over-saturation of CO_2 with respect to atmospheric equilibrium was observed systematically at the three sites, although significantly more marked at Norman's Pond. The higher values of pCO_2 and atmospheric CO_2 fluxes obtained at Norman's Pond, than in the adjacent open waters of the Great Bahama Bank, suggest a comparatively stronger heterotrophy at Norman's Pond. This is most likely related to the organic carbon inputs to the water column and sediments from the dense mangrove forest surrounding Norman's Pond. The larger amplitude of pCO_2 daily variations observed, during the Norman's Pond 24 h cycles, is probably due to higher biological activity than in the adjacent open waters of the Great Bahama Bank. This is corroborated by a tentative estimation of Gross Primary Production based on simple computations. We speculate that calcification could also contribute to some extent to different amplitude of the pCO_2 daily variations between the mangrove pond and the open waters of the Great Bahama Bank.

INTRODUCTION

Based on organic carbon flux budgets in the temperate coastal ocean, the overall picture of net ecosystem metabolism is that open continental shelves—bordered by a continental margin—are net autotrophic. These areas are net exporters of organic carbon and potential sinks for atmospheric CO_2. Near-shore systems influenced by anthropogenic and/or terrestrial organic carbon inputs, in particular estuaries, are net heterotrophic (Smith and Mackenzie 1987; Gattuso et al. 1998; Mackenzie et al. 2000; Rabouille et al. 2001).

This picture was recently confirmed by direct measurements of the air-water gradient of pCO_2 with a sufficient temporal and spatial resolution to allow the annual integration of the computed air-water CO_2 fluxes. Open continental shelves are net sinks for atmospheric CO_2 (Tsunogai et al. 1999; Borges and Frankignoulle 2001, 2002a, 2002b; DeGranpre et al. 2002; Borges and Frankignoulle 2003), while estuaries are net sources of CO_2 to the atmosphere (Frankignoulle et al. 1998; Borges and Frankignoulle 1999; Cai et al. 2000; Raymond et al. 2000; Borges and Frankignoulle 2002c).

Other coastal ecosystems that could be significant sources of CO_2 are the waters surrounding mangrove forests. Although the mangrove ecosystem as a whole (aquatic, below- and above-ground compartments) is net autotrophic; aquatic primary production is often limited by high turbidity, canopy shadow and large changes in salinity. In addition, the water column and sediments receive important quantities of leaf and wood litter from the overlying canopy. Export of labile organic carbon from mangroves to adjacent aquatic systems, although variable from one site to another is often considered to be low. The water column and the sediment metabolisms are largely net heterotrophic (see Alongi 1998; Gattuso et al. 1998; Jennerjahn and Ittekkot 2002, for reviews). Consequently,

pCO$_2$ values should be high and mangrove surrounding waters should act as a net source of CO$_2$ to the atmosphere, although the magnitude of the corresponding CO$_2$ emission has not yet been quantified. Few published data are available on dissolved inorganic carbon (DIC) variability in the water column of mangrove ecosystems, and, to our best knowledge, these were from two Indian mangrove creeks (Ghosh et al. 1987), from a Brazilian mangrove creek (Ovalle et al. 1990) and from Florida Bay, influenced by input waters from the mangrove fringe (Millero et al. 2001).

We report pCO$_2$ daily variations in Norman's Pond, a cove surrounded by a dense mangrove forest and on the open waters of the Great Bahama Bank, using a novel autonomous measuring device.

SITE DESCRIPTION

The Great Bahama Bank is a shallow (about 5 m) carbonate platform (95000 km^2 of which 7100 km^2 of land) that encompasses a variety of tropical environments: coral reefs, seagrass meadows and mud/ sand flats with mangroves. Sediments are almost exclusively formed of calcium carbonate mainly as aragonite. Coral reefs cover an area of about 1800 km^2; are present close the islands shore and along the platform margins. The main species of hermatypic corals that contribute to reef-building are: *Montastrea annularis*, *M. cavernosa*, *Acropora palmata*, *A. cervicornis*, *Siderastrea siderea*, *Diploria labyrinthiformis* and *Porites porites*. Seagrass beds are found in lagoons and sheltered bays and the three most encountered species are: *Thalassia testudium*, *Syringodium filiforme* and *Halodule wrightii*. Mangrove forests are along the margins of many lagoons and sheltered bays and exhibit the typical zonation (from shore landward): *Rhizophora mangle*, *Avicennia germinans*, *Laguncularia racemosa* and *Conocarpus erectus*.

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 within the southern part of Norman's Pond Cay (Fig. 1) and connected
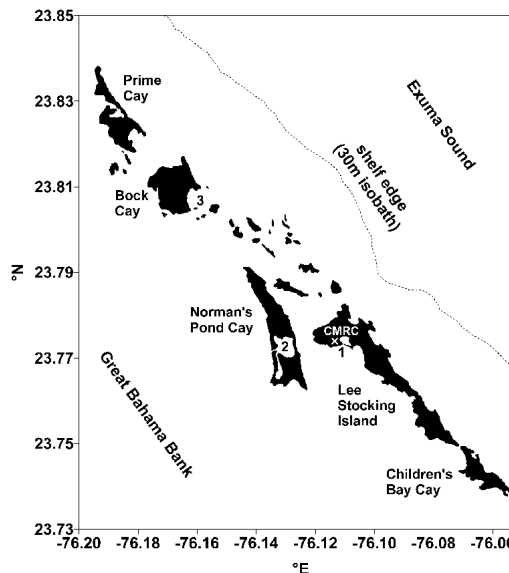

FIG. 1. Study site map showing the four stations where 24 h measurement cycles were carried out. 1. In front of the Caribbean Marine Research Centre (CMRC) (04-05 December 2000); 2. Norman's Pond (10-11 and 14-15 December 2000); 3. Near Bock Cay (12-13 December 2000).

to the island leeward shore by a tidal channel which floods and drains the pond.

MATERIALS AND METHODS

The Floating Equilibrator System (FES) consists of a torus rubber buoy (external diameter 140 cm) with a stainless steel frame on which are mounted: an equilibrator, 3 waterproof cases, a solar panel and several meteorological sensors (Fig. 2). All the variables are logged with a sampling interval of one minute and the overall autonomy of the system is about 30 h.

The equilibrator is a Plexiglas cylinder (height: 80 cm, diameter: 10 cm) filled with marbles to increase exchange surface area. Pumped sample water runs (3 L min^{-1}) from the top to the bottom of the equilibrator and air is pumped upwards (3 L min^{-1}). This equilibrator can work without clogging in very turbid waters and has a fast equilibration time. The half-life time constant of equilibration is 30 sec and 99% of equilibrium is achieved in less than 2 min (Frankignoulle et al. 2001).
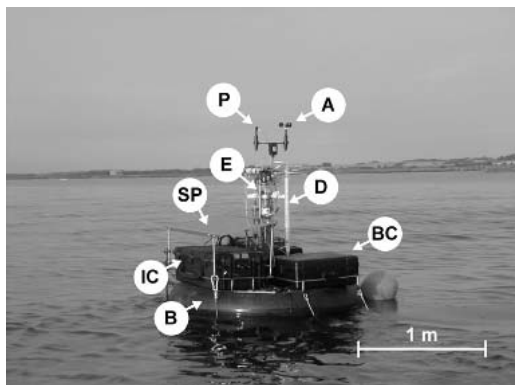
FIG. 2. Photograph of the Floating Equilibrator System (courtesy of Bruno Delille). A. anemometer; B. torus rubber buoy; BC. batteries waterproof case; D. Drierite column; E. equilibrator; IC. instrument waterproof case (containing air pump, IRGA and datalogger); P. pyranometer; SP. solar panel.

The FES includes: four 12 Volts batteries, a solar panel, air and water temperature probes (Li-Cor, Li-1400-101 and Li-1400-103), an anemometer (Young 03002VP), a data logger (Li-Cor, Li-1400), a non-dispersive infrared gas analyser (IRGA), an air pump and a water pump (Fig. 2). Recent improvements allowed adding a pyranometer (Li-Cor, Li-200-SA), a thermosalinometer (WTW 340i) and an oxymeter (WTW Oxi340), which were unavailable during the first field test, December 2000. The IRGA, air pump and data logger are enclosed in a large waterproof case ($75 \times 45 \times 25$ cm). The 4 batteries are enclosed in two smaller waterproof cases ($55 \times 45 \times 25$ cm).

The IRGA (Li-Cor, Li-6262) measures pCO_2 in air from a closed circuit, equilibrated with sample water, with an estimated accuracy of about 5 ppm. The sample air is dried with Drierite (97% $CaSO_4$, 3% $CoCl_2$) prior to measurement, and data are converted into wet air using the algorithms given by Dickson and Goyet (1994). During the December 2000 field test experiment, the IRGA was calibrated using pure nitrogen (Air Liquide Belgium) and a gas mixture with a CO_2 molar fraction of 708 ppm (National Oceanic and Atmospheric Administration).

For the first time in field conditions, the FES was tested in the Bahamas at three locations, in December 2000. The system was deployed, anchored, and data acquisition started 2 h before dusk. Two 24 h cycles were carried out in Norman's Pond, on 10-11 and 14-15 December. One 24 h cycle was carried out in front of the CMRC (Caribbean Marine Research Centre) and another near Bock Cay, on 04-05 and 12-13 December, respectively (see Fig. 1 for exact location of stations).

RESULTS

In Norman's Pond, the range of pCO_2 variations was 385-750 ppm during 10-11 December and 395-690 ppm for 14-15 December (Fig. 3A). The daily change of pCO_2 during 14-15 December cycle followed the general pattern expected from diel alternation between photosynthesis and respiration (decrease of pCO_2 during daytime until sunset and increase during night until dawn). During the 10-11 December cycle, there is a very rapid drop of pCO_2 around 08:00, which occurred at high tide. This is likely related to a significant intrusion of outer seawater into the pond. The pond is separated from surrounding sea by a sill of about 0.5 m and the intrusion of outer seawater can only occur if the tide is high enough to submerge the sill.

The daily change of pCO_2 during the cycle carried out in front of the CMRC also followed the pattern expected from the diel alternation between photosynthesis and respiration (Fig. 3B). However, the increase of pCO_2 between dusk and dawn is about 15 ppm, one order of magnitude lower than the one observed during both cycles in Norman's Pond (about 250 ppm). At Bock Cay, the daily changes of pCO_2 are erratic and are probably related to the advection of different water masses with distinct pCO_2 signatures (Fig. 3B).

Temperature variation affects the equilibrium constants of dissolved inorganic carbon; in particular the CO_2 solubility coefficient (pCO_2 rises about 4% for a temperature increase of 1°C). This phenomenon associated to the temperature diurnal cycle is in open oceanic regions the primary source of daily scale variation of pCO_2 in surface waters, as shown by Goyet and
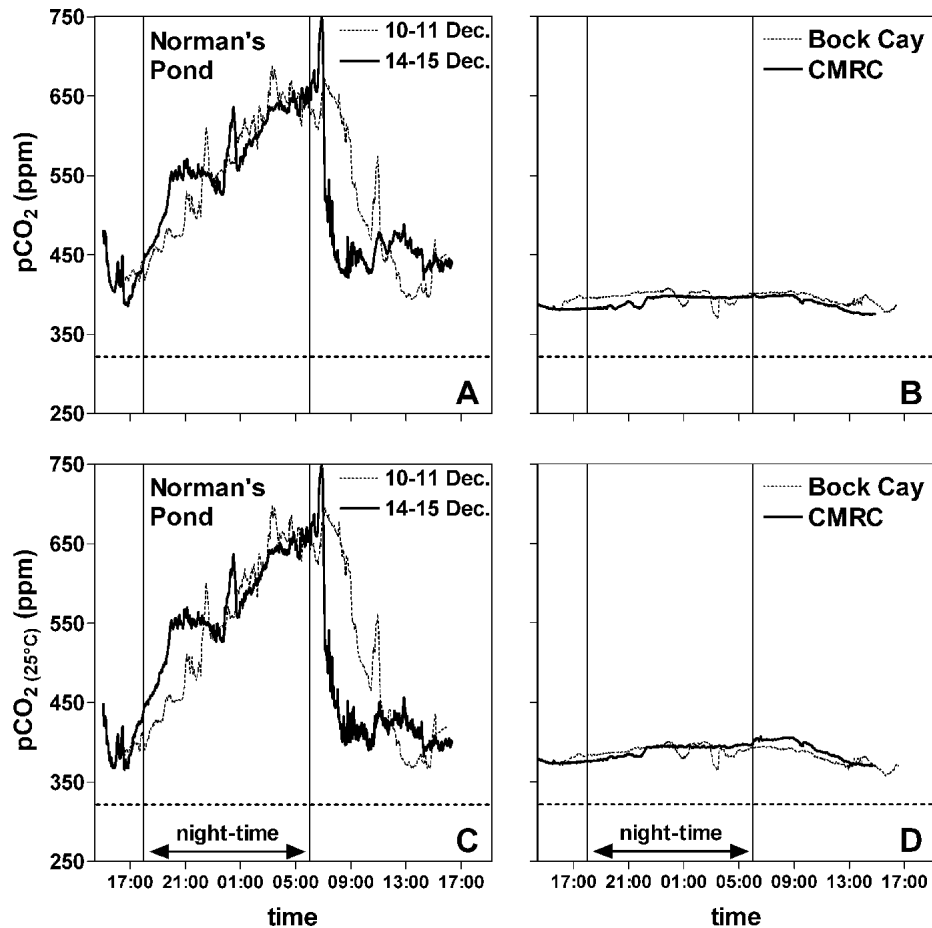
FIG. 3. Variations of pCO$_2$ at in-situ temperature (ppm), pCO$_2$ normalized to a constant temperature of 25°C (pCO$_2$ $_{(25°C)}$ in ppm), water temperature (°C) and wind speed (m s^{-1}) during 24 h at three stations (refer to Fig. 1 for exact locations). The anemometer malfunctioned during the cycle in front of the CMRC. For this cycle, the hourly wind speed data from the CMRC meteorological station are shown and these were interpolated to obtain values every minute.

Peltzer (1997) in equatorial Pacific Ocean and by Bates et al. (1998) in Sargasso Sea. To filter the effect of temperature and focus on the potential biological factors affecting pCO$_2$, the pCO$_2$ values were normalized to a constant temperature of 25°C (pCO$_2$ $_{(25°C)}$) using the algorithm proposed by Copin-Montégut (1988). This approach is widely used in the interpretation of pCO$_2$ data at daily scale (Oudot and Andrié 1989; Robertson et al. 1993; Yamashita et al. 1993; Borges and Frankignoulle 2001). The patterns of pCO$_2$ $_{(25°C)}$ (Fig. 3C and D) are very similar to those of pCO$_2$ at in-situ temperature during the four 24 h cycles (Fig. 3A

and B). We conclude that biological activity is the major factor controlling pCO$_2$ at daily scale in Norman's Pond, despite large amplitude of the daily temperature cycle (about 3°C, Fig. 3E). The amplitude of the daily temperature cycle is smaller at Bock Cay and in front of the CMRC (about 1°C, Fig. 3F). This is probably related to an enhanced diurnal heat exchange in the shallower and semi-enclosed Norman's Pond.

From the wind speed and pCO$_2$ measurements, we calculated the air-water flux of CO$_2$ during the four 24 h cycles. The flux of CO$_2$ across the air-sea interface (F) is computed from the air-sea gradi-
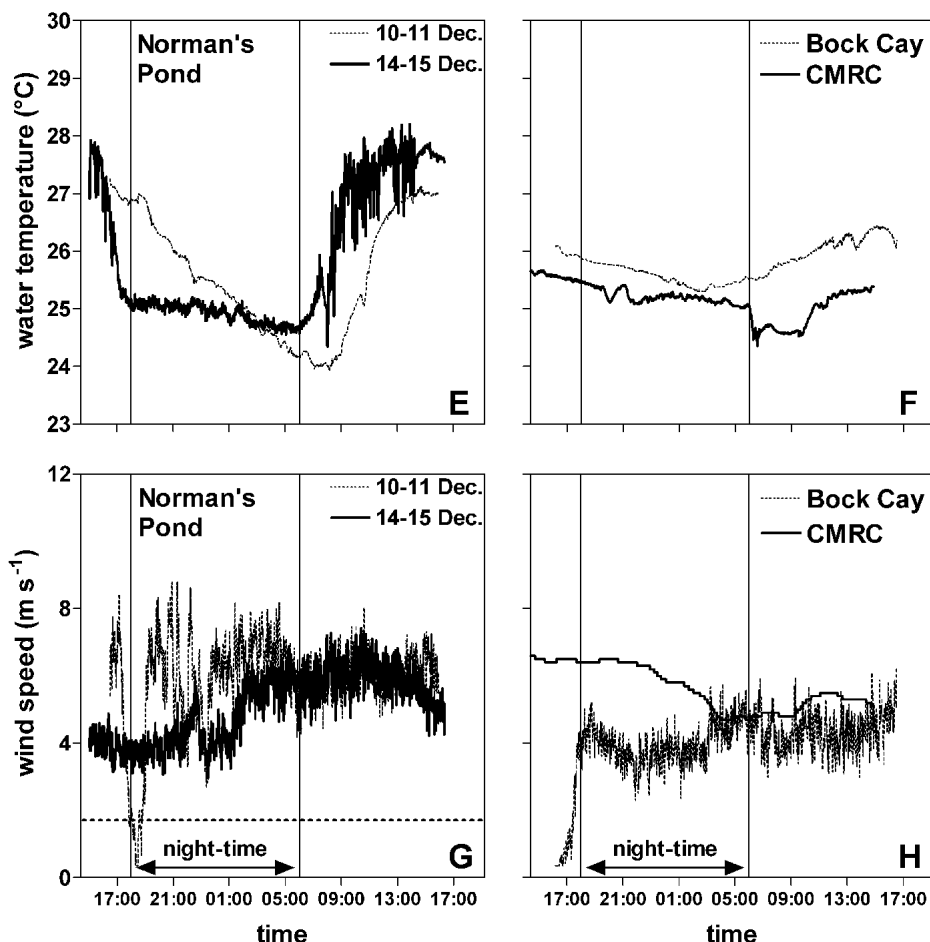
FIG. 3. Cont.

ent of pCO_2 ($\Delta pCO_2 = pCO_{2\ water} - pCO_{2\ atmosphere}$), the gas transfer velocity (k) and the solubility coefficient of CO_2 (α), using the equation:

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

We applied the algorithm of k as a function of wind speed proposed by Wanninkhof (1992) and the CO_2 solubility coefficient given by Weiss (1974). To compute ΔpCO_2, we used the atmospheric pCO_2 data from Ragged Point reference station (Barbados, 13°10′N 59°26′W) of the air sampling network of the National Oceanic and Atmospheric Administration/Climate Monitoring and Diagnostics Laboratory/Carbon

Cycle Greenhouse Gases Group (available from the internet at http://www.cmdl.noaa.gov/). The atmospheric pCO_2 data were converted into wet air values using the algorithms given by Dickson and Goyet (1994). Wind speeds were referenced to a height of 10 m using the algorithm given by Johnson (1999).

The atmospheric CO_2 fluxes computed for the two cycles in Norman's Pond are about 10 times larger than those at Bock Cay and CMRC (Table 1). This is mainly due to the significantly higher ΔpCO_2 values at Norman's Pond. The wind speeds recorded at Norman's Pond were also slightly higher than at Bock Cay and in front of the CMRC (Table 1 and Fig. 3G and H). Using an average wind speed of 6.1

TABLE 1. Average ± standard deviation of wind speed (m s^{-1}), air-water gradient of CO_2 (ΔpCO_2 in ppm), air-water flux of CO_2 computed using the gas transfer velocity algorithm of Wanninkhof (1992) (F in mmol m^{-2} day^{-1}) and number of recorded data points (N) during the 24 h cycles carried out at 3 stations (refer to Fig. 1 for exact locations).

Station	Date	Wind speed (m s^{-1})	ΔpCO_2 (ppm)	F (mmol m^{-2} day^{-1})	N
Norman's Pond	10-11 Dec.	6.4 ± 1.3	157 ± 83	16.0 ± 11.0	1521
Norman's Pond	14-15 Dec.	7.5 ± 1.7	172 ± 88	25.2 ± 16.3	1407
CMRC	04-05 Dec.	5.7 ± 0.7	31 ± 7	2.4 ± 0.6	1549
Bock Cay	12-13 Dec.	5.0 ± 1.2	38 ± 7	2.4 ± 0.9	1462

m s^{-1}, we recomputed the atmospheric CO_2 fluxes that remain significantly higher in Norman's Pond (14.2 ± 7.4 and 15.5 ± 8.0 mmol m^{-2} day^{-1} for the 10-11 and 14-15 December cycles, respectively) than in front of the CMRC and at Bock Cay (2.8 ± 0.7 and 3.4 ± 0.6 mmol m^{-2} day^{-1}, respectively).

DISCUSSION

Higher values of pCO$_2$, pCO$_{2\ (25°C)}$ and atmospheric CO_2 fluxes were observed at Norman's Pond than in the adjacent open waters of the Great Bahama Bank (near Bock Cay and in front of the CMRC). These differences are probably related to higher heterotrophy at Norman's Pond related to the presence of a dense mangrove forest, and, concomitant organic carbon inputs to the water column and sediments.

Also, the larger amplitude of the pCO$_2$ and pCO$_{2\ (25°C)}$ diurnal variations observed during the Norman's Pond 24 h cycles could reflect a higher biological activity (benthic and/or pelagic primary production and respiration) than in the adjacent open waters of the Great Bahama Bank. However, note that besides the rates of biological activity, the daily signal of pCO$_2$ and pCO$_{2\ (25°C)}$ is also modulated by depth of the water column. From the daily change of DIC it is possible to estimate the rates of biological activity at ecosystem level (pelagic and benthic components in a non-stratified system). The time course of DIC during daytime depends on Gross Primary Production (GPP) minus Autotrophic Respiration (AR), minus Heterotrophic Respiration (HR). The time course of DIC during nighttime depends on the sum of AR and

HR. Assuming that the rates of AR and HR are the same during daytime and nighttime; it is possible to compute GPP from the diurnal cycle of DIC. Based on the observed pCO$_2$ and temperature values and using a Total Alkalinity (TAlk) value of 2.340 mmol kg^{-1}, we computed the DIC change during daytime (from dawn to dusk) at Norman's pond, during the 10-11 December 24 h cycles (Fig. 3A and E). Assuming a depth of 2 m, GPP is estimated to 35.9 mmol m^{-2} h^{-1}. The same computations were made from the data obtained in front of the CRMC (Fig. 3B and F) and the corresponding estimation of GPP is 5.5 mmol m^{-2} h^{-1}, assuming a depth of 5 m. The larger amplitude of pCO$_2$ and pCO$_{2\ (25°C)}$ changes during the Norman's Pond 24 h cycles than in the adjacent open waters of the Great Bahama Bank are indeed related to higher rates of biological activity. These are probably related to the inputs to the pond of nutrients and organic carbon from Normand's Pond Cay, with a likely significant contribution from the mangrove forest.

However, the above computations are based on the assumption that only GGP, AR and aerobic HR control the DIC signal. Other biogeochemical processes such as anaerobic degradation and calcification probably also strongly contribute to DIC dynamics in the study sites. Indeed, in mangrove ecosystems, the inputs of porewater with high TAlk and DIC contents related to diagenetic anaerobic processes strongly affect the chemical properties of the creek water column (Ovalle et al. 1990; Borges et al. 2003). Benthic calcification is expected to be low in Norman's Pond due to high turbidity and haline stress, unlike the open waters of the Great Bahama Bank

(*e.g.* Broecker and Takahashi 1966). A higher rate of calcification (by coral reefs and/or calcifying algae) in the open waters of the Great Bahama Bank compared to Norman's Pond could also explain to some extent the lower amplitude of the pCO_2 and pCO_2 $_{(25°C)}$ diurnal variations. The close coupling of calcification and photosynthesis (at both physiological and ecosystem levels) buffers the pCO_2 variations in the surrounding waters as shown for instance in Spencer Gulf by Smith and Veeh (1989). However, in absence of complementary data on another parameter of the dissolved inorganic carbon system (either TAlk or DIC), it is not possible to address this question in more detail from the present data-set.

CONCLUSIONS

The first field test of a novel autonomous measuring device, the Floating Equilibrator System, was successfully carried out in the Great Bahama Bank, in December 2000. We carried out two 24 h cycles of pCO_2, water temperature and wind speed measurements in Norman's Pond, one in front of the Caribbean Marine Research Centre and another near Bock Cay.

Over-saturation of CO_2 with respect to atmospheric equilibrium was observed systematically at the three sites, although significantly more marked at Norman's Pond. The higher values of pCO_2 and atmospheric CO_2 efflux obtained at Norman's Pond than in the adjacent open waters of the Great Bahama Bank (near Bock Cay and in front of the CMRC) suggest stronger heterotrophy at Norman's Pond. This is likely related to the organic carbon inputs to the water column and sediments from the dense mangrove forest surrounding Norman's Pond.

At Norman's Pond and in front of the CMRC, we computed a tentative estimation of Gross Primary Production based on the observed daily change of pCO_2. These computations suggest that the larger amplitude of the pCO_2 daily variations observed during the Norman's Pond 24 h cycles is probably due to a higher biological activity

than in the adjacent open waters of the Great Bahama Bank. This higher biological activity is probably related to the terrestrial organic carbon and nutrient inputs to the pond from Norman's Pond Cay.

In the study sites, dissolved inorganic carbon dynamics are probably strongly influenced by other biogeochemical processes such as diagenetic anaerobic degradation and calcification, although from the present data-set it is not possible to address this matter in more detail.

LITERATURE CITED

Alongi, D. M. 1998. *Coastal Ecosystem Processes*, Boca Raton, Florida: CRC Press.

Bates, N. R., T. Takahashi, D. W. Chipman, and A. H. Knap. 1998. Variability of pCO_2 on diel to seasonal timescales in the Sargasso Sea near Bermuda. *J. Geophys. Res.* 103:15567-15585.

Borges, A. V., and M. Frankignoulle. 1999. Daily and seasonal variations of the partial pressure of CO_2 in surface seawater along the Belgian and southern Dutch coastal areas. *J. Marine Syst.* 19:251-266.

Borges, A. V., and M. Frankignoulle. 2001. Short-term variations of the partial pressure of CO_2 in surface waters of the Galician upwelling system. *Progr. Oceanogr.* 51:283-302.

Borges, A. V., and M. Frankignoulle. 2002a. Distribution of surface carbon dioxide and air-sea exchange in the upwelling system off the Galician coast. *Glob. Biogeoch. Cycles* 16:4/1-14.

Borges, A. V., and M. Frankignoulle. 2002b. Aspects of inorganic carbon dynamics in the upwelling system off the Galician coast. *J. Marine Syst.* 32:181-198.

Borges, A. V., and M. Frankignoulle. 2002c. Distribution and air-water exchange of carbon dioxide in the Scheldt plume off the Belgian coast. *Biogeochemistry* 59:41-67.

Borges, A. V., and M. Frankignoulle. 2003. Distribution of surface carbon dioxide and air-sea exchange in the English Channel and adjacent areas. *J. Geophys. Res.* 108(C5):10,1029 doi:2000JC000571.

Borges, A. V., S. Djenidi, G. Lacroix, J. Théate, B. Delille, and M. Frankignoulle. 2003. Atmospheric CO_2 flux from mangrove surrounding waters. *Geophys. Res. Lett.* 30(11):1558 doi: 10.1029/2003GL017143.

Broecker, W. S., and T. Takahashi. 1966. Calcium carbonate precipitation on the Bahama bank. *J. Geophys. Res.* 71:1575-1601.

Cai, W.-J., W. J. Wiebe, Y. Wang, and J. E. Sheldom. 2000. Intertidal marsh as a source of dissolved inorganic carbon and a sink of nitrate in the Satilla River-estuarine complex in the southeastern U.S. *Limnol. Oceanogr.* 45:1743-1752.

Copin-Montégut, C. 1988. A new formula for the effect of temperature on the partial pressure of carbon dioxide in seawater. *Mar. Chem.* 25:29-37.

DeGranpre, M. D., G. J. Olbu, C. M. Beatty, and T. R. Hammar. 2002. Air-sea fluxes on the US Middle Atlantic Bight. *Deep-Sea Res. II* 49:4355-4367.

Dickson, A.G., and C. Goyet. 1994. *Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water*, ORNL/CDIAC-74.

Frankignoulle, M., G. Abril, A. Borges, I. Bourge, C. Canon, B. Delille, E. Libert, and J.-M. Théate. 1998. Carbon dioxide emission from European estuaries. *Science* 282:434-436.

Frankignoulle, M., and A. V. Borges. 2001. European continental shelf as a significant sink for atmospheric CO_2. *Glob. Biogeochem. Cycles* 15:569-576.

Frankignoulle, M., A. V. Borges, and R. Biondo. 2001. A new design of equilibrator to monitor carbon dioxide in highly dynamic and turbid environments. *Water Res.* 35:1344-1347.

Gattuso, J.-P., M. Frankignoulle, and R. Wollast. 1998. Carbon and carbonate metabolism in coastal aquatic ecosystems. *Annu. Rev. Ecol. Syst.* 29:405-433.

Ghosh, S., T. K. Jana, B. N. Singh, and A. Choudhury. 1987. Comparative study of carbon dioxide system in virgin and reclaimed mangrove waters of Sundarbans during freshet. *Mahasagar Bull. Nat. Instit. Oceanogr.* 20:155-161.

Goyet, C., and E. T. Peltzer. 1997. Variation of CO_2 partial pressure in surface seawater in the equatorial Pacific Ocean. *Deep-Sea Res. I* 44:1611-1625.

Jennerjahn, T. C., and V. Ittekkot. 2002. Relevance of mangroves for the production and deposition of organic matter along tropical continental margins. *Naturwissenschaften* 89:23-30.

Johnson, H. K. 1999. Simple expressions for correcting wind speed data for elevation. *Coast. Eng.* 36:263-269.

Mackenzie, F. T., L. M. Ver, and A. Lerman. 2000. Coastal-zone biogeochemical dynamics under global warming. *Int. Geol. Rev.* 42:193-206.

Millero, F. J., W. T. Hiscock, F. Huang, M. Roche, and J. Z. Zhang. 2001. Seasonal variation of the carbonate system in Florida Bay. *Bull. Mar. Sci.* 68:101-123.

Oudot, C., and C. Andrié. 1989. Short-term changes in the partial pressure of CO_2 in eastern tropical Atlantic surface seawater and in atmospheric CO_2 mole fraction. *Tellus* 41B:537-553.

Ovalle, A. R. C., C. E. Rezende, L. D. Lacerda, and C. A. R. Silva. 1990. Factors affecting the hydrochemistry of a mangrove creek, Sepetiba Bay, Brazil. *Estuar. Coast. Shelf S.* 31:639-650.

Rabouille, C., F. T. Mackenzie, and L. M. Ver. 2001. Influence of human perturbation on carbon, nitrogen, and oxygen biogeochemical cycles in the global coastal ocean. *Geochim. Cosmochim. Ac.* 65: 3615-3641.

Raymond, P. A., J. E. Bauer, and J. J. Cole. 2000. Atmospheric CO_2 evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary. *Limnol. Oceanogr.* 45:1707-1717.

Robertson, J. E., A. J. Watson, C. Langdon, R. D. Ling, and J. W. Wood. 1993. Diurnal variation in surface pCO_2 and O_2 at 60°N, 20°W in the North Atlantic. *Deep-Sea Res. II* 40:409-422.

Smith, S. V., and F. T. Mackenzie. 1987. The ocean as a net heterotrophic system: implications from the carbon biogeochemical cycle. *Glob. Biogeochem. Cycles* 1:187-198.

Smith, S.V., and H. H. Veeh. 1989. Mass balance of biogeochemically active materials (C,N,P) in a hypersaline gulf. *Est. Coast. Shelf Sci.* 29:195-215.

Tsunogai, S., S. Watanabe, and T. Sato. 1999. Is there a continental shelf pump for the absorption of atmospheric CO_2? *Tellus* 51B:701-712.

Wanninkhof, R. H. 1992. Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.* 97:7373-7382.

Weiss, R. F. 1974. Carbon dioxide in water and seawater: the solubility of a non-ideal gas. *Mar. Chem.* 2:203-215.

Yamashita, E., F. Fujiwara, X. Liu, and E. Ohtaki. 1993. Measurements of carbon dioxide in the Seto Inland Sea of Japan. *J. Oceanogr.* 49:559-569.