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Oxygen and carbon dioxide fluxes at the water-sediment interface of a tropical lagoon

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ABSTRACT: Oxygen demand, carbon dioxide release and total alkalinity shift were calculated from changes in oxygen, pH and total alkalinity produced by bottom dark incubations at the water-sediment interface of the 3 bottom types identified in a southwest lagoon in New Caledonia. Total sediment oxygen demand (ΔO_2) was corrected from nonbiological oxygen demand (NBOD) in order to obtain the apparent biological activity ($\Delta O_2°$). Total carbon dioxide flux (ΔCO_2) was corrected from total alkalinity shift in order to estimate organic carbon processes. The resulting mean carbon dioxide flux ($\Delta CO_2°$ = 2.58 mmol m^{-2} h^{-1}, SE = 0.12) exceeded biological oxygen demand ($\Delta O_2°$ = 1.60 mmol m^{-2} h^{-1}, SE = 0.08). The highly significant ratio estimates from functional regression lines of $\Delta CO_2°$ on ΔO_2 and $\Delta CO_2°$ on $\Delta O_2°$ gave a total community respiratory quotient (CRQ) of 1.17 (SE = 0.06) and an organic respiratory quotient (CRQ°), involving only direct biological processes, of 1.42 (SE = 0.07) for the lagoon. The significance and the use of these ratios are discussed in order to calculate the anaerobic metabolism proportion (40.3 % of total metabolism for an aerobic respiratory quotient of 0.85). Thus, the simultaneous measurement in the field of O_2 fluxes and CO_2 fluxes, corrected from appropriate alkalinity changes, allows a rapid approach for estimating carbon production at the water-sediment interface of undisturbed communities.

KEY WORDS: Carbon flux · Metabolism · Tropical lagoon

INTRODUCTION

Although bottom oxygen uptake has been used to estimate rates of organic matter consumption by benthic organisms and oxidation of organic material, total oxygen demand of sediment alone is inadequate to estimate total benthic metabolism (Pamatmat 1977). Organic matter decomposition can occur without oxygen as a terminal oxygen acceptor and an appreciable part of the metabolism proceeds through pathways of nitrate, manganese, iron, and sulfate respiration (Jørgensen 1977, Sørensen et al. 1979). Anaerobic respiration through chemical oxidation, including what is called 'chemical oxygen demand', contributes to the total oxygen demand and depends on the balance of electron acceptors in the sediment (Andersen et al. (e.g. nitrate and sulphate reduction, methanogenesis, fermentations) because natural assemblages of bacteria are net carbon dioxide producers (Marty et al. 1989). In order to relate total sediment oxygen demand (ΔO_2) to biological carbon dioxide production ($\Delta CO_2°$) at the water-sediment interface, the total community respiratory quotient (CRQ = $\Delta CO_2°/\Delta O_2$) is usually measured. This value is useful in stoichiometric calculations related to decomposition processes and it characterises whole ecosystem or community metabolism where both aerobic and anaerobic respiration and chemical oxidation occur simultaneously (Andersen & Kristensen 1988). It is generally considered that simultaneous measurement of carbon dioxide release and oxygen demand in dark incubations of marine sediments allows the calculation of an integrated

A field method was developed in the southwest lagoon of New Caledonia to (1) determine the community respiratory quotient considered as a conversion factor to transform oxygen demand to carbon fluxes, and (2) estimate the relative importance of benthic aerobic and anaerobic metabolisms at the water-sediment interface of undisturbed communities.

MATERIAL AND METHODS

Study site. During a cruise of the OV 'Alis', bottom incubation experiments and sample collections were carried out at 14 stations (Fig. 1) in the southwest lagoon of New Caledonia from 10 to 20 December 1991 and from 6 to 9 January 1992 (Garrigue et al. 1992b). Depths ranged from 6.7 to 17.0 m. Bottom water temperature varied from 23.78 to 27.78 °C. Salinity ranged from 35.55 to 36.01‰. Sampling sites were located in communities previously defined as mud deposits (5 stations), grey-sand bottoms (6 stations) and white-sand bottoms (3 stations), which represented 35, 50 and 15% respectively of the lagoon bottom (Chardy et al. 1988). At each station triplicate enclosure experiments simulating dark conditions were performed.

Incubation procedure. Oxygen and carbon dioxide fluxes at the water-sediment interface were simultaneously measured in the water trapped in enclosures according to the incubation methods described in Boucher & Clavier (1990). Three replicate PVC cores (0.2 m^2) were pushed by SCUBA divers ca 10 cm into the sediment at a distance of 1 m from each other. The openings of the cores were then sealed with clear acrylic hemispheres to trap a known volume of bottom water, varying from 51.8 to 64.5 l according to the depth of core insertion into the substrate. Injection of a chemical photosynthesis inhibitor (DCMU) into the enclosures (5×10^{-5} mol l^{-1}), according to a procedure described by Garrigue et al. (1992a) allowed the measurement of respiration at ambient light. Gusher galley pumps ensured a gentle closed-circuit flow, allowing good mixing of the water trapped in the incubation chambers without particulate resuspension. Incubations began at 09:00 h after oxygen and pH logger calibrations and underwater deployment of the enclosures and lasted 5 h until 14:00 h, a duration producing no critical oxygen depletion (<80% saturation), which could have modified linear oxygen demand.

Nonbiological oxygen demand (NBOD) experiments were carried out on 15 incubations. Each enclosure

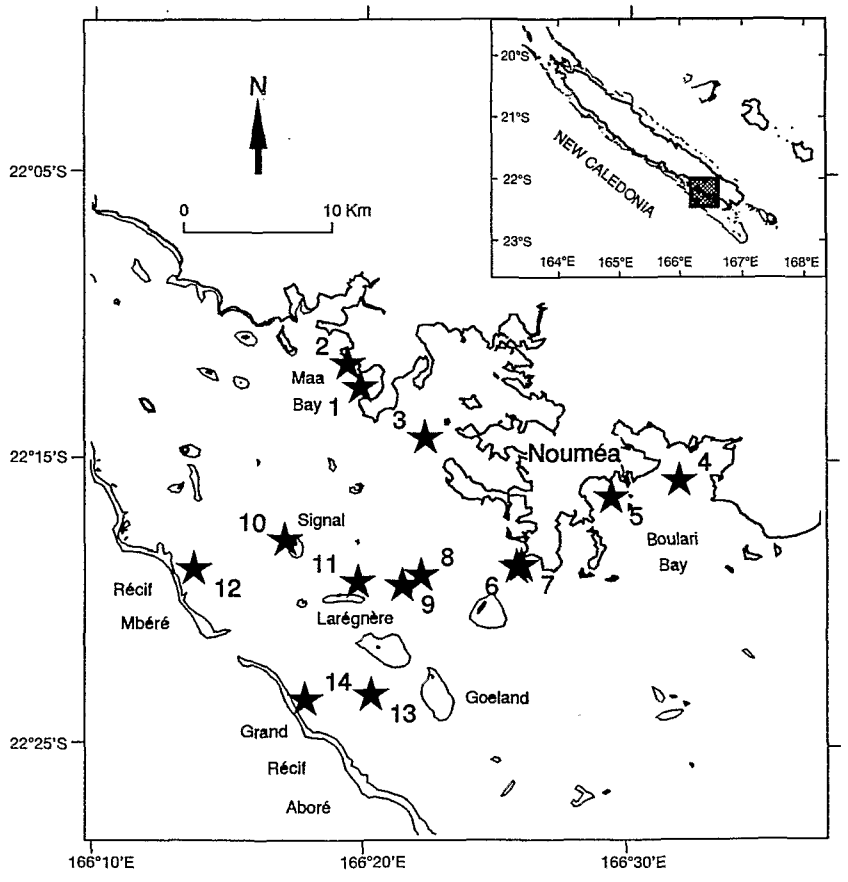


Fig. 1. Location of sampling sites in the southwest lagoon of New Caledonia. Mud deposits (with depth) are:
1: Maa Bay I, 12 m;
2: Maa Bay II, 13 m;
3: Dumbea Bay, 17 m;
4: Boulari Bay, 14 m;
5: Magenta Bay, 14 m.
Grey-sand bottoms are:
6: Rocher à la Voile I, 10 m;
7: Rocher à la Voile II, 10 m;
8: Sèche Croissant I, 10 m;
9: Sèche Croissant II, 15 m;
10: Signal, 17 m;
11: Larégnère, 16 m.
White-sand bottoms are:
12: Récif Mbéré II, 12 m;
13: Goeland, 12 m;
14: Grand Récif Aboré, 15 m

received an injection of 4 l of 40 % neutralised formalin in order to obtain a ca 2.5 to 3 % dilution which stops biological activity ($\Delta O_2°$). Oxygen uptake was measured for 4 h to obtain a linear recording of NBOD. NBOD was expressed as a percentage of total oxygen demand.

Oxygen and pH loggers. Oxygen demand was recorded *in situ* with a 3-channel oxygen logger respirometer built by the ORSTOM Center of Nouméa (3 Yellow Spring Instrument YSI 58 oxymeters refitted in a waterproof container). Data were stored in a Squirrel analogue recorder and later transferred on board to a computer. The 3 polarographic probes were calibrated every morning in moist air.

The pH logger was built by the AIMS laboratory (Townsville, Australia) according to a technology developed by Barnes (1983) and later adapted by Chisholm et al. (1990) and Gattuso et al. (1993). Three Radiometer GK2401C combined pH electrodes were fitted in pressure-compensated cells connected to preamplifier boxes. pH was measured every second, and averaged and recorded every minute. Linear regression of the 300 pH values recorded over 5 h was calculated. Then the pH values corresponding to the initial and final sampling time, when alkalinity could be measured, were calculated.

Total alkalinity. Incubation water was collected by SCUBA divers using 100 ml syringes, at the beginning and at the end of the incubation. Samples were analysed immediately after collection. A total of 50 ml of incubation water was injected through a Sweenex 0.8 µm filter to remove particulate $CaCO_3$ material. Total alkalinity (TA) was measured on board by the potentiometric automatic method (Culberson et al. 1970) with a Tacussel Titrator TT-processor 2600S and an EBX2 20 ml automatic burette. Titration involved the continuous measurement of the pH of a seawater sample where a known volume (15 ml) of HCl 0.01 N was continuously added. A total of 8 replicate measurements were performed at the beginning and at the end of each incubation, i.e. 24 samples at the start and at the finish of the experiment. Alkalinity flux (ΔTA: mEq m^{-2} h^{-1}) was expressed as the difference of final TA and initial TA, corrected for incubation duration and surface of the enclosure.

Flux calculation. Oxygen flux (mmol m^{-2} h^{-1}) was expressed as the slope of the linear regression of oxygen content in the incubation water versus time. As biological oxygen demand should only include oxidation by living organisms, its flux was expressed as:

$$\Delta O_2° = \Delta O_2 - \mathrm{NBOD}$$

The total CO_2 concentration in the incubation water was calculated according to Strickland & Parsons (1972), using the formula given in Oviatt et al. (1986). ΔCO_2 (mmol m^{-2} h^{-1}) during incubation was determined by the difference of CO_2 concentration at the beginning and at the end of the incubation, taking into account ambient pH, alkalinity, temperature and salinity. This flux not only depends on organic carbon variation ($\Delta CO_2°$), but also on the alkalinity shift at the interface related to the dissolution and precipitation of $CaCO_3$ ($\Delta CaCO_3$), and to the consumption of electron acceptors other than molecular oxygen: $\Delta CO_2° = \Delta CO_2 - x\mathrm{TA}$. We used $x = 0.5$, as we considered that TA is only influenced by precipitation (negative flux) or dissolution (positive flux) of $CaCO_3$, the total CO_2 content of seawater being lowered or increased by 0.5 mol for each equivalent of TA change (Skirrow 1975, Gattuso & Jaubert 1990, Chisholm & Gattuso 1991), and sulphate respiration which predominates in the tropical environment (Skyring & Chambers 1976, Kristensen et al. 1991).

The total community respiratory quotient was calculated as: $\mathrm{CRQ} = |\Delta CO_2°/\Delta O_2|$. This quotient should be used to calculate carbon fluxes from total oxygen demand in sediments. In order to calculate the relative contributions of aerobic and anaerobic metabolism, oxygen fluxes must be corrected from NBOD. The organic community respiratory quotient (CRQ°) is:

$$\begin{aligned}\mathrm{CRQ}° &= |\Delta CO_2°/\Delta O_2°| = |(\Delta CO_2°_{an} + CO_2°_{ox})/\Delta O_2°| \\ &= |(\Delta CO_2°_{ox}/\Delta O_2°) + (\Delta CO_2°_{an}/\Delta O_2°)| \\ &= |\mathrm{RQ} + (\Delta CO_2°_{an}/\Delta O_2°)|\end{aligned}$$

$$CO_2°_{an} = (\mathrm{CRQ}° - \mathrm{RQ}) \times |\Delta O_2°|$$

where $\Delta O_2°$ = biological oxygen demand; $\Delta CO_2°$ = total organic CO_2 flux (corrected from TA shift); $\Delta CO_2°_{ox}$ = CO_2 flux resulting from aerobic metabolism; $\Delta CO_2°_{an}$ = CO_2 flux resulting from anaerobic metabolism; CRQ° = community respiratory quotient for organic carbon; and RQ = aerobic respiratory quotient.

The proportion of anaerobic metabolism (ANQ = anaerobic quotient × 100) was calculated as follows:

$$\mathrm{ANQ} = \Delta CO_2°_{an}/CO_2° = (\mathrm{CRQ}° - \mathrm{RQ}) \times \Delta O_2°/\Delta CO_2°$$

$$\Delta O_2°/\Delta CO_2° = 1/\mathrm{CRQ}$$

$$\mathrm{ANQ} = (\mathrm{CRQ}° - \mathrm{RQ})/\mathrm{CRQ}° = 1 - (\mathrm{RQ}/\mathrm{CRQ}°)$$

Statistical analysis. ANOVAs were performed on 3 groups of stations corresponding to the 3 bottom types. Multiple range tests of the relationships among variables were performed to detect homogeneous groups of stations using least significant differences (LSD), with a confidence interval of 95 % (Sokal & Rohlf 1981). Since both CO_2 and O_2 fluxes were subjected to natural variability and measurement errors, functional regression (Ricker 1973) was applied for metabolic quotient calculations (Jacques & Pilson 1980, Gattuso & Jaubert 1990).

Table 1. Mean values (standard errors in parentheses) of carbon dioxide and oxygen demand at the 3 different bottom types of the southwest lagoon of New Caledonia: ΔCO_2 and $\Delta CO_2°$: total carbon dioxide and organic carbon dioxide fluxes (mmol m^{-2} h^{-1}); ΔO_2 and $\Delta O_2°$: total sediment oxygen demand and biological oxygen demand (mmol m^{-2} h^{-1}). W: percentage of the lagoon surface occupied by mud deposits (MD), grey-sand bottom (GSB) and white-sand bottom (WSB). Lagoon: mean value of investigated stations. Lagoon (WM): mean values corrected from the surface occupied in the lagoon (weighted mean)

Community	W	N	ΔCO_2	$\Delta CO_2°$	ΔO_2	$\Delta O_2°$
MD	0.35	15	1.65 (0.14)	1.43 (0.09)	−1.46 (0.05)	−0.84 (0.06)
GSB	0.50	18	3.81 (0.19)	3.37 (0.19)	−2.97 (0.15)	−2.22 (0.14)
WSB	0.15	9	2.79 (0.21)	1.98 (0.42)	−1.80 (0.07)	−1.30 (0.15)
Lagoon		42	2.82 (0.10)	2.38 (0.09)	−2.18 (0.08)	−1.53 (0.12)
Lagoon (WM)			2.90 (0.10)	2.48 (0.09)	−2.27 (0.07)	−1.60 (0.08)

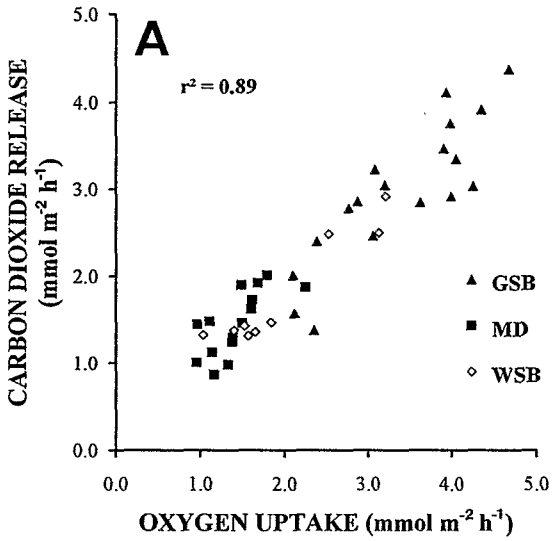
RESULTS

pH and TA evolution

Calculated pH values in the enclosed water, at ambient temperature, ranged from 8.152–8.367 at the beginning to 8.119–8.315 at the end of the incubation. Values of the slope of the regression lines of pH versus time ranged from −0.006 to −0.027 pH unit h^{-1}. TA increased from 2.310–2.402 at initial time to 2.319–2.414 mEq l^{-1} at final time. TA flux values ranged from 0.00 to 2.76 mEq m^{-2} h^{-1} with a mean value of 0.86 mEq m^{-2} h^{-1}.

CO_2 and O_2 fluxes

ΔCO_2 and $\Delta CO_2°$ ranged from 0.96 to 5.17 and from 0.96 to 4.67 mmol m^{-2} h^{-1} respectively. ΔO_2 and $\Delta O_2°$ ranged from 0.87 to 4.38 and 0.50 to 3.27 mmol m^{-2} h^{-1} respectively. The mean values of each flux (Table 1) were significantly different for the 3 bottom types (ANOVA, $p < 0.001$). The highest values were re-



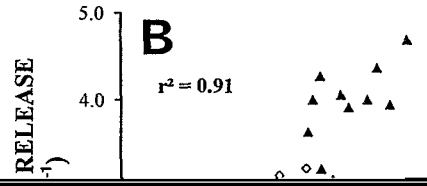


Table 2. Values of CRQ and CRQ° (standard error in parentheses) calculated by GM regression for mud deposits (MD), grey-sand bottoms (GSB), white-sand bottoms (WSB) and the

With a mean value of respiratory quotient (RQ = 0.85) based on aerobic respiration of animals and the chem-

Andersen & Hargrave (1984) proposed a method for correcting total oxygen demand from chemical oxygen uptake in order to calculate aerobic respiration, whereas they considered release of carbon dioxide in the dark as an integrated measure of aerobic respiration, nitrate and sulphate respiration and methanogenesis. In our study, the resulting ratio (CRQ° = 1.42 for the whole lagoon), which is always greater than CRQ, involves direct biological processes and allows the respective contribution of anaerobic and aerobic

of subtidal sediments (Hargrave & Phillips 1981) was explained only with anaerobic respiration processes since CO_2 is the end product of all aerobic and anaerobic metabolism.

Factors affecting CO_2 fluxes

Many metabolic processes in a benthic community may modify the flux of carbon dioxide without simulta-

more important limiting factors for an estimation of car- lithotrophs, which use O_2 both for carbon oxidation

organic matter degradation in marine sediments (Anderson et al. 1986, Kerner 1993). Anaerobic metabolism is of the same order of magnitude in mud deposits and white-sand bottoms (47 and 49% respectively) and higher than in grey-sand bottoms (35%). It is anticipated that anaerobic metabolism results from refractory organic matter accumulation according to processes which are different in coastal zones and back-reef bottoms. In mud deposits, anaerobic metabolism is stimulated by an increased deposition of particulate organic matter (Clavier et al. in press) whereas in white-sand bottoms, these metabolisms result from end products of biomass degradation (small food web and primary production: Boucher & Clavier 1990). The lower proportion of anaerobic metabolism observed in grey-sand bottoms does not indicate what happens in these sediments because macrophytes are aerobic and their contribution to total metabolism reduces apparent anaerobiosis.

CONCLUSIONS

The close correlation between carbon dioxide release and oxygen demand at the water-sediment interface confirms that CO_2 and O_2 fluxes are closely coupled processes in lagoon sediments. Simultaneously measuring both fluxes in the field on undisturbed communities allows an assessment of a realistic benthic metabolic quotient. The pH/alkalinity method,

the AIMS laboratory (Townsville) were chosen with the advice of Dr J. P. Gattuso (URA CNRS 1453), E. Gill and G. Macnaughton (AIMS workshop: Electronic and Mechanical Division). We thank Dr P. J. Lambshead (Museum of Natural History, London) for correcting the English.

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