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Analysis of the seawater CO_2 system in the barrier reef–lagoon system of Palau using total alkalinity-dissolved inorganic carbon diagrams

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Abstract

We studied the seawater carbon dioxide (CO_2) system in the Palau coral reef by measuring total alkalinity (TA) and total dissolved inorganic carbon (DIC). Variation in the CO_2 system on the reef flat and in the lagoon was analyzed by TA–DIC diagrams, taking into accounts the differing residence times of seawater. CO_2 in the offshore water was relatively stable in space and time, but on the reef flat it was subject to rapid (about 3 h) and substantial changes due to photosynthesis and calcification during the day and due to respiration and calcification at night. Water flowed into the lagoon where decomposition of organic matter and continuing calcification occurred over relatively long residence times (~30 d). Despite the spatial and temporal variations, the center of the lagoon had relatively constant TA and DIC values similar to the mean values for the entire lagoon. A long-term 30–40% decrease in reef productivity and calcification has occurred over the last decade, primarily a result of degradation of the reef environment following a major coral reef bleaching event in 1998. This is reflected in decreases in the differences in TA and DIC between offshore lagoon waters and those in center of the lagoon.

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Introduction

Coral reefs play a significant role in global biogeochemical cycles. They are involved in the production of calcium carbonate ($CaCO_3$) and their bioactivity accounts for >10% of the calcification occurring in the world's oceans, although reefs only have 0.17% the area of the oceans (Smith 1978; Milliman and Droxler 1996; Iglesias-Rodriguez et al. 2002). In general, coral reef environments can be divided into the reef flat and lagoon. The reef flat is the shallow part of the coral reef where active photosynthesis and calcification ($CaCO_3$ production) occur and where water has a short residence time of only a few hours. The lagoon is the relatively deep part of the reef where water has a residence time from a few days to several months, and where organic matter and $CaCO_3$ transported from the reef flat or adjacent land are deposited and decomposed (Kawahata et al. 2000; Suzuki et al. 2001). In some lagoon environments, the autochthonous production of biological matter, including $CaCO_3$, is also important (Smith 1978; Yamano et al. 2002).

Photosynthesis and calcification affect the seawater CO_2 system. Photosynthesis and calcification alter the dissolved inorganic carbon (DIC) and total alkalinity (TA), such that when 1 mol of organic carbon is produced, the DIC decreases by 1 mol, while the TA does not change. When 1 mol of $CaCO_3$ is produced, the TA decreases by 2 mol and the DIC by 1 mol. From these relationships, TA and DIC measurements allow us to evaluate photosynthesis and calcification rates (e.g., Gattuso et al. 1996) and these metabolic processes can be displayed graphically on TA–DIC diagrams as different, independent vectors (Suzuki 1995; Kawahata et al. 1997).

Suzuki and Kawahata (2003) developed TA–DIC diagrams for a number of coral reef lagoon environments. They normalized their results with respect to salinity and were able to demonstrate the effects of accumulated calcification occurring over relatively long residence times on the lagoon system. In some lagoon systems, such as the northern Great Barrier Reef, they showed that the DIC was affected by the input and subsequent oxidation of organic matter delivered by rivers. Contours showing the fugacity of CO_2 (fCO_2) on their TA–DIC diagrams allowed them to conclude that coral reefs are a primary source of atmospheric CO_2, and changes in a reef system are determined by both metabolic processes and residence time. Because their analysis was qualitative, they were only able to show a general pattern of variation within a lagoon. This is because their data were restricted temporally to a single survey and spatially to a single system of surface lagoon waters.

Coral reefs are highly productive, and large variations in TA and DIC occur in space and time, such that general trends across an entire reef system cannot be derived from restricted data. No attempts have been made to fully analyze a mix of both reef flat and lagoon data on a single TA–DIC diagram. On the shallow reef flat, TA and DIC change rapidly within a short residence time, whereas in the lagoon, TA and DIC change more slowly and have relatively long residence times. Consequently, in analyzing TA–DIC diagrams, there is a primary requirement to define appropriate residence times for both the reef flat and lagoon. Much spatial and temporal data are required, which must include vertical profiles within the lagoon. When comparing TA–DIC diagrams that cover different survey times, diurnal variation on the reef flat must also be accommodated.

This paper explores the seawater CO_2 system in a coral reef system that possesses a deep lagoon to ascertain the factors that affect it, such as biological metabolic processes, seawater residence times, and carbon input from rivers. We conducted field surveys of the Palau barrier reef in the western equatorial Pacific over 4 years from 1998 to 2002. This reef has a relatively deep lagoon. Its mean depth is 20 m and the maximum depth 55 m. Intensive surveys of the lagoon and reef flat were conducted to determine representative sampling sites that provided adequate spatial and temporal coverage of the productivity characteristics of the lagoon and reef flat. The measured data were analyzed quantitatively using TA–DIC diagrams, taking full account of seawater residence times, air–sea exchange of CO_2, and carbon input from rivers. The analysis has been interpreted in terms of changes in the ecosystem that affect the seawater CO_2 system. The Palau reef has undergone severe degradation, induced principally by a major, worldwide, coral reef bleaching event in 1998 (Bruno et al. 2001; Kayanne et al. 2002). The information we present has allowed this degradation of the ecosystem to be quantified and the impact on the coral reef carbon cycle to be evaluated.

Materials and methods

Geographic setting—The Palau barrier reef is located in the western equatorial Pacific. It extends from 7° to 8°N lat. and 134° to 135°E long. (Fig. 1A). The main island, Babeldaob, and other small islands form an archipelago in which a well-developed oceanic barrier reef lies to the west of the islands.

To the north, the islands are made up of volcanic rock on which flat terraces have been eroded up to 200 m above sea level. In the south, the islands consist of limestone, and many are small and mushroom shaped. Babeldaob Island possesses a few mangrove-infilled rivers whose catchment area is shown in Fig. 1A.

The weather at Palau has two distinct seasons. The dry season extends from February to May, during which time northeasterly trade winds prevail. The wet season runs from July to September, when winds are mainly from the northwest or southwest. The annual average precipitation is 3,700 mm. The average sea surface temperature is 29°C, and the annual range is <2.5°C in normal years (Morimoto et al. 2002).

The reef flat has a depth of 1–3 m and separates the lagoon with its average depth of 20 m from the open ocean, which is a few thousand meters deep 10 km from the reef (Hata et al. 1998). We established an east–west (EW) sampling line from Malakal Harbor that traversed 10 km of the lagoon and 2 km of the reef flat, and extended 10 km offshore in the direction of the prevailing current (Fig. 1B).

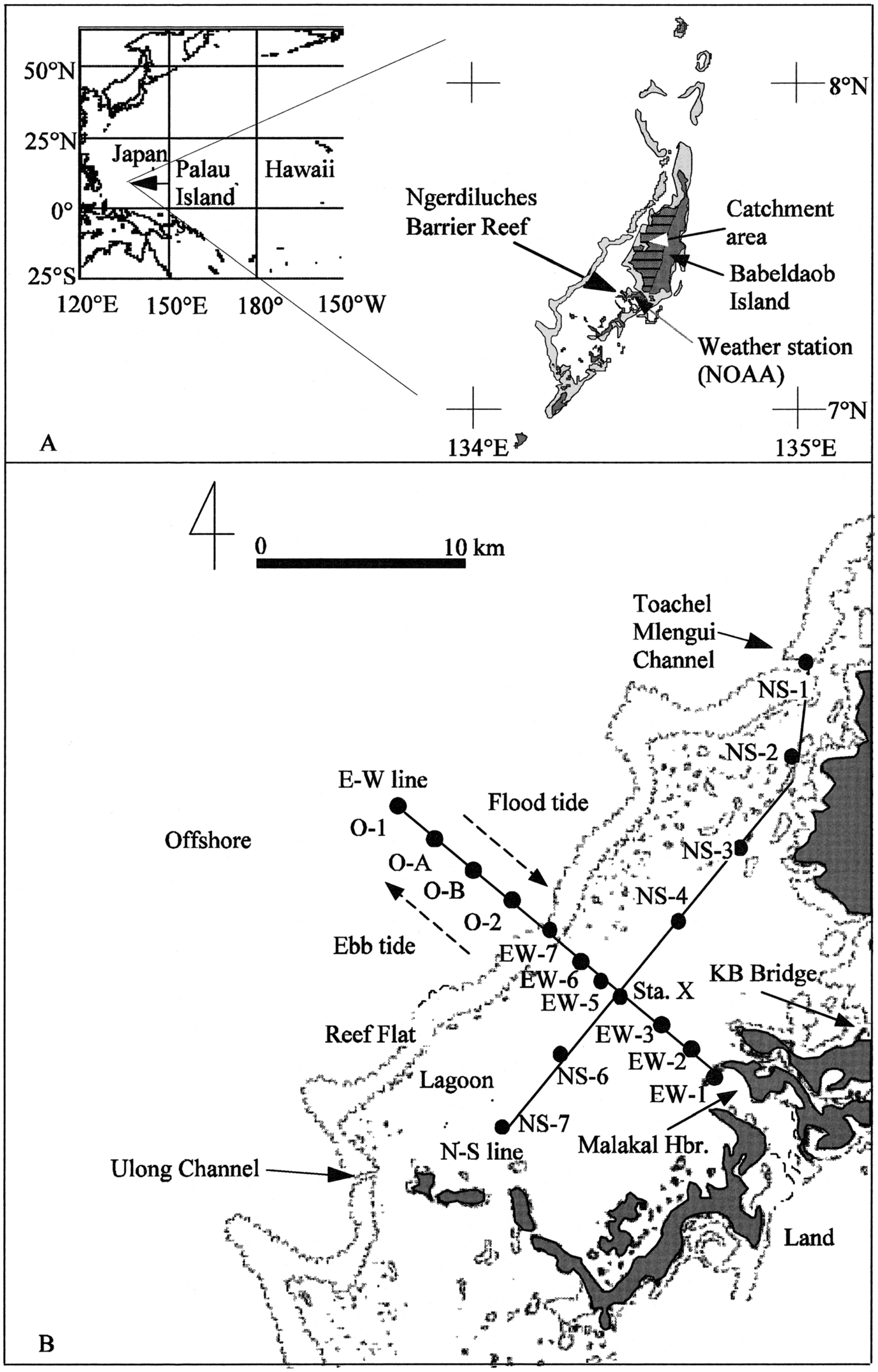

Fig. 1. Palau barrier reef. (A) Location of Palau. (B) Study site. The EW line is oriented in the direction of the current, and the NS line is perpendicular to the EW line. The EW and NS lines cross at Sta. X. Dashed arrows indicate the directions of the flood and ebb tides. Arrows indicate the main channels (openings), where we measured vertical profiles. The catchment area affecting the reef system is indicated by hatching in (A). Note the location of the NOAA weather station.

To determine any impacts of the adjacent land and lagoonal channels on the chemistry of the reef system, we established an additional north–south (NS) sampling line perpendicular to the EW line. The two crossed at the center of the lagoon, at Sta. X. The NS line extended from the northern Toachel Mlengui Channel, which is 10–70 m deep with a cross section of 28×10^3 m^2, to the southern Ulong Channel, which is 5–20 m deep with a cross section of 10×10^3 m^2. Two other channels were present in the sampled area: KB Bridge (15–30 m deep and 9×10^3 m^2 in cross section) and Malakal Harbor in the east (30–40 m deep and 25×10^3 m^2 in cross section).

Reef biota—The coral coverage was surveyed along a same transect on the reef flat (around EW-7 in Fig. 1B) before and after the 1998 bleaching event (Kayanne et al. 2005). In 1994, reef-building corals with thick branches (*Acropora digitifera*) dominated and had a mean coverage of 8.1%. Following the bleaching, living corals, mainly *Acropora* species, decreased to one-sixth of their original coverage (1.4%) with most of the *Acropora* colonies dying. Subsequently, the reef flat supported mainly brown algae (Turbinaria and Sargassum) with a mean coverage of 15%. In addition to corals, benthic foraminifera also play a significant role in carbonate production on the reef flat (Hallock 1981).

In the lagoon, many patch reefs reach the sea surface. They range in diameter from tens of meters to several kilometers, with coral coverage consisting mainly of *Porites* species, sometimes exceeding 80% (Kayanne et al. 2002). Benthic foraminifera also occur in the shallow part of the lagoon (Hallock 1981). Information on water-column phytoplankton is sparse, but the chlorophyll *a* (Chl *a*) levels are 0.3–0.5 μg L^{-1} in the lagoon water and always exceed the offshore levels of 0.1–0.2 μg L^{-1} (Hata et al. 1998).

Physical environment—The chart of Palau published by the U.S. Defense Mapping Agency (1996) was used to provide information on water depth. We divided our study area into a 0.9-km $\times$ 0.9-km grid consisting of 480 quadrats and determined the mean depth of each quadrat. The area, length, and width of both the reef area and catchment area of the rivers affecting this reef system (Fig. 1A) were estimated from a topographic map. Table 1 summarizes the physical properties of the Palau barrier reef. The mean depth of the area occupied by the 480 lagoon quadrats is 20 m, with a maximum depth of 55 m. The total area of the 480 quadrats is equivalent to 4.1×10^8 m^2. From the average depth and the area of the lagoon, the total water volume was calculated as 8.2×10^9 m^3 with 95% of the volume occurring in depths from 0–30 m and 5% occupying depths >30 m. The area, length, and mean width of the barrier reef flat were estimated as 7.1×10^7 m^2, 4.3×10^4 m, and 1.6×10^3 m, respectively. The average depth of the reef flat is 2 m, with an average tidal range at Palau of 1.5 m (Fig. 2B). The catchment affecting this reef system (Fig. 1A) has an area of 2.0×10^8 m^2. The average velocity across the reef flat measured by a current meter (Argonaut-XR, SonTek, San Diego, CA) over 13 tidal cycles, was 11 cm s^{-1} (Fig. 2A). At flood tide, water flows into the lagoon from offshore, whereas at ebb tide water flows out of the lagoon (Fig. 2A). This flow pattern across the reef flat is quite reproducible, with the inflows and outflows roughly balancing (data not shown). This pattern is repeated in the salinity measurements (Fig. 2D). Incoming offshore water has a higher salinity (33.8–33.9) than outgoing lagoon water (33.5–33.6).

Table 1. Summary of the properties of the Palau barrier reef.

Lagoon	
Area (km^2)	407
Depth (m)	
Average	20
Deepest	55
Total water volume (m^3)	8.2×10^9
Volume (%)	
0–30 m	95
>30 m	5
Barrier reef flat	
Area (km^2)	71
Length (km)	43
Width (km)	1.6
Water depth (m)	2
Average tidal range (m)	1.5

All the properties, except for water depth and average tidal range of barrier reef flat, were read from the chart published by the U.S. Defense Mapping Agency (1996). See text for more details.

Salinity and temperature profiles from the surface to the bottom were measured at each station on the NS and EW lines using a salinity temperature depth (STD) profiler, except for the offshore stations where measurements were made from the surface to a depth of about 200 m, which is well below the thermocline.

The mean residence time of seawater in the lagoon was estimated using two different methods. One was based on the simple assumption of complete mixing and exponential decay from original seawater (Endoh 1999), where *d* is the average tidal range (m), *D* is the average water depth (m), and *t* is the exchange times (once every 12.5 h because of the semidiurnal tide at Palau), *d*/*D* of the original seawater is exchanged and mixed completely with newly introduced seawater at each tidal cycle. Thus the change rate of the original seawater concentration is expressed by

$$\frac{\Delta C}{\Delta t} = -\frac{d}{D}C(t) \qquad (1a)$$

where $\Delta C/\Delta t$ is the concentration change at each tidal cycle, $C(t)$ is the concentration just before the exchange. Equation 1a can be rewritten as

$$\frac{\Delta C}{C(t)} = -\frac{d}{D}\Delta t \qquad (1b)$$

Equation 1b can be solved by integrating it:

$$C(t) = C(0)\exp[(-d/D)t] \qquad (2)$$

where $C(0)$ is the initial concentration of the original seawater, and $C(0)$ equals 1 (only made up of the original seawater at the initial state). Here we define the residence

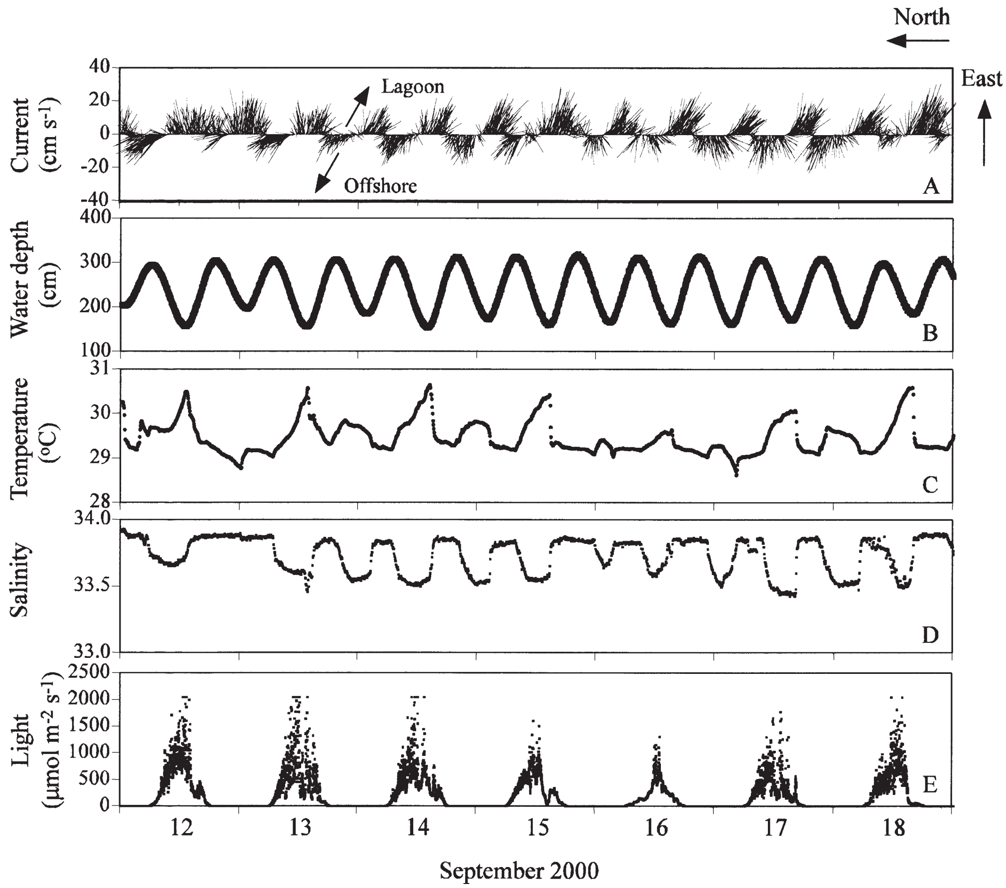

Fig. 2. Physical parameters measured on the reef flat (EW-7) in September 2000. (A) Current (cm s^{-1}), (B) water depth (cm), (C) water temperature (°C), (D) salinity, and (E) light intensity (μmol m^{-2} s^{-1}).

time, $\tau_1(d)$ when $C(t)$ becomes less than 0.01, which is equivalent to more than 99% of the original seawater being exchanged. You can relate t and τ_1 by Eq. 3.

$$\tau_1 = \frac{24}{12.5} t \tag{3}$$

where 12.5 is the number of hours each tidal cycle takes.

The other method uses the difference in salinity between the lagoon and offshore water and the equation of Smith and Jokiel (1978) with a little modification:

$$\tau_2 = \frac{D}{(p + r - v)} \left(\frac{S_O - S_L}{S_O} \right) \tag{4}$$

where p is the mean daily precipitation, r is the mean daily river discharge, v is the evaporation rate, and S_O and S_L are the mean salinity of offshore and lagoon water, respectively. Here, v is calculated as:

$$v = 0.14\,(p_0 - p_h)\,w \tag{5}$$

where w is the wind speed (m s^{-1}), and p_0 and p_h are the water vapor pressure in the air at the sea surface and at ground level, determined using the temperature, dew point, and water vapor pressure of seawater (Smith and Jokiel 1978). Local climatic data were compiled from NOAA reports, and the mean data for the 1 month immediately preceding each survey period was used. The water vapor pressure, p_0, was calculated using the equation of Weiss and Price (1980) by assuming 100% humidity for a given salinity and seawater temperature. The relative humidity was calculated from the average temperature and dew point at each period using the NOAA data, and p_h was calculated from p_0 and the relative humidity, obtained from the mean temperature and the mean dew point of about 80% in Palau as reported by NOAA.

The river discharge was obtained from the equation:

$$V_Q = 1000\,AP \exp(-e_0/P) \tag{6}$$

where V_Q is the monthly runoff (m^3 $month^{-1}$), A is the watershed area (km^2), P is monthly precipitation (mm $month^{-1}$), and e_0 is the evapotranspiration rate (mm $month^{-1}$) calculated as:

$$e_0 = 1.0 \times 10^9 \exp\left(-4.62 \times 10^3/T\right) \tag{7}$$

where T is the monthly air temperature (K) (Schreiber 1904; cf. the LOICZ web site http://www.loicz.org/public/loicz/products/r_and_s/13report.pdf). This model is robust for tropical and subtropical areas. The daily river discharge rate per area of lagoon (r in Eq. 4) was obtained by

Table 2. Residence time of seawater in the Palau barrier reef in each study period.

	Mar 2002	Mar 2001	Sep 2000	Apr 2000	Jan 1998	Mean
Average depth, D (m)	20	20	20	20	20	
Precipitation, p (mm d^{-1})	2.7	6.4	12.1	6.3	7.2	
River discharge, r (mm d^{-1})	0.1	1.0	3.2	0.9	1.3	
Offshore salinity, S_O	34.30	33.75	33.84	33.77	34.22	
Lagoon salinity, S_L	34.25	33.54	33.49	33.60	33.98	
Wind speed, w (m s^{-1})	2.7	2.5	3.0	2.7	2.4	
Lagoon SST (°C)	29.0	28.6	29.4	29.6	28.5	
Air temperature (°C)	28.6	28.3	27.7	28.2	27.9	
Dew point (°C)	23.9	24.1	24.1	24.6	24.1	
Relative humidity (%)*	75.3	77.6	80.4	80.5	79.5	
Water vapor pressure in the air (kPa), p_0†	3.93	3.84	4.02	4.07	3.82	
Water vapor pressure at sea surface (kPa), p_h†	2.95	3.04	3.10	3.19	3.09	
Evaporation rate (mm d^{-1}), v‡	3.7	2.8	3.9	3.3	2.4	
Residence time, τ_2 (d)§	−32	27	18	26	23	24±4
Residence time, τ_1 (d)‖	29	29	29	29	29	29

The weather data were compiled from those reported by a NOAA station in Palau. Datum for τ_2 in March 2002 was excluded from the calculation of mean residence time because the salinity differences were too small for the period.

* Relative humidity is calculated from mean temperature and mean dew point (about 80% in Palau).

† p_0 assumes 100% humidity calculated with water temperature and salinity from Weiss and Price (1980). p_h is calculated by multiplying the saturated water vapor pressure at mean temperature by relative humidity.

‡ $v = 0.14\ (p_0 - p_h)\ w$ (Smith and Jokiel 1978).

§ $\tau_2=[D/(p + r - e)]\ [(S_O - S_L)/S_O]$ (a little modification to the equation given by Smith and Jokiel 1978).

‖ This residence time τ_1 is evaluated from the complete mixing method. See the text for more details.

dividing V_Q by the number of days per month and by the lagoon area.

Table 2 summarizes the calculated residence time for seawater in the lagoon using both methods. Substituting the average tidal range, d = 1.5 m, and average water depth, D = 20 m, into Eq. 2, τ_1 was calculated to be 29 d. Using Eqs. 4–7, we determined the residence time (τ_2) to be 23, 26, 18, and 27 d for January 1998, April 2000, September 2000, and March 2001, respectively. The salinity difference was too small (0.05) in March 2002 to allow calculation of τ_2. The calculated residence time τ_2 averaged across the four seasons was 24 d and is in reasonable agreement with τ_1 (29 d).

Sampling procedures—The seawater CO_2 system was studied intensively on the reef flat near EW-7 (Fig. 1B) from 15 to 21 April and from 13 to 18 September 2000 using the flow respirometry method described by Marsh and Smith (1978). Kayanne et al. (2005) have described the reef flat community and its metabolic processes in detail. The water was sampled using a 5-liter Go-Flo Niskin bottle, and the water samples for TA and DIC were bottled in 500-mL borosilicate glass bottles (Duran, Schott®) with 500 μL of saturated mercuric chloride ($HgCl_2$) solution (6.9 g per 100 mL) added to each sample for preservation. Water was also sampled for salinity.

Water from the lagoon and offshore were sampled and preserved as described previously in January 1998, April 2000, September 2000, and March 2002. A limited number of samples were collected at Sta. X in February and August 1999, and March 2001. In the lagoon, vertical water samples were obtained every 10 m from the surface to the bottom at most stations with the most intensive sampling undertaken at Sta. X. At the offshore stations, where the maximum depth was a few hundred meters, we collected water at depths of 0 (surface), 10, 20, 40, 80, and 160 m at O-1 and O-2, but at the surface only at O-A and O-B. River water was sampled from near NS-2 in March 2001 and again in March 2002.

Laboratory analysis and data processing—In 1998, TA was determined using an open-cell titration method based on the Gran procedure (Hansson and Jagner 1973) and DIC was determined using a TOC-5000 analyzer (Shimadzu) according to the method of Weisburd et al. (1995). In 1999, both TA and DIC were determined using a closed-cell analyzer constructed using the directions in the Department of Energy (DOE) handbook (DOE 1994), but after 2000, TA and DIC were determined using a newly developed flow-through–type analyzer. Details of the TA and DIC determinations can be found elsewhere (Kimoto et al. 2001, 2002; Watanabe et al. 2004). The accuracy and precision of the TA and DIC measurements were better than 3 and 2 μmol kg^{-1} for TA and 3 and 2 μmol kg^{-1} for DIC, respectively (Watanabe 2004; Watanabe et al. 2004), which were checked against certified reference materials (CRMs) distributed by A. Dickson (Scripps Institution of Oceanography). Errors associated with our sampling and preservation protocol were tested using the filtered, poisoned seawater for 2 years, and our accuracy was within 2 μmol kg^{-1} (0.1%) for both TA and DIC.

In 1998 and 1999, salinity was measured using a STD profiler (model AST-500, Alec Electronics). After 2000, salinity was determined using a Portasal salinometer (8410A, Guideline Instruments) along with the STD measurement. The Portasal was calibrated daily at the beginning of each batch using IAPSO standard seawater to ascertain its accuracy. The temperature change in the

Table 3. CO_2 system and physical parameters of the Palau barrier reef in various years.

Survey period Unit	Offshore/ lagoon‡	Salinity	SST °C	TA μmol kg^{-1}	DIC μmol kg^{-1}	fCO_2§ Pa	nTA μmol kg^{-1}	nDIC μmol kg^{-1}	ΔnTA μmol kg^{-1}	ΔnDIC μmol kg^{-1}	n	Sunshine hour‡ min d^{-1}
Mar 2002	O	34.30	28.4	2,242.2	1,925.9	39.5	2,288.0	1,965.2	43.6 (5.0)	21.2 (5.7)	4	368
	L	34.25	29.0	2,196.3	1,902.3	43.2	2,244.4	1,944.0			4	
Mar 2001*	O	33.75	28.5	NM	NM	NM	2,285.9	1,940.6	46.8 (1.7)	10.3 (3.9)	0	476
	L	33.54	28.6	2,145.7	1,849.8	39.3	2,239.1	1,930.3			5	
Sep 2000	O	33.84	29.3	2,208.5	1,874.8	34.9	2,284.4	1,939.2	36.9 (9.6)	13.3 (9.6)	8	332
	L	33.49	29.4	2,150.5	1842.9	38.4	2,247.5	1,926.0			26	
Apr 2000	O	33.77	29.1	2,206.5	1,877.1	35.6	2,286.6	1,945.3	48.7 (7.7)	17.8 (6.4)	8	335
	L	33.60	29.6	2,148.4	1,850.4	40.6	2,237.9	1,927.5			12	
Aug 1999*	O	NM	NM	NM	NM	NM	2,285.9	1,940.6	43.5 (4.5)	22.3 (1.6)	0	331
	L	32.81	NM	2,102.1	1,798.3	NM	2,242.4	1,918.3			2	
Feb 1999†	O	NM	NM	NM	NM	NM	2,285.9	1,940.6	47.7	28.5	0	355
	L	33.81	NM	2,162.1	1,847.1	NM	2,238.2	1,912.1			1	
Jan 1998	O	34.22	NM	2,227.8	1,855.7	NM	2,278.6	1,898.0	63.9 (10.7)	31.8 (9.0)	2	269
	L	33.98	28.5	2,150.2	1,811.8	NM‖	2,214.7	1,866.2			4	

Data in the parentheses indicate standard deviation (1 SD). n: number of data points. NM: not measured.
* The nTA and nDIC values for February 1999, August 1999, and March 2001 are averaged offshore values for all the other seasons, excluding January 1998, because no offshore samples were collected.
† Total sunshine hours for the 1-month period before the survey were averaged from the NOAA data.
‡ O and L indicate samples from the offshore and the lagoon, respectively.
§ fCO_2 is calculated from TA and DIC.
‖ Not calculated because of systematic errors in TA and DIC.

laboratory was kept within 1°C to prevent analyzer drift. The data obtained with the STD profiler were calibrated against the values obtained with the salinometer.

The effects of dilution by rain or evaporation on TA and DIC were regarded as proportional and were compensated for by using salinity normalization as follows:

$$\mathrm{nTA(nDIC)} = \mathrm{TA(DIC)}35/S \quad (8)$$

where nTA(nDIC) is the normalized TA (DIC) for a salinity of 35; and S is the salinity of the sample. fCO_2 is calculated from DIC, TA, salinity, and sea surface temperature using thermodynamic constants (Mehrbach et al. 1973 as modified by Dickson and Millero 1987). The air–sea exchange of CO_2 can be calculated from the difference in fCO_2 in air and water (ΔfCO_2), the solubility of CO_2 at a given temperature and salinity (Weiss 1974), and the gas transfer velocity (Eq. 29 in McGillis et al. 2001). The unit for fCO_2 is microatmospheres (μatm) in all the calculations above. The unit is converted from microatmospheres to Pa by multiplying a factor of 0.101325 (1 atm equals 101,325 Pa).

To measure total organic carbon (TOC, which is equivalent to dissolved organic carbon [DOC] plus particulate organic carbon [POC]), we sampled 30 mL of seawater, which were preserved by adding $HgCl_2$ to provide a final concentration of 10 ppm before being kept at room temperature before analysis (Torreton 1999). The TOC was measured using a high-temperature catalytic oxygen method with a nondispersive infrared analyzer as the detector (Model TOC-5000, Shimadzu). A calibration line was made by measuring standard solutions prepared from glucose. Seawater samples were assigned values against this calibration line.

Duplicate 10-mL samples were collected and stored frozen at −20°C until analyzed for nutrients. Nutrient concentrations for nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+), and phosphate (PO_4^{3-}) were determined colorimetrically using an autoanalyzer (AACS III, BRAN + RUEBBE).

Results

The CO_2 system in offshore water—Table 3 summarizes the offshore surface CO_2 system and associated parameters. In January 1998, the nTA and nDIC of the offshore surface water were 2,278.6 ± 3.3 μmol kg^{-1} and 1,898.0 ± 3.3 μmol kg^{-1}, respectively (n = 2 and all data are shown as means ± 1 SD). In April 2000, a conspicuous thermocline developed from 50 to 80 m, and nTA and nDIC increased to 2,292–2,305 μmol kg^{-1} and over 2,000 μmol kg^{-1} at 80 and 160 m, respectively. In September 2000, the offshore water was well-mixed down to 80 m and nTA and nDIC showed little variation from the surface to 80 m. The averaged data for the mixed layer of offshore surface water in both April and September 2000 had values for nTA and nDIC that were similar. nTA was 2,286.6 ± 1.2 in April and 2,284.4 ± 1.1 μmol kg^{-1} in September, while nDIC was 1,945.3 ± 3.2 in April and 1,939.2 ± 4.4 μmol kg^{-1} in September (n = 8). The water below the April 2000 thermocline had relatively high values for nTA and nDIC (up to 2,305 μmol kg^{-1} and 2,160 μmol kg^{-1}, respectively), with a high salinity (up to 34.8) and low temperatures (down to 12°C). In March 2002, only surface sampling was performed with values for nTA and nDIC of 2,288.0 ± 4.2 μmol kg^{-1} and 1,965.2 ± 4.4 μmol kg^{-1}, respectively (n = 3).

Calculated values of fCO_2 from TA and DIC determined at known salinities and temperatures are shown in Table 3. The calculated fCO_2 was 35.6 ± 1.1, 35.0 ± 1.1, and 39.5 ±

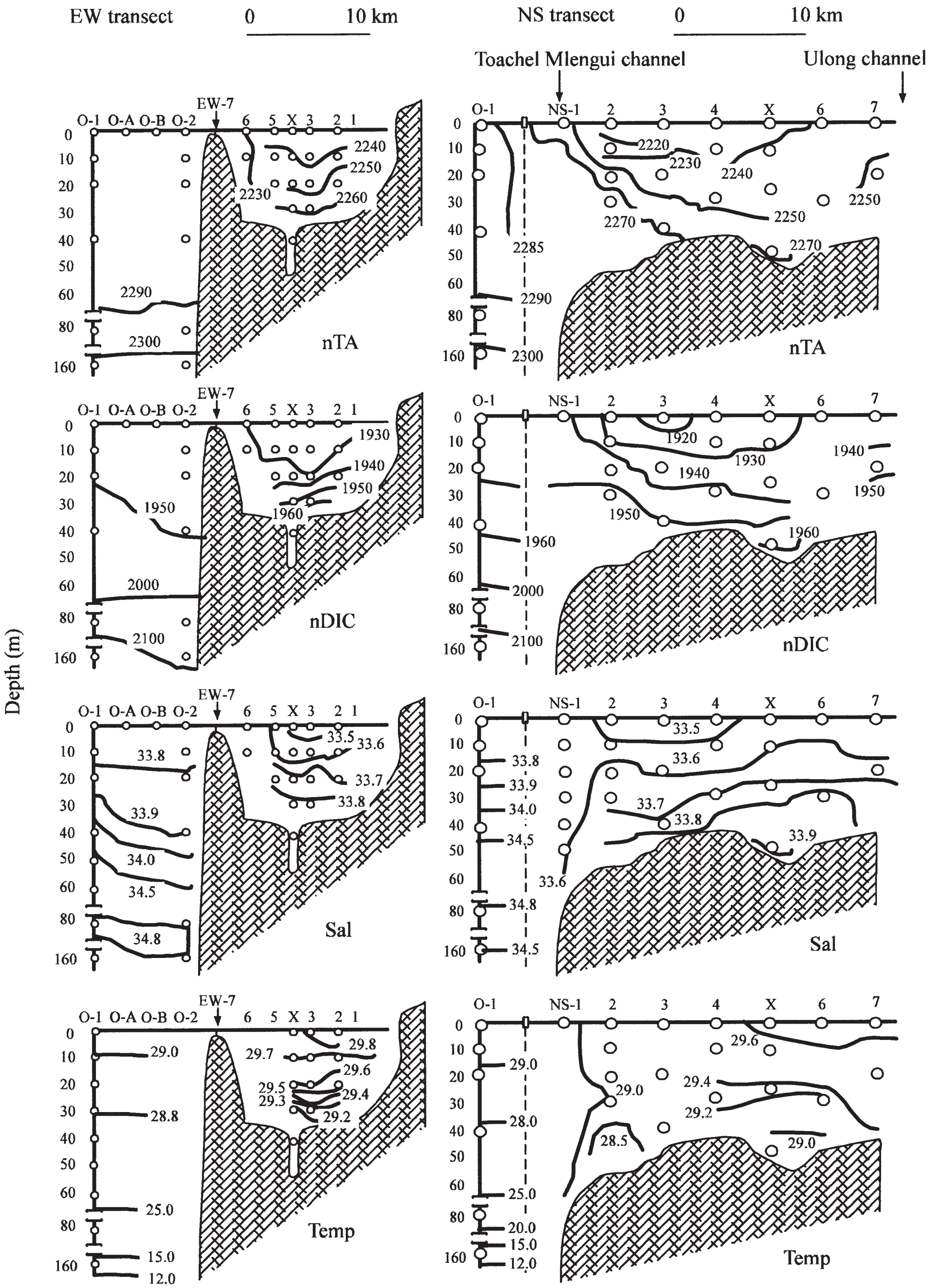

Fig. 3. Typical vertical profiles of nTA (μmol kg^{-1}), nDIC (μmol kg^{-1}), salinity, and temperature (°C) along the EW and NS transects in April 2000. Circles indicate sampling points.

1.2 Pa in April 2000, September 2000, and March 2002, respectively. An error associated with fCO$_2$ calculation from TA and DIC was evaluated based on the method of Dickson and Riley (1978). No calculations were made for 1998 because the relevant DIC data contain systematic errors arising from the analytical methods used. In the fCO$_2$ calculation, the concentrations of phosphate (0.00–0.04 μmol L^{-1}) and silica (1.5–4.6 μmol L^{-1}; Kayanne et al. 1993) are quite low and their effect on total alkalinity can safely be ignored.

Spatial variation of CO_2 system in the Palau barrier reef—Figure 3 shows representative vertical profiles of nTA, nDIC, salinity, and temperature obtained in April 2000. On the EW transect, no difference was observed among stations, with each exhibiting a gradual increase in nTA, nDIC, and salinity from the surface to the bottom. The bottom water had values close to those of offshore surface water. On the NS transect, spatial variation occurred near the large channels (NS-1 or NS-2) and islands (NS-2, NS-3). The data from NS-1 and NS-2 at depths of 20 and 30 m displayed values close to those of offshore water. The surface nTA at NS-2 and NS-3 was relatively low by about 20 μmol kg^{-1}, compared with the other stations in the lagoon. River water near NS-2 (Fig. 1A) affected the reef system. It had average values for March 2001 and March 2002 of 350 $\pm$ 43 (n = 3) μmol kg^{-1} and 700 $\pm$ 416 (n = 3) kg^{-1} for TA and DIC, respectively, where the salinity is zero.

Figure 4 shows nTA–nDIC diagrams for April and September 2000. Offshore mixed-layer waters were taken from the surface to approximately 50-m depth. The diagram shows net processes, such as net photosynthesis and net calcification. In the lagoon, temporal differences occurred between April and September. In April, the surface (shallower than 30 m) and bottom waters (deeper than 30 m) in the lagoon had distinctly different values, whereas in September, the surface and bottom waters had similar values. Data from around Sta. X gave means for nTA and nDIC of 2,237.9 $\pm$ 5.6 μmol kg^{-1} and 1,927.5 $\pm$ 4.2 μmol kg^{-1} (n = 12, 1 SD) in April and 2,247.5 $\pm$ 9.7 μmol kg^{-1} and 1,926.0 $\pm$ 8.8 μmol kg^{-1} (n = 12, 1 SD) in September (Table 3). Similar values were obtained from around Sta. X in February 1999, August 1999, March 2001, and March 2002. In January 1998, nTA was 2,214.7 $\pm$ 10.5 μmol kg^{-1} (n = 4), which was significantly lower ($p < 0.001$, t-test), by 20–30 μmol kg^{-1}, than the nTA determined in other sampling periods. The calculated mean fCO_2 in the lagoon was 40.6 $\pm$ 1.3, 38.4 $\pm$ 1.2, 39.3 $\pm$ 1.3, and 43.2 $\pm$ 1.4 Pa in April 2000, September 2000, March 2001, and March 2002, respectively (Table 3).

On the reef flat where the residence time of water is only a few hours (2.8 h calculated from the reef flat width of 1.6 km [Table 1] and the mean current speed of 15 cm s^{-1}) a large daytime decrease occurred in nTA and nDIC in both April and September 2000 (Fig. 4). Decreases occurred from the offshore value at flood tide and from the lagoon value at ebb tide. At night, nDIC increased at flood tide from the offshore value. From the daytime production slope of 0.50 $\pm$ 0.09 shown by vectors 1 to 3 in Fig. 4, the calculated ratio of net ecosystem production to calcification is (3.09 $\pm$ 0.75) : 1 (mean $\pm$ 1 SD, n = 3), indicating that the level of photosynthesis is three times that of calcification. From the nighttime production slope of -1.17 ± 0.18 for vector 4 in Fig. 4, the calculated ratio of respiration to calcification is (2.74 $\pm$ 0.27) : 1 (95% confidence limit for vector 4), indicating that respiration is the dominant process but calcification also occurs at night.

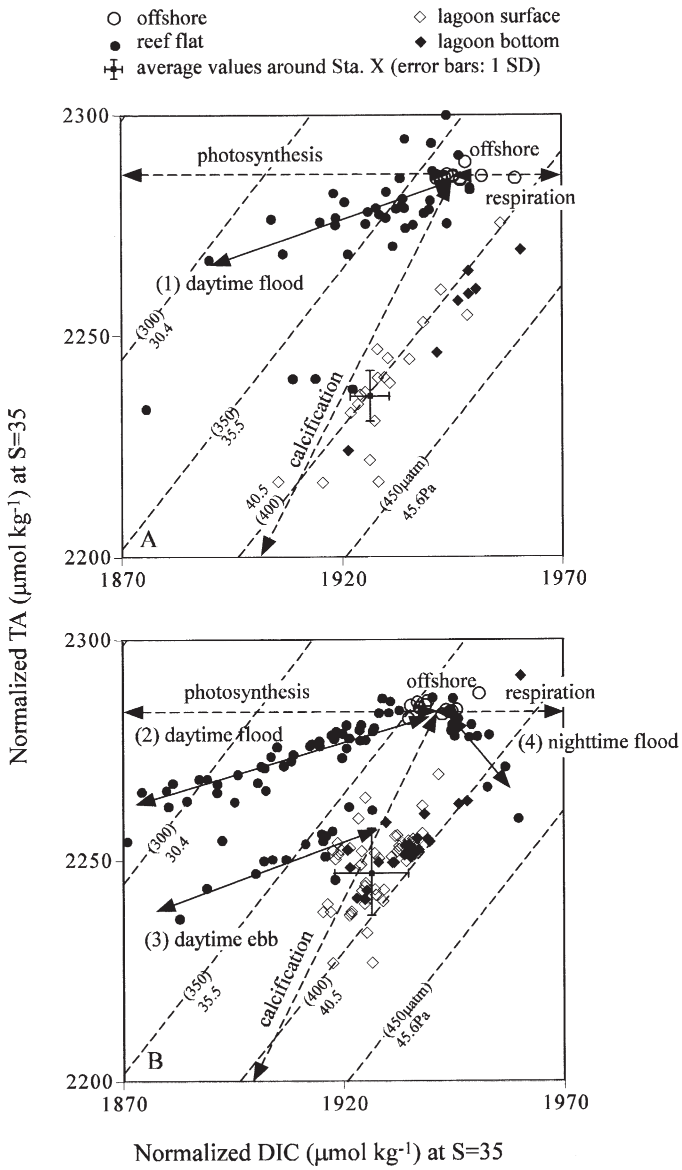

Fig. 4. Temporal and spatial variation in the CO_2 system of the Palau barrier reef in (A) April and (B) September 2000. The open circles, diamonds, and closed circles represent the offshore, lagoon, and reef flat data, respectively. The open and closed diamonds show lagoon data from the surface to 30 m and from >30 m, respectively. The dotted arrows indicate changes due to photosynthesis, calcification, and respiration; the production trend on the reef flat is shown as the sum of these vectors. The numbered vectors indicate the productivity on the reef flat: 1 and 2: daytime productions at flood tide, 3: daytime production at ebb tide, and 4: nighttime production at flood tide. Diagonal dotted lines are contour for fCO_2 between 30.4 and 45.6 Pa (300 and 450 μatm).

Organic matter and nutrients—Organic carbon was sampled without filtration in the Palau study. The TOC concentration was 79 $\pm$ 2.5 μmol kg^{-1} (mean $\pm$ 1 SD, n = 7) in the lagoon (Table 4), while in the river it was 186 $\pm$ 52 μmol kg^{-1} (n = 9) or about twice the lagoon value, although large variation occurred between samples.

Nutrients levels are summarized in Table 4 and were low in the reef and offshore (NO_3^- + NO_2^-, 0.06–0.18 μmol kg^{-1}; NH_4^+, 0.33–0.68 μmol kg^{-1}; PO_4^{3-}, 0.05–0.07 μmol kg^{-1}), in good agreement with previous studies (e.g., Hata 2003). The values were slightly higher in the river (NO_3^- + NO_2^-, 1.1 μmol kg^{-1}; NH_4^+, 1.5 μmol kg^{-1}; PO_4^{3-}, 0.3 μmol kg^{-1}).

Table 4. Organic carbon and nutrients concentrations in the Palau barrier reef in March 2001 and March 2002.

Site	NO_3^-		NO_2^-		NH_4^+		PO_4^{3-}		TOC	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Lagoon	0.04	0.06	0.02	0.02	0.38	0.25	0.04	0.02	79	2.5
Offshore	0.06	0.06	0.01	0.01	0.68	0.61	0.04	0.01	NM	NM
Reef flat	0.13	0.08	0.05	0.07	0.33	0.09	0.05	0.02	NM	NM
River	0.47	0.12	0.54	0.29	1.49	0.85	0.28	0.21	186	52

Units in μmol kg^{-1}. NM: not measured.

Gas exchange and riverine carbon transport—The air–sea exchange of CO_2 can be evaluated from empirical equations using wind velocity and the fCO_2 difference (ΔfCO_2) between air and water (McGillis et al. [2001] was used, which gives the largest gas flux under this condition). The only year for which all the necessary data were available for the calculation is 2000. For April and September 2000, the calculated lagoon water fCO_2 was 40.6 ± 1.3 and 38.4 ± 1.2 Pa, respectively (Table 3). The atmospheric fCO_2 was 35.9 Pa for April and 36.2 Pa for September (Table 5; Kayanne et al. unpubl. data), with measurement accuracy of 0.5 Pa (Kayanne et al. 2005). Differences in air–water fCO_2 were significantly smaller than zero in April ($p < 0.001$) and in September ($p < 0.10$). From the differences in the air–water fCO_2, and the wind speeds obtained every 3 h during these periods, 0.0–9.4 m s^{-1} (2.7 ± 1.7 m s^{-1}, mean ± 1 SD, $n = 256$, April) and 0.0–7.2 m s^{-1} (average 3.1 ± 1.8 m s^{-1}, mean ± 1 SD, $n = 209$, September), the calculated gas-exchange flux is −1.3 ± 0.6 (April) and −0.7 ± 0.4 mmol m^{-2} d^{-1} (September); the negative values indicating degassing from the sea surface to the atmosphere.

From Eqs. 6 and 7, the river discharge into the lagoon in April and September 2000 was 1.1×10^8 and 3.9×10^8 m^3 month^{-1}. From the organic and inorganic carbon concentrations and the river discharge, the TA flux from the river into the lagoon in April and September 2000 was 0.3 ± 0.04 and 1.1 ± 0.1 mmol m^{-2} d^{-1}, the DIC flux was 0.6 ± 0.4 and 2.2 ± 1.3 mmol m^{-2} d^{-1}, and the TOC flux was 0.2 ± 0.07 and 0.6 ± 0.2 mmol m^{-2} d^{-1}, respectively.

Discussion

Physical environment and the reef water CO_2 system—The offshore values of nTA and nDIC were similar in April and September 2000 and March 2002 (Table 3). The nTA values were particularly consistent during these three periods: 2,284.4 ± 1.2 (mean ± 1 SD, $n = 8$), 2,286.6 ± 1.1 ($n = 8$), and 2,288.0 ± 4.4 μmol kg^{-1} ($n = 3$). Values determined in earlier studies are consistent with these results. In April 1992 Kayanne et al. (1993) determined an nTA of 2,285.7 ± 4.5 μmol kg^{-1} ($n = 6$) and in July 1994 Suzuki (1995) obtained a value of 2,284.7 μmol kg^{-1} ($n = 1$). Therefore, the offshore surface water can be considered to be a constant end member of the Palau barrier reef system.

Temporal differences were observed between April and September 2000. In April 2000, clear vertical gradients existed in nTA and nDIC (Fig. 3) (from 0 to 20 m nDIC = 1,927.5 ± 5.6 μmol kg^{-1}, nTA = 2,237.9 ± 7.6 μmol kg^{-1} [$n = 12$]; from 30 m to the bottom nDIC = 1,953.8 ± 13.6 μmol kg^{-1}, nTA = 2,264.9 ± 10.0 μmol kg^{-1} [$n = 17$]), whereas in September, nDIC and nTA were similar from the surface to the bottom (from 0 to 20 m, nDIC = 1,926.0 ± 8.5 μmol kg^{-1} and nTA = 2,247.5 ± 9.5 μmol kg^{-1} [$n = 26$]; and from 30 m to the bottom, nDIC = 1,934.4 ± 8.7 μmol kg^{-1} and nTA = 2,253.1 ± 6.1 μmol kg^{-1} [$n = 20$]). Although the layer of water mass deeper than 30 m has significantly higher values of nTA and nDIC under well-stratified conditions, such as in April 2000 (Fig. 3), this water mass occupies only 5% of the total lagoon water volume (Table 1) and would have little influence on the mean value if it were to mix with the surface layer; the increase of 1–3 μmol kg^{-1} (μmol kg^{-1}) is within the analytical error. By contrast, the deep water value is easily modified where it mixes efficiently with surface water. The mean residence time for τ_2 was 26 and 18 d, respectively, in April and September. The shorter residence time calculated for September might arise from such efficient mixing. The resultant water exchange could lead to the surface water exhibiting higher values, with the shorter residence time reflected in smaller accumulated changes and values approaching those of offshore water. Correspondingly, the bottom water would possess lower values as a result of efficient mixing with surface water. Thus the CO_2 system varies with water mixing or stratification within the system.

Effects of CO_2 gas exchange and nutrient uptake on the CO_2 system—Lagoon water fCO_2 is always supersaturated compared with atmospheric or offshore surface water fCO_2 (both around 35.5 Pa), which can be seen from the contours for fCO_2 in Fig. 4. The gas-exchange rate was calculated to be −1.3 ± 0.6 (April) and −0.7 ± 0.4 mmol m^{-2} d^{-1} (September) in 2000. The gas-exchange changes DIC only, not TA. At this rate the lagoon mixed-layer (0–20 m) DIC will be decreased only by 0.9 to 1.7 μmol kg^{-1} during the residence time of ~30 d. As can be clearly seen in Fig. 4, a 10 to 30 μmol kg^{-1} decrease in DIC is needed to reach equilibrium with atmospheric fCO_2, but the gas exchange in Palau is too small because of the weak wind speed. Assuming only calcification occurs and gas-exchange efficiency is 0, 25, 50, 75, and 100% for Sep 2000, the slope on TA–DIC diagram between original, offshore water, and lagoon water becomes 2, 1.75, 1.56, 1.40, and 1.27, respectively. The slopes for 0% and 100% exchanges are represented on Fig. 4 by a calcification line

Table 5. TA and DIC flux calculations for the Palau barrier reef.

Data used for calculation	Unit	Jul 1994		Apr 2000		Sep 2000	
ΔnTA	μmol kg^{-1}	74.6±5.3 (4)		48.7±7.7 (12)		36.9±9.6 (26)	
ΔnDIC	μmol kg^{-1}	34.2±9.2 (4)		17.8±6.4 (12)		13.3±9.6 (26)	
Lagoon fCO_2	Pa	41.9±1.1‖		40.6±1.3		38.4±1.2	
fCO_2 in air	Pa	35.3±0.5‖		35.9±0.5¶		36.2±0.5¶	
Riverine TOC*	μmol kg^{-1}	200±65 (7)		200±65 (7)		200±65 (7)	
Riverine DIC*	μmol kg^{-1}	700±416 (3)		700±416 (3)		700±416 (3)	
Riverine TA*	μmol kg^{-1}	350±43 (3)		350±43 (3)		350±43 (3)	
Residence time τ_1	d	29		29		29	
Residence time τ_2	d	30		26		18	
Lagoon depth	m	20		20		20	
Lagoon area	m^2	4.1×10^8		4.1×10^8		4.1×10^8	
Reef flat area	m^2	7.1×10^7		7.1×10^7		7.1×10^7	
Catchment area	m^2	2.0×10^8		2.0×10^8		2.0×10^8	
Precipitation	mm d^{-1}	7.9		6.3		12.1	
Wind speed	m s^{-1}	3.2±0.8 (32)		2.7±1.7 (256)		3.0±1.8 (209)	
Salinity		33.62±0.10 (4)		33.60±0.10 (12)		33.49±0.03 (23)	
Temperature	°C	28.3±0.3 (4)		28.3±0.2 (12)		29.4±0.2 (23)	
River flux							
River discharge, V_Q†	m^3 d^{-1}	6.3×10^5		3.7×10^5		1.3×10^6	
DIC flux	mmol m^{-2} d^{-1}	1.1±0.7		0.6±0.4		2.2±1.3	
TA flux	mmol m^{-2} d^{-1}	0.5±0.06		0.3±0.04		1.1±0.1	
TOC flux	mmol m^{-2} d^{-1}	0.3±0.1		0.2±0.07		0.6±0.2	
Reef flat							
P_{n_reef}‡	mmol m^{-2} d^{-1}	−97±52		−25±17		−25±17	
G_{n_reef}‡	mmol m^{-2} d^{-1}	−130		−74		−74	
Whole reef system							
Residence time used		τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
ΔTA_0	mmol m^{-2} d^{-1}	−53±3.8	−51±3.6	−35±5.4	−39±6.0	−27±6.8	−43±10.9
ΔDIC_0	mmol m^{-2} d^{-1}	−26±7.0	−25±6.7	−13±4.7	−15±5.4	−12±8.7	−18±13.0
ΔDIC_{calc}	mmol m^{-2} d^{-1}	−27±1.9	−26±1.8	−17±2.7	−19±3.0	−14±3.4	−22±5.5
ΔDIC_{gas}§	mmol m^{-2} d^{-1}	−1.8±0.4	−1.8±0.4	−1.3±0.6	−1.3±0.6	−0.7±0.4	−0.7±0.4
ΔDIC_{org}	mmol m^{-2} d^{-1}	2.9±7.3	2.8±6.9	5.3±5.5	5.8±6.2	2.0±9.3	4.3±14.1
Lagoon							
P_{n_lagoon}	mmol m^{-2} d^{-1}	11.8±9.7	11.7±9.3	8.3±6.6	9.0±7.4	4.6±11.0	7.2±16.6
G_{n_lagoon}	mmol m^{-2} d^{-1}	−19.9	−18.9	−13.9	−16.3	−9.5	−18.8

Data after ± indicate calculated errors. Data in parentheses indicate number of data points. P_{n_reef}, G_{n_reef}, P_{n_lagoon} and G_{n_lagoon} indicate reef flat net ecosystem production, net ecosystem calcification, lagoon net ecosystem production, and lagoon net ecosystem calcification, respectively.

* Results in March 2002 and March 2003.

† Calculation based on LOICZ web site.

‡ Kayanne et al. (2005).

§ Calculated using the equation from McGillis et al. (2001).

¶ Kayanne et al. unpubl. data.

‖ Kawahata et al. 1997.

(slope = 2) and fCO_2 is represented by contour lines (slopes = ~1.3). The plots in Fig. 4 indicate that calcification is predominant and that gas exchange is not a significant process in Palau.

In this study we calculated fCO_2 from TA and DIC. This will cause large errors in the calculated values, about 3% (1.0 Pa) under the measurement accuracy of TA and DIC. Even with this error, the release of CO_2 from the lagoon is much smaller than the biological fluxes and does not affect the flux calculations significantly. But when studying some environments in which CO_2 gas exchange plays an important role in CO_2 fluxes, it is better to measure fCO_2 directly (accuracy ~1%) or to calculate it from pH-TA or pH-DIC (accuracy ~1.5%) (Anderson et al. 1999).

Relative humidity (RH) was assumed to be 100% in the atmosphere–water boundary in the gas-exchange calculation. By changing RH to 80%, which is about the mean value of atmospheric RH in Palau, fCO_2 in the atmosphere increases by 0.3 Pa, thus making the air–sea difference lower by 0.3 Pa. This error is smaller than the error of calculated seawater fCO_2 (~1.0 Pa) and is not of great importance in the gas-exchange calculation in this study.

Strictly speaking, the uptake of NO_3 and NH_4 during photosynthesis causes a small change in TA (Brewer and

Goldman 1976). When 1 mol of NO_3 is consumed, TA increases by 1 mol, while when 1 mol of NH_4 is consumed, TA decreases by 1 mol (Anderson et al. 1999). Assuming that the primary producers have a Redfield C : N : P ratio, 106 : 16 : 1, and all the nitrogen used is nitrate (ammonia), then TA will increase (decrease) by 0.16 (0.14) mol when 1 mol of organic carbon is produced (e.g., Chen 2002). This will decrease (increase) the estimate of organic carbon production by 7.5 (7.4) % and increase (decrease) the estimate of inorganic carbon production by about the same strength, which is dependent on the magnitude of organic carbon production. The error of this magnitude is negligible because the natural variability of CO_2 system parameters is larger than this (usually >20%, see Table 3).

Formation process of the reef water CO_2 system analyzed by TA–DIC diagrams—The effect of metabolic processes in the biological community on the seawater CO_2 system can be explored using TA–DIC diagrams (Fig. 4). Even allowing for the temporal and spatial variation in the lagoon water CO_2 system, the values obtained near the center of the lagoon at Sta. X are about the mean values for all stations and can be regarded as representative of the lagoonal seawater composition (Fig. 4). Consequently, the significant differences in nTA and nDIC are those between the offshore mixed layer values and the lagoon surface mixed layer values near the center of the lagoon (EW-3 to 5 and NS-4 to 6). Here, these differences are defined as ΔnTA and ΔnDIC.

Table 5 summarizes TA and DIC fluxes calculations for the Palau barrier reef to quantitatively evaluate net ecosystem production and calcification rate. In April and September 2000, ΔnTA was -48.7 ± 7.7 and -36.9 ± 9.6 μmol kg^{-1}, and ΔnDIC was -17.8 ± 6.4 and -13.3 ± 9.6 μmol kg^{-1}, respectively. ΔnTA in April and September 2000 differed significantly ($p < 0.001$, *t*-test). From the residence times (τ_1 and τ_2), the depth D, and ΔnTA and ΔnDIC, the fluxes in TA and DIC (ΔTA and ΔDIC) can be calculated from next equations:

$$\Delta\mathrm{TA}\left(\mathrm{mmol\ m^{-2}\ d^{-1}}\right) = -\Delta\mathrm{nTA}\,\sigma\,\mathrm{D}/\tau \quad (9)$$

$$\Delta\mathrm{DIC}\left(\mathrm{mmol\ m^{-2}\ d^{-1}}\right) = -\Delta\mathrm{nDIC}\,\sigma\,\mathrm{D}/\tau \quad (10)$$

where σ is density of seawater (kg dm^{-3}). Calculated ΔTA $= -34 \pm 5.4$ to -38 ± 6.0 and -26 ± 6.8 to -42 ± 10.9 mmol m^{-2} d^{-1}, and ΔDIC $= -13 \pm 4.7$ to -14 ± 5.4 and -9 ± 8.7 to -15 ± 13.0 mmol m^{-2} d^{-1} for April and September 2000, respectively. Subtracting the river TA, DIC, and TOC inputs, as discussed in the previous paragraph, and defining the first two differences as $\Delta\mathrm{TA}_0$ and $\Delta\mathrm{DIC}_0$,

$$\Delta\mathrm{TA}_0\left(\mathrm{mmol\ m^{-2}\ d^{-1}}\right) = \Delta\mathrm{TA} - \text{river TA flux} \quad (11)$$

$$\Delta\mathrm{DIC}_0\left(\mathrm{mmol\ m^{-2}\ d^{-1}}\right) = \Delta\mathrm{DIC} - \text{river DIC flux} - \text{river TOC flux} \quad (12)$$

and assuming that all of the TOC is respired back to DIC, the calculated values of $\Delta\mathrm{TA}_0$ range from -35 ± 5.4 to -39 ± 6.0 and from -27 ± 6.8 to -43 ± 10.9 mmol m^{-2} d^{-1}, and those of $\Delta\mathrm{DIC}_0$ from -13 ± 4.7 to -15 ± 5.4 and from -12 ± 8.7 to -18 ± 13.0 mmol m^{-2} d^{-1} for April and September 2000, respectively (Table 5). The change in the DIC flux associated with calcification ($\Delta\mathrm{DIC_{calc}}$) is half of $\Delta\mathrm{TA}_0$, and hence $\Delta\mathrm{DIC_{calc}}$ ranges from -17 ± 2.7 to -19 ± 3.0 and from -14 ± 3.4 to -22 ± 5.5 mmol m^{-2} d^{-1} for these same periods. The DIC flux related to gas exchange ($\Delta\mathrm{DIC_{gas}}$) is -1.3 ± 0.6 and -0.7 ± 0.4 mmol m^{-2} d^{-1} over these same intervals, as discussed previously, such that the DIC flux related to organic production ($\Delta\mathrm{DIC_{org}}$) can be calculated as 5.3 ± 5.5–5.8 ± 6.2 and 2.0 ± 9.3–4.3 ± 14.1 mmol m^{-2} d^{-1} for April and September 2000, respectively, given that

$$\Delta\mathrm{DIC}_0 = \Delta\mathrm{DIC_{calc}} + \Delta\mathrm{DIC_{gas}} + \Delta\mathrm{DIC_{org}} \quad (13)$$

The positive values indicate net respiration in the system.

Kayanne et al. (2005) estimated the reef flat net ecosystem production ($P_{\mathrm{n\_reef}}$) and calcification ($G_{\mathrm{n\_reef}}$) as -25 ± 17 (mean $\pm$ 1 SE) and -74 mmol m^{-2} d^{-1} from surveys performed in April and September 2000, respectively. Only half of this production on the reef flat (i.e., production at flood tide) affects the change in values of TA and DIC over that of lagoon water.

In the following equations, the net ecosystem production and calcification in the lagoon are defined as $P_{\mathrm{n\_lagoon}}$ and $G_{\mathrm{n\_lagoon}}$:

$$\Delta\mathrm{DIC_{org}}(\mathrm{lagoon\_area} + \mathrm{reef\_area}) = \frac{1}{2}(P_{\mathrm{n\_reef}})(\mathrm{reef\_area}) + P_{\mathrm{n\_lagoon}}(\mathrm{lagoon\_area}) \quad (14)$$

$$\Delta\mathrm{DIC_{calc}}(\mathrm{lagoon\_area} + \mathrm{reef\_area}) = \frac{G_{\mathrm{n\_reef}}(\mathrm{reef\_area})}{2} + G_{\mathrm{n\_lagoon}}(\mathrm{lagoon\_area}) \quad (15)$$

Substituting all the data into Eqs. 14 and 15, we can calculate $P_{\mathrm{n\_lagoon}}$ with two calculated residence times as 8.3 ± 6.6 (τ_1) to 9.0 ± 7.4 (τ_2) and 4.6 ± 11.0 to 7.2 ± 16.6 mmol m^{-2} d^{-1}, and $G_{\mathrm{n\_lagoon}}$ is calculated as -13.9 to -16.3 and -9.5 to -18.8 mmol m^{-2} d^{-1}, for April and September 2000, respectively.

Clearly, the quantitative analyses of the TA–DIC diagrams shows that the shallow reef flat with its abundant reef-building organisms and sufficient light exhibits large areal photosynthesis and calcification, whereas in the deep lagoon, with fewer organisms and less light, respiration equals or is larger than photosynthesis, although calcification can still occur. TA and DIC change in the direction of photosynthesis or calcification, and from the vector analyses such as that just performed, we can estimate the metabolism of the subsystem (lagoon), which is not directly measured.

Smith and Jokiel (1978) and Smith et al. (1984) reported carbon fluxes due to biological metabolic activity in two shallow (3 and 6 m average depth) lagoons in the central tropical Pacific. They showed that $P_{\mathrm{n\_lagoon}}$ ranged from -5.8 to -14.2 mmol m^{-2} d^{-1} and $G_{\mathrm{n\_lagoon}}$ from -2.5 to

-13.7 mmol m^{-2} d^{-1} for the 3 and 6 m deep lagoons, respectively. The calcification rate in the lagoon in our Palau study was almost identical to their value, whereas the pattern of photosynthesis at Palau is totally different from their result. The shallow lagoons they studied exhibited positive net ecosystem production (i.e., autotrophic), whereas the deep lagoon we studied exhibited negative net ecosystem production (i.e., heterotrophic) although bearing large errors. It appears that shallow ($\sim$5 m) lagoons perform rather like a reef flat in that they receive sufficient sunlight to allow for positive net ecosystem production and calcification, although the flux may be an order of magnitude smaller than reef flat. Conversely, a deep lagoon performs differently and has a negative net ecosystem production that is fueled in part by organic matter delivered from the productive reef flat. Such a lagoon may show positive calcification.

Long-term decrease in reef productivity—We have included data for Sta. X during April 1992 and July 1994 from Kayanne et al. (1993) and Suzuki (1995) to see the long-term change in reef productivity. ΔnTA and ΔnDIC decreased from 1992 until 2002, especially as for ΔnTA (Fig. 5 and Table 5). Differences between before 1998 and after 1998 are significant ($p < 0.001$), and differences between 1992 and 1994 and between 1992 and 1998 are also significant ($p = 0.05$). Both the residence time of the lagoon water and the magnitude of the productivity of the entire coral reef system influence the values of ΔnTA and ΔnDIC. The calculated residence times (τ_2) for April 1992 and September 2000 (11 and 18 d, respectively) were significantly shorter than for all other periods (23–30 d). One reason for this might lie in the mixing of the lagoon water observed in both September 2000 in this study and in April 1992 by Kayanne et al. (1993). The salinity difference in Eq. 4 ($S_O - S_L$) was quite small in April 1992, and this might arise from significant errors in the calculation. But a shorter residence time in April 1992 is inconsistent with the larger values of ΔnTA and ΔnDIC determined in April 1992. Moreover, variation in ΔnTA and ΔnDIC for other periods cannot be explained from the residence time alone. Certainly, the differences in ΔnTA and ΔnDIC before and after 1998 are too large to be explained by changes in residence time caused by lagoon water mixing. Instead, these differences might arise from changes in the productivity of the coral reef.

The average minutes of sunshine per day for the 1-month period preceding each survey were calculated from NOAA data (Table 5). In April 1992, the sunshine levels were high (565 min d^{-1}). This period corresponded to an El Niño event, and this fine weather might have enhanced the biological activity in the reef and hence increased ΔnTA. However, with the exception of April 1992, neither the change in residence time nor the sunshine hours can explain the changes in ΔnTA.

Kayanne et al. (2005) reported a decrease in productivity on the reef flat after the bleaching event in 1998. The community net production, respiration, gross production, and calcification in April and September 2000 were 32%, 46%, 44%, and 57% of their July 1994 values, respectively.

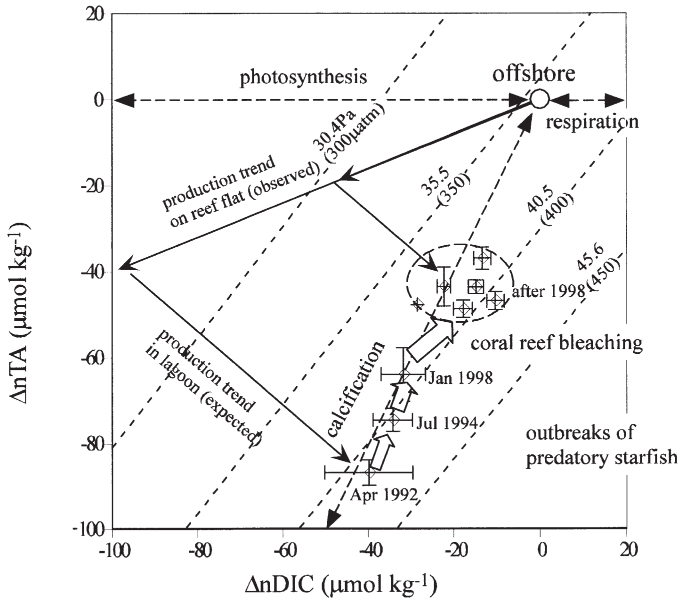

Fig. 5. Long-term changes in the TA and DIC differences between the offshore and lagoon waters (ΔTA and ΔDIC). DIC and TA are normalized to a salinity of 35. Data for 1992 and 1994 are cited from Kayanne et al. (1993) and Suzuki (1995), respectively. The dashed arrows indicate changes due to photosynthesis, respiration, and calcification. Diagonal dotted lines are contour for fCO_2 between 30.4 and 45.6 Pa (300 and 450 μatm). The error bars indicate 1 SE for the lagoon nDIC and nTA. ΔnTA for after 1998 differed significantly from those before 1998 ($p < 0.001$), and ΔnTA for Apr 1992 differed significantly from Jul 1994 and Jan 1998 ($p = 0.05$).

Corals in the relatively deep lagoon areas were also influenced by the high 1998 temperature and their coverage decreased, as reported by Bruno et al. (2001). In addition, ΔnTA and ΔnDIC decreased each year beginning in 1992. This might have been due to the decrease in coral coverage before 1998, possibly related to outbreaks of *Acanthaster planci*, a predatory starfish, in the mid to late 1990s that caused near total coral mortality at some sites (Bruno et al. 2001). The ΔnTA for years after 1998 decreased by 27%, 37%, and 46% of the values for January 1998, July 1994, and April 1992, respectively. Clearly, the year-to-year decrease in productivity of the reef system over the last decade has been reflected in the CO_2 system of the lagoon waters.

As calculated earlier for 2000, the fluxes can be calculated for July 1994. The reef flat calcification and net ecosystem production rate were reported to be 130 and 97 $\pm$ 52 (mean $\pm$ 1 SE) mmol m^{-2} d^{-1}, respectively (Kayanne et al. 2005). Kawahata et al. (1997) found the lagoon and atmospheric fCO_2 to be 41.9 $\pm$ 1.1 and 35.3 $\pm$ 0.5 Pa during the same period. The precipitation and wind speed during this period were 7.9 mm d^{-1} and 1.8–5.4 m s^{-1} (daily averaged data, 3.2 $\pm$ 0.8 m s^{-1}, mean $\pm$ 1 SD, $n = 32$). The calculated fluxes were as follows: ΔTA_o, -51 ± 3.6 to -53 ± 3.8 mmol m^{-2} d^{-1}; ΔDIC_o, -25 ± 6.7 to -26 ± 7.0; ΔDIC_{calc}, -26 ± 1.8 to -27 ± 1.9; ΔDIC_{gas}, -1.8 ± 0.4; ΔDIC_{org}, 2.8 ± 6.9 to 2.9 ± 7.3;

P_{n_lagoon}, 11.7 ± 9.3 to 11.8 ± 9.7; and G_{n_lagoon}, −18.9 to −19.9 mmol m^{-2} d^{-1} (Table 5). Note that in 2000, the lagoon calcification decreased by 60–70% of 1994 values. The lowered calcification rate in the lagoon may be attributed to decreased coral coverage here (Bruno et al. 2001), as well as to the activity of other calcareous organisms, such as foraminifers. The present reef environment is certainly unable to support the number of heterotrophic organisms, such as fish, that it once did.

Together with a decline in organic production on the reef flat (Kayanne et al. 2005), both the reef flat and the lagoon calcification decreased drastically after the bleaching event in 1998. The bleaching event was observed worldwide, and in regions where the corals did not recover after the bleaching, the same trends must have occurred. Because coral reef calcification is estimated to account for >10% of the calcium input to the world ocean (Smith 1978; Milliman and Droxler 1996; Iglesias-Rodriguez et al. 2002), if serious degradation of coral reef environments and the resultant decrease in calcification (over 30%) observed by this study occurs worldwide it must have a significant impact on the global carbon and calcium cycles.

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