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Journal of Marine Systems 66 (2007) 140–149
JOURNAL OF MARINE SYSTEMS
www.elsevier.com/locate/jmarsys

Measurement of air–water CO_2 transfer at four coastal sites using a chamber method

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Received 5 October 2005; accepted 7 April 2006
Available online 25 September 2006

Abstract

We measured the air–water CO_2 flux in four coastal regions (two coral reefs, one estuary, and one coastal brackish lake) using a chamber method, which has the highest spatial resolution of the methods available for measuring coastal air–water gas flux. Some of the measurements were considerably higher than expected from reported wind-dependent relationships. The average k_{600} values for Shiraho Reef, Fukido Reef, Fukido River, and Lake Nakaumi were 1.5 ± 0.6, 3.2 ± 0.3, 0.69 ± 0.26, and 2.2 ± 0.9 (mean ± S.D.) times larger than the wind-dependent relationships. Results were compared with current-dependent relationships and vertical turbulence intensity (VTI). VTI is an index of water-surface stirring and is calculated from near-surface vertical velocity. Although some measurements from the reefs and river closely matched those expected from wind-dependent relationships, others were considerably higher. All data were correlated with VTI and were qualitatively explained by bottom macro-roughness enhancement. In Lake Nakaumi, results tended to differ from the wind-dependent relationships, and the difference between the measured and expected gas-transfer velocity was correlated with biological DO changes and/or the intensity of density stratification. We found these factors to have important effects on coastal gas flux. In addition, the chamber method was an effective tool for evaluating coastal gas flux.

Keywords: Air-water CO2 flux; Coastal area; Current effect; Biological effect

1. Introduction

Air–water gas transfer is determined by physical, chemical, and biological surface-water conditions. On the open ocean, wind stress is thought to be the dominant factor affecting the water surface. Consequently, the gas-transfer velocity has been calculated from the wind speed 10 m above the water surface (e.g., Liss and Merlivat,

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0924-7963/$ - see front matter
doi:10.1016/j.jmarsys.2006.04.010

1986; Wanninkhof, 1992). In coastal regions, field measurements have shown a different relationship between gas-transfer velocity and wind speed (Marino and Howarth, 1993; Carini et al., 1996; Raymond and Cole, 2001). In addition, factors other than wind speed affect water-surface conditions. Thus, such factors should be incorporated in calculations of coastal air–water gas flux.

Early studies of air–water gas transfer indicated that water currents at shallow depths affect the gas-transfer velocity (O'Connor and Dobbins, 1958; Owens et al., 1964; Langbein and Durum, 1967). O'Connor and Dobbins (1958) demonstrated this with a simple formula:

$$k_{600} = 1.72\sqrt{u/h}$$

where k_{600} is the transfer velocity normalized at a Schmidt number (*Sc*) of 600, u is the current speed (cm/s), and h is the water depth (m). This formula indicates that strong currents at shallow depths increase the gas transfer velocity. Recently, Moog and Jirka (1999a,b) demonstrated that bottom macro-scale elements enhance gas transfer. In an estuarine system, Zappa et al. (2003) showed that gas-transfer velocity measurements were consistent with the formula of O'Connor and Dobbins relationship (hereafter, OD58) under low-wind conditions.

In addition, Upstill-Goddard et al. (2003) reported that the air–water transfer velocity of methane was enhanced when methane-oxidizing bacteria were added to their water-tank experiment. They suggested that this result could be applied to gas transfer in the field (Upstill-Goddard et al., 2003). However, Goldman et al. (1988) and Frew et al. (1990) suggested that phytoplankton-generated organic matter can decrease the gas-transfer velocity, because plankton exudates can affect the dissipation rate of near-surface turbulence.

This prior research clearly indicates that factors other than wind speed can regulate air–water gas transfer. For example, Zappa et al. (2003) measured gas transfer in an estuary and found that current speed was correlated with the gas-transfer velocity. Furthermore, they demonstrated that the turbulent dissipation rate captures many of the driving processes, including wind and currents, and may thus provide a method to scale the gas-transfer rate (Zappa et al., 2003). Here, we account for the effects of bottom macro-roughness enhancement. To evaluate the factors regulating coastal gas transfer, high temporal and spatial resolution are required to capture variable coastal site conditions. In addition, multi-point measurements are necessary to compare gas transfer among several sites. The Gradient flux technique (McGillis et al., 2001; Zappa et al., 2003) and direct measurement of near-surface turbulence satisfy these requirements. However, these methods require a platform at each measurement site, and thus, multi-point measurement is difficult. Furthermore, these methods cannot be used at sites where platform construction is unfeasible (e.g., because of depth) because the motion of a small boat or vessel would make it difficult to adjust for these measurements.

The chamber method provides the only way to produce enough temporal and spatial resolution for coastal gas-transfer measurement without a platform. This method is ideal for evaluating coastal gas flux under limited conditions (Kremer et al., 2003) and has been used successfully for some coastal measurements (e.g., Frankignoulle, 1988). However, the validity of the chamber method has been debated, despite studies verifying that results using this method were consistent with those from other methods, such as the mass balance technique. The primary criticism of the chamber method is that the chamber device blocks wind stress. However, Kremer et al. (2003) showed that air turbulence inside the chamber, which was generated by an attached fan, increased gas flux by only 2–12% under weak wind conditions. They indicated that the direct regulating factor of gas transfer is near-surface liquid turbulence generated by wind stress and that turbulence entering the chamber under the water surface is not affected by the device (Kremer et al., 2003). Another criticism of the method is that the chamber pressure against the current generates unnatural turbulence on the water surface. Frankignoulle (1988) used a drifting system to avoid this unnatural turbulence. In addition, Belanger and Korzum (1991) compared results from different sizes of chambers and found that differences in gas transfer were caused by temperature and pressure changes inside the chamber.

We measured CO_2 flux and the gas-transfer velocity (k) to test the effects of current including bottom macro-roughness enhancement and biological activity on the air–water CO_2 transfer velocity in coastal regions. To analyze these effects, we used the chamber method because multi-point measurement with high temporal and spatial resolution was required. These measurements were performed under weak current conditions to avoid current-generated unnatural turbulence. In addition, we measured temperature and pressure changes within the chamber to monitor the biases found by Belanger and Korzum (1991). Air–water gas flux and gas-transfer velocity were measured in two coral reefs, one estuary, and one brackish coastal lake. We compared the results with current parameters and with temporal changes in dissolved oxygen (DO) concentrations (an index of biological activity).

2. Locations and methodology

Measurements were conducted at the Fukido and Shiraho reefs (24°29′N 124°13′E and 24°24′N 124°15′N, respectively) and the Fukido River (24°28′N 124°14′E) on Ishigaki Island, Okinawa Prefecture, Japan, as well as at the coastal Lake Nakaumi (35°28′N 133°14′E–135°28′N 133°11′E) in Shimane Prefecture, Japan. On Ishigaki Island, measurements were made in July and August 2003, whereas at Lake Nakaumi, measurements were taken in July 2003 and August 2004. Measurements were taken during the summer because wind conditions at these sites are usually moderate at that time; we think other seasonal effects were not significant for this study.

The Shiraho and Fukido reefs are situated on the southeastern and northwestern coasts of Ishigaki Island, respectively. These reefs have widths of 500–1000 m, mean depths of 1–3 m, and average tidal ranges of 1.5 m. Measurement sites were located in the middle of the reef flats where coral zonation could be found. The density of coral appeared to be higher at Fukido Reef than at Shiraho Reef. The Fukido River is small (the largest width and depth are ~10 m and ~2 m, respectively) and has either a sand or mud bed. This river flows through a mangrove forest and enters Fukido Reef. The measurement site was located approximately 100 m from the swash.

Lake Nakaumi is a semi-enclosed brackish coastal lake connected to the Japan Sea by a channel. The lake area is 60 km^2 and the average depth is 6 m. Because the Japan Sea has a relatively shallow tidal level (0.2–0.4 m), there is minimal tidal effect on Lake Nakaumi. Lake Nakaumi has high chlorophyll concentrations (1995 range was 5–70 μg/L; Nakata et al., 2000) and a high density stratification because of the salinity difference between the surface and the bottom. The measurement site was located in the middle of the lake.

Water conditions (temperature, salinity, pH, DO) were measured at approximately 1m in depth using a water quality sensor (Hydrolab H20; Hach Environmental, Loveland, CO, USA). Air and water fCO_2 were measured using an fCO_2 analyzer through an equilibrator system (detailed in Saito et al., 1995), which has an estimated accuracy of 1%. All measurements were taken either from a small boat or a fixed observatory tower. Data used from the bottom layer in Lake Nakaumi (at ~ 7 m) were measured by the Ministry of Land Infrastructure and Transport of

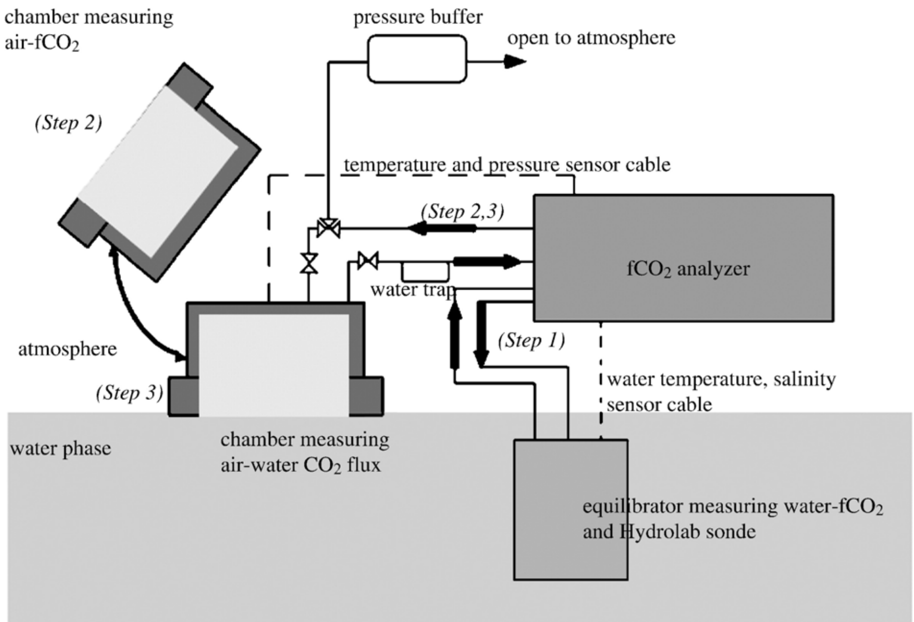

Fig. 1. Flow diagram of the flux measurement system. The chamber floated on the water surface during flux measurements and was open to the atmosphere during air–fCO_2 outside-chamber measurements prior to flux measurements (see Fig. 2). The air inside the chamber was circulated by an air-line (solid line) and through an fCO_2 analyzer (described in Saito et al., 1995). A water trap and a pressure buffer were attached to the air-line to prevent water intrusion into the fCO_2 analyzer and to maintain constant pressure inside the chamber. Temperature and pressure inside the chamber were monitored every 10 s using a data logger built into the fCO_2 analyzer (the dashed line represents the temperature and pressure sensor cable). Water–fCO_2 and other chemical conditions (temperature, salinity, pH, DO) were measured using an equilibrator and a Hydrolab sonde every 10 s. Steps of each procedure are indicated and are explained in Fig. 2.

Japan (published data; cf., http://www1.river.go.jp/cgi/SiteInfo.exe?ID=307041287705350).

We measured the air–water CO_2 flux and the gas-transfer velocity using a chamber method (Fig. 1). The chamber was a rectangular Plexiglas box (50 cm long and wide, 22 cm high, volume of 55 L and surface area of 0.25 m^2), and was moored to an anchored small boat or the fixed tower. The chamber was connected to an fCO_2 analyzer with a teflon tube to measure fCO_2 of the atmosphere and inside the chamber. The procedure of flux measurement was 1) water–fCO_2 measurement by the equilibrator for ~10 min, 2) atmospheric fCO_2 measurement with the chamber open to the atmosphere (Fig. 1) for ~20 min, 3) flux measurement with a chamber floating on the water surface for 20–30 min, and 4) water–fCO_2 measurement again (Figs. 1 and 2). The calculation of CO_2 flux ($F_{(n)}$; μmol s^{-1} m^{-2}) is as follows,

$$F_{(n)} = \frac{fCO_{2(n+1)}/RT - fCO_{2(n)}/RT}{10} \times \frac{V}{S}$$

where $fCO_{2(n)}$ (μatm) is the fugacity of CO_2 in the chamber measured every 10 s. The $fCO_{2(n)}$ was calibrated by the pressure measured using a barometer attached to the chamber. R and T are the gas constant and the temperature measured using a thermometer attached to the chamber, respectively. V and S are the volume and area of the chamber, respectively ($V/S = 0.22$ m). Flux values were calculated every 10 s and results were averaged over 15–25 min for each measurement. Because the fluctuation in $fCO_{2(n)}$ raw data did not change significantly over 10 s, the gas density (fCO_2/RT) had to be approximated to a continuous line or curve. Past studies using chamber methods have used linear fitting (Frankignoulle, 1988; Borges et al., 2004) and exponential fitting (Wanninkhof and Knox, 1996). Theoretically, gas density should be fitted with an exponential curve, but some of the gas densities we measured did not change as expected from theory. This mismatch between measurements and theory was potentially caused by the change in transfer velocity during measurement. We used quadratic fitting because it produced the highest correlation coefficients. The CO_2 transfer velocity (k) was calculated every 10 s from the measured CO_2 flux, air–water ΔfCO_2, and solubility (K). All k mentioned in this study were averaged over every measurement and normalized at $Sc = 600$.

$$k_{600} = \frac{F}{K \Delta fCO_2} (600/Sc)^{-0.5}$$

The solubility of CO_2 and the Sc number were calculated from empirical formulas by Weiss (1974) and Jähne et al. (1987), respectively, using measured water temperature and salinity.

To test the current effect, we measured horizontal current speed in the reefs and river using a current

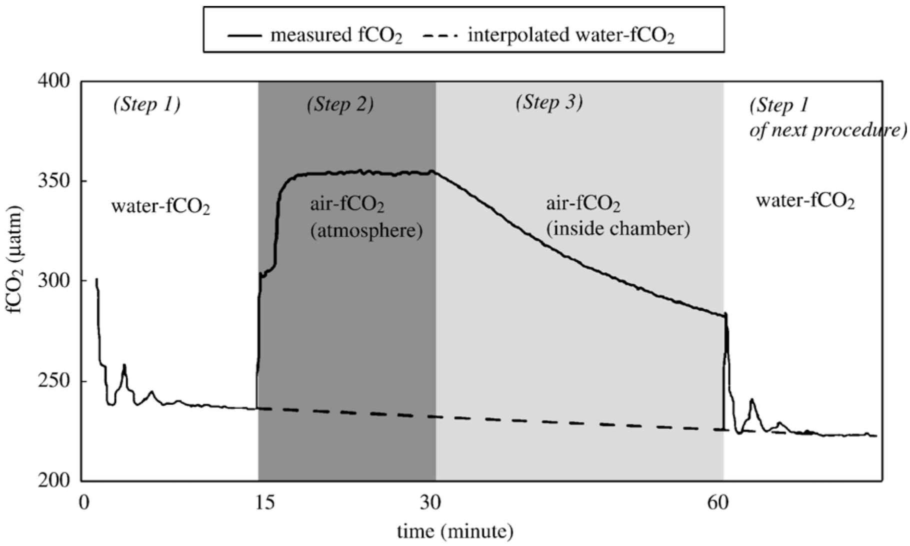

Fig. 2. Example of CO_2 flux measurement steps. First, water–fCO_2 was measured for ~10 min using an equilibrator (*Step 1*). Second, the atmospheric air–fCO_2 was measured for ~20 min using a chamber that was open to the atmosphere (*Step 2*; see Fig. 1). Third, flux was measured for 20–30 min using a chamber floating on the water surface (*Step 3*). The solid and dashed lines indicate the measured and interpolated fCO_2, respectively. Because this device cannot measure water– and air–fCO_2 simultaneously, water–fCO_2 during the measurement of air–fCO_2 was calculated using interpolation. All data for the first 5 min of each step were ignored because of high instability.

velocimeter (Alec Compact EM; Alec Electronics Co., Kobe, Japan) in 2003. In 2004, we measured current speed in three dimensions using an acoustic Doppler velocimeter (Nortek Vector; Nortek AS, Rud, Norway), at a depth of 0.16–0.50 m for 10 min every flux measurement. The sampling rate of the current speed in three dimensions was 4 Hz (the Nyquist frequency is 2 Hz). In addition, we measured wave height simultaneously with current. In Lake Nakaumi, it was difficult to set up a velocimeter because of the depth, so current measurements were not taken.

We used wind data that were available from other sources. At Fukido River and Fukido Reef, we used data from an observatory (located 5 km from the sites) of the Japan Meteorological Agency. At Shiraho Reef, we obtained wind data from an anemometer (located 1 km from the measurement sites) maintained by a research group from the Tokyo Institute of Technology. At Lake Nakaumi, we used wind data from an observatory (located <100 m from the measurement site) of the Ministry of Land Infrastructure and Transport of Japan. All wind measurement sites were on land, except at Lake Nakaumi. Wind data were referenced to a 10 m height using the logarithmic law (Kondo, 2000).

3. Results

Water conditions and physical data (current, depth, wind speed, fetch) of the sites were summarized (Table 1). At the reefs, water conditions were nearly identical to those of the ocean, except water–fCO_2 and DO, which were affected by higher temperatures and algal photosynthesis inside corals. Physical conditions were characterized by a weak current (<14 cm/s) and shallow depth (<1.8 m). At Fukido River, chemical conditions included high water–fCO_2 and low DO values, both the result of organic-matter decomposition. Current speed was <20 cm/s and depth was 1.4–1.8 m. Significant wave height at both reefs and the river were approximately 3–4 cm and <1 cm, respectively. Fetch in both reefs was <1 km because the distance from the measurement site to the reef edge was <1 km. Fetch in the river was almost zero because the measurement site was surrounded by a mangrove forest. At Lake Nakaumi, chemical conditions differed between the surface and the bottom layer because of strong density stratification that changed in intensity with climate. Water–fCO_2 and DO in the surface layer were affected by phytoplankton activity, with the former always at undersaturated levels (18–77%) and the latter always at oversaturated levels (111–139%) during the measurement period. This biological effect appeared to be stronger in 2004 than in 2003 because DO saturation was higher in 2004 (122–139%) than in 2003 (111–116%). In 2003, the difference in salinity between the surface and the bottom was stronger (18–19 psu) than normal (9–16 psu; Nakata et al., 2000), whereas it was weaker in 2004 (<5 psu). We did not measure current data because of the difficulty of setting up a velocimeter, but surface and bottom current speed have been estimated to be quite weak (<10 cm/s at the surface and bottom; Moriwaki et al., 2003). The fetch at Lake Nakaumi was approximately 5 km, which was

Table 1
Chemical and physical data for the measurement sites

Site data	Shiraho Reef	Fukido Reef	Fukido River	Lake Nakaumi		
				Daytime 2003	Daytime 2004	Nighttime 2004
Water temp (°C)	29.0–31.7	30.0–31.1	29.3–30.7	20.7–21.0	27.8–27.9	27.4–27.8
Salinity (psu)	29.8–32.7	32.8–32.2	24.8–30.2	2.38–2.79	21.3–22.7	22.9–23.4
pH	8.21–8.46	8.24–8.31	7.34–8.21	7.52–7.94	8.24–8.29	8.21–8.31
DO (mg/L)	6.46–12.7	6.79–8.87	2.8–5.98	9.5–10.2	9.1–9.6	8.3–9.4
Water–fCO_2 (μatm)	226.4–538.9	378.9–527.6	372.8–6422.2	44.3–110.0	223.3–250.9	230.0–279.9
Current speed (cm/s)	7.5–10.1	1.3–14.1	2.6–19.9	1[c]	1[c]	1[c]
Depth (m)	1.0–1.7	1.5–1.7	1.4–1.7	6.9	6.7	6.8
Wind speed (m/s)	3.2–4.2	3.8–4.8	2.0–4.0	3.9–4.3	5.5–6.8	5.3–8.3
Fetch (km)	<1[a]	<1[a]	Almost zero[b]	5	5	5

Water temperature, salinity, pH, dissolved oxygen (DO), water–fCO_2, current speed, depth, wind speed and wind fetch are shown.
Fetch values are rough estimates and consider wind direction.
Measurements were taken on 29 July 2003, 7 August 2003, 8 August 2003 to 6 August 2004, 16 July 2003, 21 August 2004, and 21–22 August 2004, for Shiraho Reef, Fukido Reef, Fukido River, Lake Nakaumi 2003 daytime, Lake Nakaumi 2004 daytime, and Lake Nakaumi 2004 nighttime, respectively.

[a] Distance from the measurement site to the reef edge where wind waves break.

[b] Measurement sites were surrounded by mangrove forest, so the practical fetch was considered ~ 0.

[c] These are bottom current speed and rough estimates from the residence time of the lake.

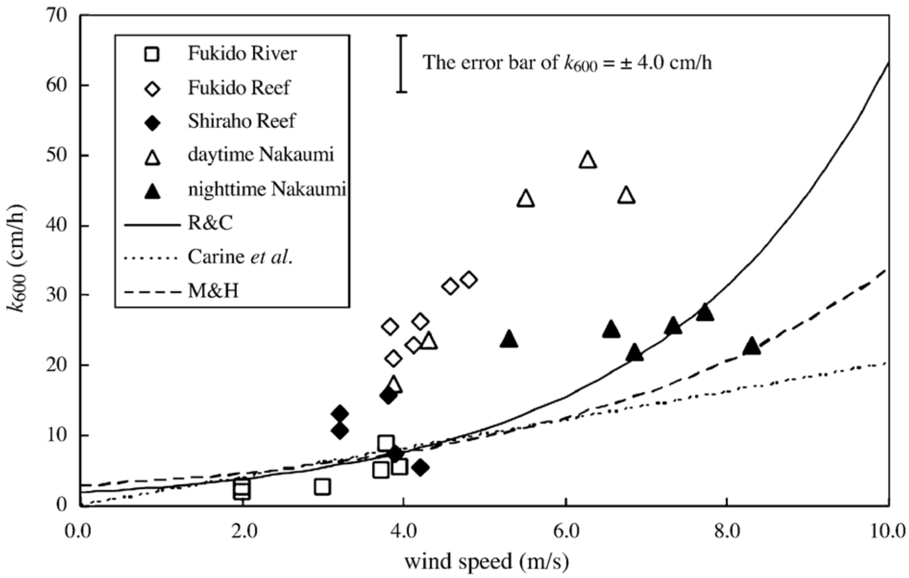

Fig. 3. k_{600} vs. wind speed. The dashed, dotted, and solid lines show the relationships from Marino and Howarth (1993), Carini et al. (1996), and Raymond and Cole (2001), respectively. Open squares, open diamonds, solid diamonds, open triangles, and solid triangles, indicate measurements from the Fukido River, Fukido Reef, Shiraho Reef, Lake Nakaumi (day) and Lake Nakaumi (night), respectively. The error bar near the top of the figure indicates the chamber precision (±4.0 cm/h) calculated as 1 S.D. from results using a chamber method under nearly identical conditions.

estimated from the shape of the lake and the wind direction during measurements.

The precision of k_{600} (±4.0 cm/h) was calculated using the standard deviation of k_{600} measured under nearly identical conditions, but in different survey periods (seven data points measured at Shiraho Reef: wind speed 2–4 m/s, current speed 5–11 cm/s). Data were considered unsuitable for analysis and were omitted if CO_2 density changes inside the chamber were weakly correlated with the quadratic fitting. In this study, we set 0.90 as the threshold correlation coefficient.

All of the measured k_{600} values and wind speeds were compared (Fig. 3). The correlation between k_{600} and wind speed was weak ($r=0.65$, $n=29$). The average k_{600} for Shiraho Reef was 1.5±0.6 (mean±S.D., $n=5$) times larger than that calculated using a wind-dependent relationship (Marino and Howarth, 1993; Carini et al., 1996; Raymond and Cole, 2001: these models were determined from coastal flux measurements, and thus are applicable here). This difference was 3.2±0.3 times for Fukido reef ($n=6$), 0.69±0.26 times in the Fukido River ($n=6$), and 2.2±0.9 times in Lake Nakaumi ($n=11$). The average k_{600} of Shiraho Reef, Fukido River and nighttime data for Lake Nakaumi matched those from wind-dependent relationships within error ranges (i.e., the sum of the precision of the chamber method and the standard deviation of the three wind-dependent relationships). In contrast, the remaining values (Fukido Reef, and daytime data for Lake Nakaumi) were significantly higher than the wind-dependent relationships.

4. Discussion

Gas-transfer measurements were made under moderate wind conditions, in which previous studies having shown the chamber method performs well (Frankignoulle, 1988; Borges et al., 2004). All measurements were conducted under weak current conditions (<20 cm/s); thus, the bias from unnatural turbulence was likely negligible. The potensial effects of temperature and pressure changes inside the chamber (as noted by Belanger and Korzum, 1991) were examined using measurements from a thermometer and a barometer attached to the chamber. Chamber data were consistent with wind-dependent relationships under an environment with no notable conditions other than wind stress. We also estimated the precision (4.0 cm/h) of the chamber method, which we expected to be low relative to other methods. Although comparisons between turbulence conditions (which directly control gas-transfer velocity) inside and outside of the chamber are needed for a quantitative analysis of the chamber-method bias, we did not expect this bias to affect our results qualitatively for the above reasons.

A portion of our data was considerably higher than those from wind-dependent relationships (Marino and

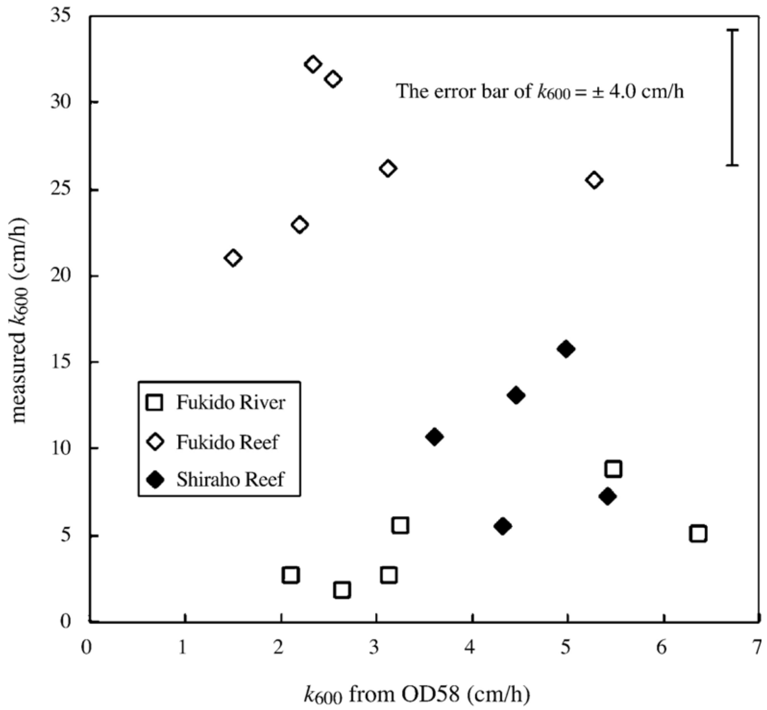

Fig. 4. Results of OD58 vs. measured k_{600}. OD58 results were calculated from equation of O'Connor and Dobbins (1958). Open squares, open diamonds, and solid diamonds are measurements from the Fukido River, Fukido Reef, and Shiraho Reef, respectively. The error bar near the top of the figure is as in Fig. 3.

Howarth, 1993; Carini et al., 1996; Raymond and Cole, 2001). Below, we analyze the regulating factors and compare the anomalies of gas-transfer velocity (Δk_{600}) with factors such as the turbulence index or abiotic parameters.

Gas-transfer velocities at the Fukido River and a portion of the Shiraho Reef were consistent with wind-dependent relationships, but gas-transfer velocities at other sites were not (Fig. 3). The Δk_{600} at the reefs were higher than those for wind relationships, and the Δk_{600} at the Fukido Reef was higher than that at the Shiraho Reef. In the reefs and the Fukido River, neither chemical nor biological effects were probable regulating factors of gas transfer because chemical and biological activity in the surface layer likely did not differ from other common coastal sites. In contrast, the current effect was substantial.

O'Connor and Dobbins (1958) reported a simple relationship (OD58) between water current, depth, and gas-transfer velocity. This formula has often been found consistent with field measurements (Zappa et al., 2003). Because the current effect was not parameterized in the wind-dependent relationships, we compared measured gas-transfer velocities with OD58 results (Fig. 4) under the assumption that the wind effect could be ignored. This assumption was legitimate because the range of wind speeds in the reefs and the river was approximately 2–5 m/s. Thus, the effect of wind stress was almost identical. The overall trend indicated that the measured data were affected by differences between measurement sites rather than the OD58 (Fig. 4).

To compare the gas-transfer velocity with a more appropriate current factor, we used the Vertical Turbulence Intensity (VTI) as an index of the intensity of turbulence:

$$\mathrm{VTI} = \sqrt{\overline{(w - \overline{w})^2}}$$

where w is vertical current speed (m/s) measured using an acoustic Doppler velocimeter. Because VTI equals the square root of twice the average vertical turbulence energy of vertical motion, it should be highly correlated with the gas-transfer velocity. The accuracy of VTI was 1%, which was calculated from the accuracy of the velocimeter. We compared the VTI and measured Δk_{600} values (Fig. 5). Linear correlations (r=0.88, n=9) were observed at two sites, but at Fukido Reef, there was no clear relationship (r=0.24, n=6). We expected that the VTI more adequately accounted for the difference in turbulence intensity and gas transfer between Fukido

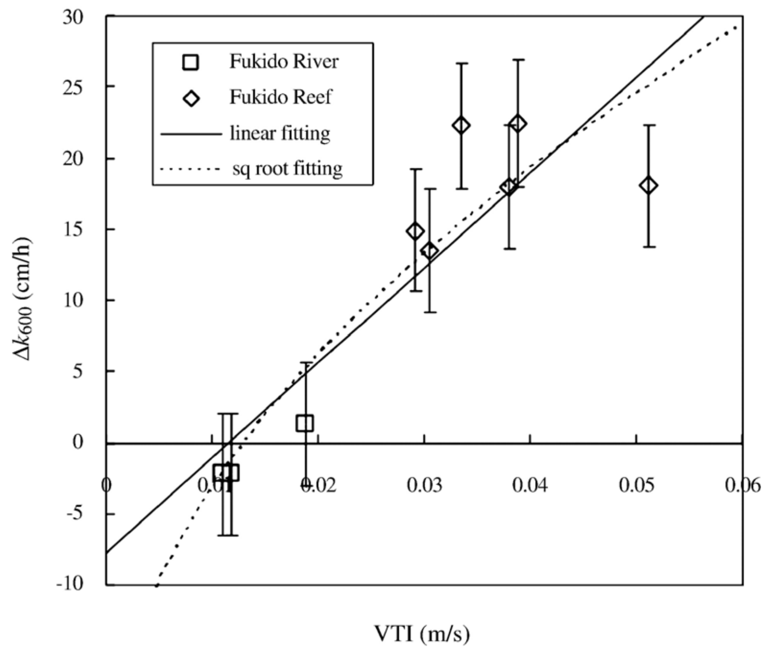

Fig. 5. Δk_{600} vs. VTI. Δk_{600} was calculated as the measured k_{600} minus the average of three wind-dependent relationships (Marino and Howarth, 1993; Carini et al., 1996; Raymond and Cole, 2001). Open squares and open diamonds represent measurements from the Fukido River and Fukido Reef, respectively. The solid line ($r=0.88$, $n=13$: $y=670.47x-7.82$) and dotted line ($r=0.91$: $y=223.59x^{0.5}-25.44$) indicate the fitted line or curve based on linear and square root relationships between VTI and Δk_{600}, respectively. The square-root correlation is based on a large-eddy model (Fortescue and Pearson, 1967). These models assume that the horizontal turbulence intensity is proportional to VTI and the turbulence length scale is constant. Error bars indicate the sum of the chamber precision and 1 S.D. of the above three relationships. The accuracy of VTI is 1%.

Reef and the Fukido River than the OD58, because average current speed was higher in the river than in the reef, but the VTI and k_{600} were higher in the reef.

The VTI is applicable to the large-eddy model of Fortescue and Pearson (1967). VTI (strictly, the square root of twice the turbulent energy of all three dimensions) is one of the parameters of this theoretical model. Assuming that vertical- and horizontal-turbulence current fluctuations are proportional and that the integral turbulence length scale is constant, gas-transfer velocity calculated with the surface-renewal model was proportional to the square root of VTI. The square-root correlation formulas ($r=0.91$ $n=9$; Fig. 5) provided better fits that the linear models ($r=0.88$). The weak correlation between the Δk_{600} and the VTI at Fukido Reef may have been caused by the inconstancy of the ratio of the VTI with the horizontal turbulence fluctuation and/or the turbulence length scale. Although the VTI could explain the difference in Δk_{600} between rough and flat bottoms, the measurement or estimation of the ratio and/or the turbulence length scale would be necessary to more efficiently apply the VTI as an index of current effects.

We expected that differences in VTI and gas-transfer velocity between the river and reef would be caused by bottom macro-roughness enhancement. Moog and Jirka (1999b) demonstrated that macro-scale elements in currents generated strong and complex near-surface turbulence and caused higher transfer velocity in a wind-tunnel experiment. At Fukido Reef, there were many *Porites australiensis* coral ~1 m diameter. In contrast, the Fukido River had a relatively flat bottom composed of sand or mud. Thus there was stronger turbulence in the reef, and consequently, gas-transfer velocities were higher. Unfortunately, we did not measure VTI at Shiraho Reef. However, gas-transfer velocities at the Shiraho Reef were lower than those at Fukido Reef, whereas the density of coral was lower than at Fukido Reef. This pattern appears to be inconsistent with the relationship between bottom macro-roughness enhancement and gas-transfer velocity observed at the Fukido Reef and river. In addition, data from Shiraho Reef, which were consistent with wind-dependent relationships, were measured during the lowest tide; thus, bottom macro-roughness enhancement was likely insignificant.

Most wind-dependent relationships do not include current effects, and simple models of current effect (e.g., OD58) do not include bottom macro-roughness enhancement. Therefore, one cannot use these models to compare gas transfer between sites with and without macro-scale elements. For example, Borges et al. (2004) measured gas-transfer velocities in three European estuaries using a chamber method and suggested a wind and gas-transfer velocity relationship after removing the current effect. However, they calculated current effects at all three sites using OD58. Thus, the current effect may be underestimated in their model because of a bottom macro-roughness enhancement. Moog and Jirka (1999b) reported bottom macro-roughness enhancement, but because turbulence affected by macro-scale elements is very complex, their results are likely not applied in the field where the distribution of bottom macro-scale elements and the Reynolds number of water should be different. We accounted for the qualitative differences in gas-transfer velocity and turbulence intensity between flat-bottom and relatively rough-bottom sites. To obtain a more quantitative calculation, bottom macro-roughness would have to be quantified by measuring the current profile (Lacy et al., 2005) as well as the integral turbulence length scale.

The daytime k_{600} was considerably higher than that calculated from wind speed, whereas there was no clear difference for nighttime k_{600} (Fig. 3). In addition, the daytime Δk_{600} was greater in 2003 than in 2004. In Lake Nakaumi, current effects on gas transfer were not strong because the bottom current speed was weak (< 10 cm/s), the depth was ~7 m, and bottom macro-roughness enhancement could be ignored (the bottom was composed of mud). Other factors besides wind stress or current effects may explain the Δk_{600} in Lake Nakaumi. The particularly strong photosynthetic activity and density stratification in Lake Nakaumi potentially affected gas transfer because the former would affect near-surface CO_2 density directly through photosynthesis or respiration, and the latter would affect the near-surface turbulence intensity. We used the rate of DO change (mg L^{-1} h^{-1}) and Δsalinity (bottom minus surface salinity) as parameters of the photosynthetic activity and density stratification, respectively; We did not use the change in dissolved CO_2 concentration as an index of photosynthetic activity because CO_2 concentration in water is affected by both biological effects and the carbonic buffering system. In Lake Nakaumi, we assumed that the effects of advection on abiotic surface conditions were negligible because the variables such as salinity, which do not affected by photosynthetic activity, were stable during the measurement period and the surface current was weak. The rate of change in DO was calculated from the DO concentration measured at 1m in depth, using the least-squares method.

Multiple regression analysis indicated that the change in DO and Δsalinity in Lake Nakaumi were highly correlated with Δk_{600} (r=0.85 n=11). The change in DO was proportional and Δsalinity was inversely related to Δk_{600}. Furthermore, the offset value was 21.3±3.0 cm/h (mean± S.D.), which is the expected Δk_{600} when the change in DO and Δsalinity are 0. This value should be ~0 because all probable effects in Lake Nakaumi were assumed to be removed.

Upstill-Goddard et al. (2003) demonstrated that the air–water methane flux was enhanced when methane-oxidizing bacteria were added to their water-tank experiment. They found that methane consumption in the surface layer enhanced the gradient of methane density at the surface layer and increased the methane-transfer velocity (Upstill-Goddard et al., 2003). In contrast, Frew et al. (1990) and Goldman et al. (1988) showed that the oxygen-transfer velocity decreased when there was substantial plankton near the surface because plankton-exuded organic matter changed the surface dissipation rate. The results of Upstill-Goddard et al. (2003) conflict with those of Frew et al. (1990), but the former effect likely only occurs with a specific gas, such as CO_2 or methane, which can change during photosynthesis or methane oxidation. In the context of the results of Upstill-Goddard et al. (2003), a biological effect would increase the transfer velocity of a specific gas while decreasing those of other gases. Our results were consistent with this hypothesis. However, some questions remain concerning the data from Lake Nakaumi. The increment of k_{600} was considerably higher (120±90%) than in Upstill-Goddard et al. (2003; 12±10%). Thus, the Δk_{600} could not be explained only by the biological activity suggested by Upstill-Goddard et al. (2003). Density stratification is the parameter correlated with Δk_{600}. Because Δk_{600} was inversely related to Δsalinity (our index of density stratification intensity), the strong density stratification in Lake Nakaumi may have weakened the near-surface turbulence and gas-transfer velocity. However, we did not conduct turbulence measurements in Lake Nakaumi; thus, we could not analyze the effect of density stratification. In addition, the offset value of the multiple regression analysis suggests that other factors affect gas transfer in Lake Nakaumi. Currently, the Δk_{600} analysis in Lake Nakaumi is not adequate, and requires further quantitative analyses including the construction of a more appropriate index of regulating factors, to more thoroughly explain gas transfer in Lake Nakaumi.

Acknowledgments

We thank H. Kimoto and M. Tsuda, of Kimoto Electric for help in making the chamber device used in this study. We also thank S. Yamamoto, M. Sasaki, H. Shimabukuro, and the members of the Research Center for Coastal Lagoon Environments, Shimane University, for help with field measurements.

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