

Estimating of Gas Transfer Velocity Using Triple Isotopes of Dissolved Oxygen

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The atmosphere-ocean exchange of climatically important gases is determined by the transfer velocity (k) and concentration gradient across the interface. Based on observations in the northwestern subarctic Pacific and Sagami Bay, we report here the results of the first ever application of the natural abundance of triple isotopes of dissolved oxygen (^{16}O , ^{17}O and ^{18}O) for direct estimation of k and propose a new relationship with wind speed. The k values estimated from nighttime variations in oxygen isotopes are found to be higher than the direct estimations at low wind speed ($<5\text{ m s}^{-1}$) and lower at high wind speeds ($>13\text{ m s}^{-1}$) and showed significant spatial variability. The method presented here can be used to derive seasonal and spatial variations in k and the influence of surface conditions on the value, leading to improved estimates of biogenic/anthropogenic gas exchange at the air-sea interface.

Keywords:

- Gas transfer velocity,
- stable isotopes,
- biogeochemistry,
- gas exchange,
- carbon cycle.

1. Introduction

The exchange of gases between the ocean and the atmosphere, which is still subject to major uncertainty, is an important part of the biogeochemical cycles of climatically important elements. The oceans are important net sources for several biogeochemically important gases, such as dimethyl sulphide, nitrous oxide, methane, non-methane hydrocarbons etc. These gases play very significant roles in the atmospheric chemistry and climate regulation and the rates of their sea-to-air flux is directly controlled by the transfer velocity (k). Consequently, a knowledge of air-sea exchange rates is directly relevant to a range of global issues. Accurate estimates of the air-sea exchange rate of CO_2 are critical to our perception of the global carbon cycle, over which there is currently substantial uncertainty (Schimel, 1998). The nature of the dependence of k on wind speed is central to calculating the strength of oceans as a source or sink (e.g. Takahashi *et al.*, 2002). The k value has been parameterized to obtain averages over weeks to several years, using either artificial tracers, such as SF_6 / ^3He (Watson *et al.*, 1991; Nightingale *et al.*, 2000; Ho *et al.*, 2006) or bomb radio-

carbon (Wanninkhof, 1992; hereafter W92); or using numerical models (e.g. Erickson, 1993; Woolf, 2005) including several assumptions. Later on, k was measured directly using an eddy covariance method during the Gas Ex-98 experiment in North Atlantic (Wanninkhof and McGillis, 1999; McGillis *et al.*, 2001) and GasEx-2001 in the equatorial Pacific (McGillis *et al.*, 2004). Recently, Calleja *et al.* (2005) found that plankton metabolic rates and DOC in the skin layer have a significant influence on $\Delta p\text{CO}_2$ and air-sea exchange. The presence of enriched organic carbon and microorganisms in the thin upper layer and its effect on air-sea exchange has been known for over three decades (McIntyre *et al.*, 1974). In addition to this, Frew *et al.* (2004) suggested that the presence of surfactants could reduce k by 50%. Nevertheless, the empirical parameterization of k at deep-water field sites is inappropriate for regions of shallow water depth or strong interaction between currents and bottom topography (Graham *et al.*, 2004), which suggests that any global average parameterization of k would yield large errors on the regional scale so frequent measurements of k in different regions are essential for the precise estimation of net gas exchange across the air-water interface. Here we propose a novel approach using stable oxygen isotopes for the direct estimation of k of a gas across the air-water interface and report the results obtained from

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several experiments in an open oceanic site in the western Subarctic North Pacific and a coastal region in Sagami Bay.

2. Principle of Estimating Gas Transfer Using Oxygen Isotopes

Our technique involves precise measurements of triple oxygen isotopes (^{16}O , ^{17}O and ^{18}O) in dissolved oxygen (O_2) in the mixed layer of the ocean, which is controlled by photosynthetic O_2 production, respiration, exchange with the atmosphere and mixing with underlying water. Isotopic composition and anomaly for oxygen are here defined as:

$$\delta^n\text{O} = [(n\text{O}/^{16}\text{O})_{\text{sample}}/(n\text{O}/^{16}\text{O})_{\text{air}} - 1]10^3,$$

$$^{17}\Delta = [\ln(1 + \delta^{17}\text{O}/1000) - \lambda \ln(1 + \delta^{18}\text{O}/1000)]10^6,$$

where n and λ represent the number of minor isotopes (as 17 or 18), and the ratio of mass-dependent isotope fractionation factor of ^{17}O to ^{18}O , respectively (Angert *et al.*, 2003). The value of λ for oxygen consumption by marine organisms is defined as 0.518 (Luz *et al.*, 1999). The isotopic composition of O_2 produced during photosynthesis and fractionation during respiration is the primary control on the ratios of stable oxygen isotopes in atmospheric O_2 . Photosynthetic O_2 generated by marine primary producers has an identical isotopic composition to seawater, which has an anomaly of 249 (Luz and Barkan, 2000). Although reported values of isotope fractionation during oxygen consumption by marine organisms have varied from 0.978 to 0.990 for ^{18}O (Kroopnick, 1975; Kroopnick and Craig, 1976; Bender and Grande, 1987; Quay *et al.*, 1993; Kiddon *et al.*, 1993; Nakayama *et al.*, 2007, 2008), most marine organisms share the same respiratory electron transport pathway, the cytochrome oxidase pathway (COX). This process has a constant λ value of 0.518 as described above. It is therefore important to note that $^{17}\Delta$ is not influenced by oxygen consumption in the ocean.

On the other hand, mass-independent fractionation occurs in the stratosphere, resulting in a ratio of $\delta^{17}\text{O}$ to $\delta^{18}\text{O}$ (0.62 ± 0.06 ; Lammerzahl *et al.*, 2002) that is significantly different from the mass-dependent signature. Therefore, in the $\delta^{18}\text{O}$ of dissolved O_2 , which is produced and consumed by biological processes, there is always an excess of ^{17}O in comparison to that of atmospheric O_2 , which is influenced by stratospheric O_2 (Luz *et al.*, 1999). This excess, or the anomaly ($^{17}\Delta$) in the dissolved O_2 in the surface mixed layer, is determined by the relative contributions of photosynthetically produced “normal” O_2 and “anomalous” O_2 injected from the atmosphere. If the rate of the former is known, the influx of O_2 , and thus k , can be derived using oxygen solubility at *in*

situ temperature and salinity. Although fluorescence based techniques, such as fast repetition rate fluorometry (FRRF), are promising for estimating gross oxygen production (Sarma *et al.*, 2005, 2006), their estimates involve significant uncertainty, up to 20–30%. This approach would thus yield a less accurate k . On the other hand, if anomaly changes are known in the absence of phytoplankton production, the changes in anomaly can be directly attributed to the influx of oxygen from the atmosphere and k can thus be estimated more accurately. The nighttime changes in oxygen concentrations are mainly due to air-sea exchange and community respiration. Since community respiration removes dissolved oxygen in a mass-dependent manner, it has no influence on $^{17}\Delta$. Hence, if the anomaly changes are monitored in the dark in the mixed layer, they are directly related to the influx of oxygen from the atmosphere.

If the steady state is assumed in the mixed layer, i.e., horizontal and vertical mixing has no influence on changes in oxygen levels in a given region, the changes in oxygen concentration in the mixed layer in the dark can be equivalent to the exchange of oxygen at the air-sea interface and removal through respiration, which can be written as:

$$(\text{O}_{2(t_2)} - \text{O}_{2(t_1)})d/(t_2 - t_1) = G_{\text{in}} - G_{\text{out}} - R, \quad (1)$$

where $\text{O}_{2(m)}$ is dissolved oxygen concentration (mol m^{-3}) at time t_n , d is mixed layer depth (m), G_{out} and G_{in} are respectively efflux and influx of O_2 to/from atmosphere, and R is O_2 consumption rate. The anomaly changes can be written approximately as:

$$\begin{aligned} & (\Delta_{(t_2)}\text{O}_{2(t_2)} - \Delta_{(t_1)}\text{O}_{2(t_1)})d/(t_2 - t_1) \\ & = \Delta_{\text{eq}}G_{\text{in}} - \Delta_{(t_1)}G_{\text{out}} - \Delta_{(t_1)}R, \end{aligned} \quad (2)$$

where $\Delta_{(m)}$ is $^{17}\Delta$ at time t_n and Δ_{eq} is the equilibrium constant of 16 per meg between dissolved and gas phases (Luz and Barkan, 2000).

Multiplying equation (1) by $\Delta_{(t_1)}$ results in:

$$\begin{aligned} & (\Delta_{(t_1)}\text{O}_{2(t_2)} - \Delta_{(t_1)}\text{O}_{2(t_1)})d/(t_2 - t_1) \\ & = \Delta_{(t_1)}G_{\text{in}} - \Delta_{(t_1)}G_{\text{out}} - \Delta_{(t_1)}R, \end{aligned} \quad (3)$$

then subtracting equation (3) from (2) produces the final mass balance equations (4) and (5).

$$(\Delta_{(t_2)} - \Delta_{(t_1)})\text{O}_{2(t_2)}d/(t_2 - t_1) = (\Delta_{\text{eq}} - \Delta_{(t_1)})G_{\text{in}}, \quad (4)$$

$$G_{\text{in}} = [(\Delta_{(t_2)} - \Delta_{(t_1)})/(\Delta_{\text{eq}} - \Delta_{(t_1)})]\text{O}_{2(t_2)}d/(t_2 - t_1). \quad (5)$$

Here G_{in} can also be expressed as:

$$G_{\text{in}} = k\text{O}_{2\text{sat}}, \quad (6)$$

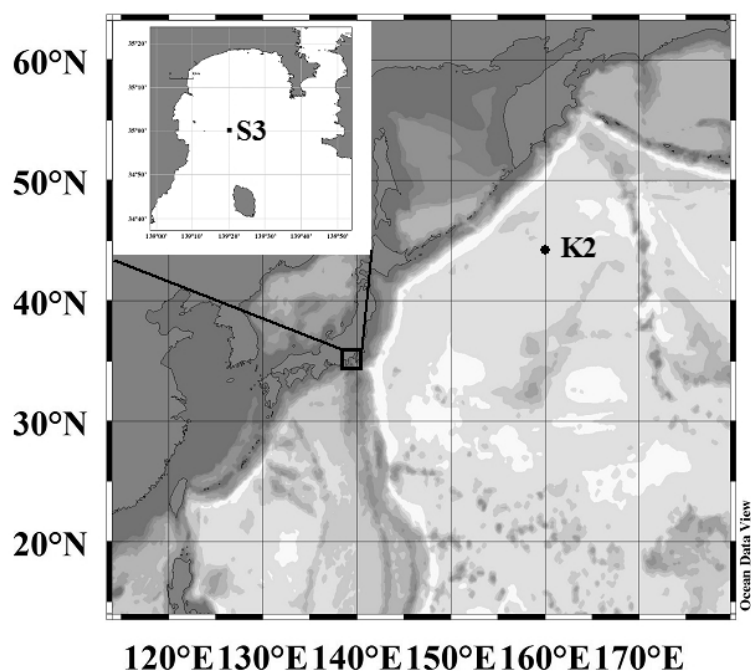


Fig. 1. Locations of stations K2 and S3 (in the inset).

where k and $O_{2\text{sat}}$ are transfer velocity (m h^{-1}) from atmosphere to ocean and oxygen saturation concentration (mol m^{-3}) at *in situ* temperature and salinity, respectively. Finally, transfer velocity (k ; m h^{-1}) can be obtained as follows:

$$k = [(\Delta_{(t_2)} - \Delta_{(t_1)}) / (\Delta_{\text{eq}} - \Delta_{(t_1)})] (O_{2(t_2)} / O_{2\text{sat}}) d / (t_2 - t_1). \quad (7)$$

3. Material and Methods

Sampling was conducted at station K2 (44°N, 160°E; water depth 5200 m; Fig. 1) in the northwestern subarctic Pacific during 24th June, 1st, 8th, and 17th July 2006 in the upper 30 m at 2 h intervals from 20:00 to 04:00 h (nighttime). Sampling was also conducted at station S3 (35°N, 139.5°E; water depth 1500 m; Fig. 1) in Sagami Bay, northwestern Pacific, during 29–30th August 2003 and 1–2nd August 2004 in the upper 40 m. The sampling at this station was done only twice, i.e., 20:00 h and 04:00 h on the next morning to examine the changes in $^{17}\Delta$ in the night due to influx of O_2 . Seawater samples were collected with 20 L Niskin bottles mounted on a Sea-Bird CTD-RMS. The water sampling methodology was adopted from Luz *et al.* (2002). About 150 mL of water sample was collected in duplicate into pre-evacuated gas extraction vessels (300 mL flasks with Louwers Hapert® O-ring stopcocks) containing 250 μL of saturated HgCl_2 solution. Water and headspace in the sampling flasks were immediately equilibrated for 24 hours at room temperature onboard and water was carefully removed leaving

only headspace gases in the flask. The flask was then connected to a preparation system to separate O_2 and Ar from N_2 , CO_2 , N_2O and water vapor following the procedure of Sarma *et al.* (2003). The standard errors of means for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ were found to be 6 and 3 per meg, respectively, and for the error on $^{17}\Delta$ to be 5 per meg.

4. Results and Discussion

4.1 Estimation of gas transfer velocity using nighttime changes in $^{17}\Delta$ in the subarctic Northwest Pacific and Sagami Bay

The diurnal variations in temperature, salinity, Chl a , $^{17}\Delta$ and horizontal wind speeds at station K2 are drawn in Fig. 2 for each observation. The temperature in the upper 30 m at station K2 increased consecutively from 24th June to 17th July 2006 (Figs. 2a–d) whereas salinity increased by 0.2 from 24th June to 01st July, then decreased by 0.4 until 17th July (Figs. 2e–h). Except on 24th June 2006, both mixed layer temperature and salinity showed marginal variations, by $<0.5^\circ\text{C}$ and 0.05 respectively during each study period of 8 hours (20:00 h to 04:00 h) (Table 1). $O_2/O_{2\text{sat}}$ decreased by 0.3 to $\sim 1\%$ in the 8 hours of the period (20:00 h to 04:00 h) due to both removal of oxygen to the atmosphere and community respiration; the magnitude of decrease was proportional to the wind speed (Table 1). On the other hand, intense vertical mixing from 24:00 h to 02:00 h occurred on 24th June 2006 due to heavy winds ($>18 \text{ m s}^{-1}$), resulting in a

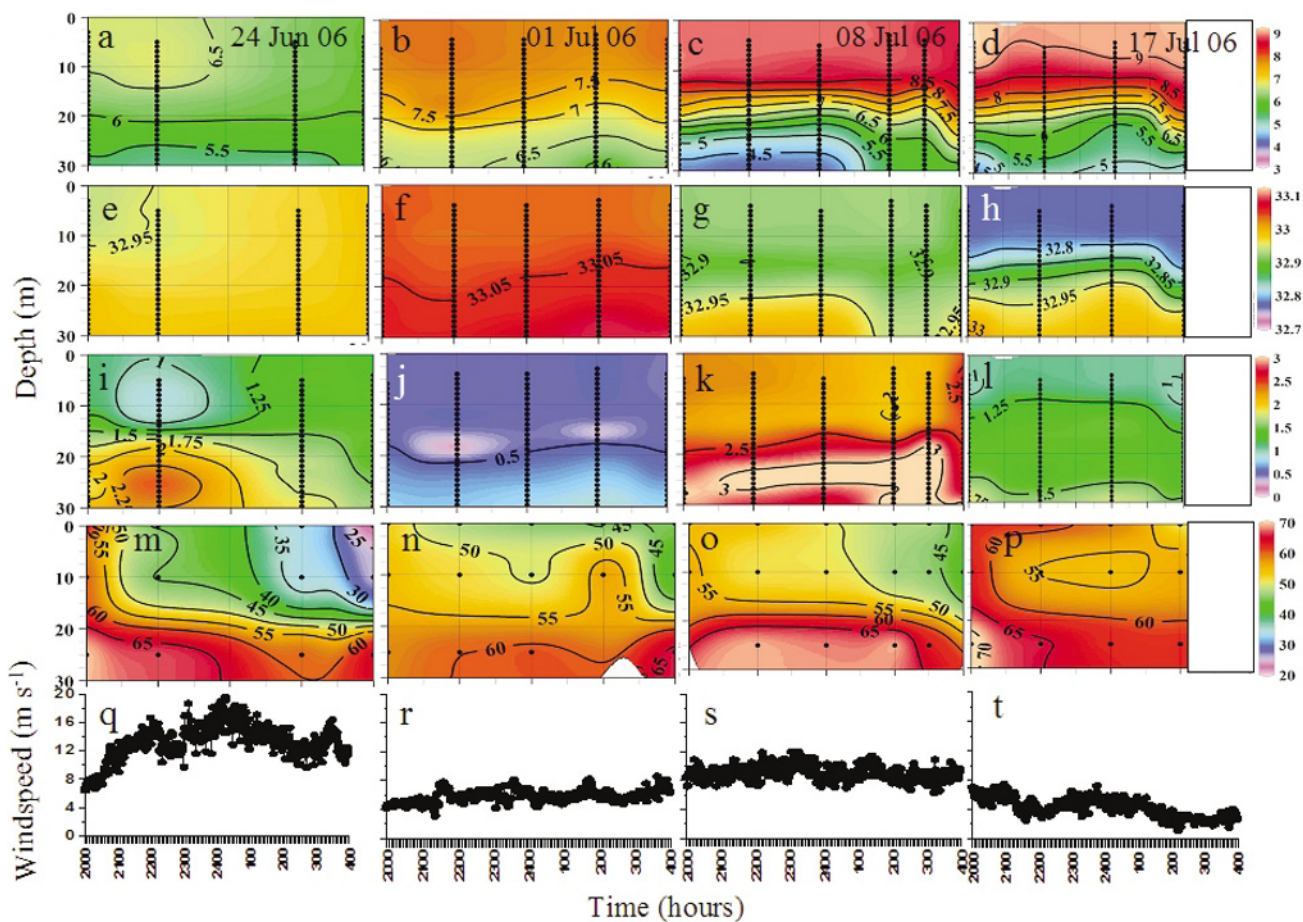


Fig. 2. Time-series variation in (a–d) Temperature ($^{\circ}\text{C}$), (e–h) Salinity, (i–l) Chlorophyll a (mg m^{-3}), (m–p) $^{17}\Delta$ (per meg) and (q–t) wind speeds (m s^{-1}) at station K2 in the northwestern subarctic Pacific.

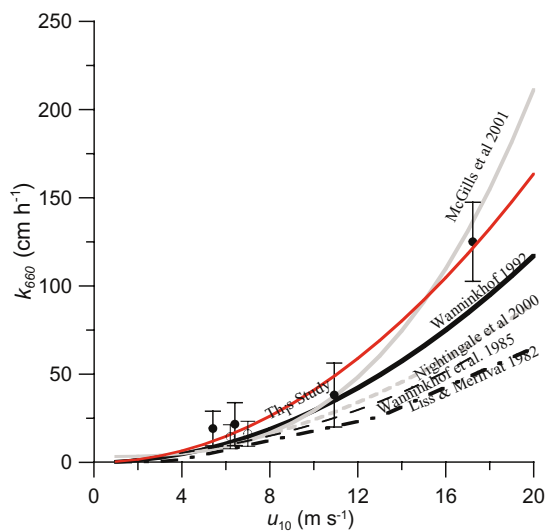


Fig. 3. Relationship between transfer velocity, normalized to Schmidt number 660, and wind speeds, normalized to 10 m height from the sea surface. Comparison with other estimates using different tracers is also shown where red line fit is generated from data collected at station K2 in the subarctic North Pacific.

Table 1. Time-series variations in triple oxygen isotopic ratios and $^{17}\Delta$ in the northwestern Subarctic Pacific and Sagami Bay.

Station	Date	Time (hours)	Temp. (°C)	Salinity	O_2/O_{2sat}	$\delta^{17}O_{air}$ (per mil)	$\delta^{18}O_{air}$ (per mil)	$^{17}\Delta$ (per meg)
K2	24-Jun-06	20:00	6.627	32.939	1.055	-0.125	-0.363	64
		22:00	6.745	32.948	1.046	0.055	0.021	44
	25-Jun-06	0:00	6.127	32.969	1.048	-0.033	-0.127	33
		4:00	6.029	32.979	1.045	-0.112	-0.26	22
	01-Jul-06	20:00	7.730	33.042	1.055	0.077	0.045	53
		22:00	7.916	33.033	1.053	0.144	0.186	48
	02-Jul-06	0:00	7.756	33.033	1.051	0.608	1.089	44
		2:00	7.680	33.034	1.052	-0.037	-0.156	44
		4:00	7.861	33.028	1.048	0.261	0.418	45
	08-Jul-06	20:00	8.839	32.914	1.078	-0.054	-0.21	55
		22:00	8.898	32.918	1.077	-0.051	-0.195	50
	09-Jul-06	0:00	8.752	32.917	1.076	-0.009	-0.108	47
		2:00	8.860	32.918	1.076	-0.043	-0.175	48
		4:00	8.742	32.919	1.074	-0.076	-0.229	43
	17-Jul-06	20:00	9.033	32.771	1.050	-0.267	-0.636	62
		22:00	8.678	32.779	1.049	0.062	0	63
18-Jul-06	0:00	8.893	32.774	1.047	-0.037	-0.184	58	
	2:00	9.006	32.771	1.049	0.069	0.036	50	
S3	29-Jul-03	20:00	26.858	33.900	1.061	-1.12	-2.375	111
	30-Jul-03	4:00	26.931	33.910	1.058	-0.609	-1.364	98
	01-Jul-04	20:00	27.012	33.881	1.059	-1.406	-2.833	62
	02-Jul-04	4:00	27.088	33.893	1.055	-0.737	-1.528	55

deepening of the mixed layer and cooling of surface waters (Figs. 2q–t). The surface Chl *a* shows strong daily variations, the highest being during 8th July and the lowest on 1st July 2006 (Figs. 2i–l); this was positively related to solar radiation (figure not shown). A subsurface Chl *a* maximum of up to 3 mg m⁻³ was found during the entire study period at a depth of 15–25 m since the photic zone (~50 m) was deeper than the mixed layer depth (mostly <20 m) and nutrients were available below the mixed layer. The mixed layer depth varied between 7 and 20 m during the study period; diurnal variations are mainly caused by variations in wind strength. Increases in surface Chl *a* were observed in association with deepening of the mixed layer due to mixing of high Chl *a* subsurface waters with the surface.

$^{17}\Delta$ was lower at the surface, and increased below the mixed layer in the Northwestern subarctic Pacific. The mixed layer $^{17}\Delta$ exhibited large diel variations during the study period, associated with wind speed (Figs. 2m–t). For instance, on 24th June 2006, the mixed layer $^{17}\Delta$ was ~62 per meg at 20:00 h, decreasing sharply to 23 per meg at 04:00 h (Fig. 2m). The wind speeds were ~8 m s⁻¹ at

20:00 h increasing sharply to ~20 m s⁻¹ at 01:00 h and decreasing back to 8 m s⁻¹ at 04:00 h (Fig. 2q). Due to intense mixing of atmospheric oxygen with the surface waters, $^{17}\Delta$ decreased by 38 per meg in 8 h on 24th June 2006. On the other hand, wind speeds, and thus oxygen influx, were uniformly high (~9.5 m s⁻¹) from 20:00 to 04:00 h during 8th July 2006 and $^{17}\Delta$ decreased from 54 to 42 per meg. By contrast, wind speeds were fairly uniform during 1st and 17th July (at 5 and 6 m s⁻¹ respectively) and the anomaly decrease was 11 and 10 per meg, respectively. Similarly, $^{17}\Delta$ decreased from 111 to 98 and 62 to 55 per meg in 8 hours (from 20:00 to 04:00 h) at station S3 in Sagami Bay during 29–30th August 2003 and 1–2nd August 2004, respectively (Table 1). This suggests that physical processes have a strong influence on $^{17}\Delta$ in the mixed layer at night. Since the influx of oxygen from the atmosphere decreases the $^{17}\Delta$ and respiration has no influence, the decrease in $^{17}\Delta$ showed a strong inverse relation to wind speed. However, one cannot expect a one-to-one correlation between wind speed and $^{17}\Delta$ as the latter is also influenced by horizontal and vertical advection of waters with different $^{17}\Delta$.

Table 2. The difference in $^{17}\Delta$ anomaly from the beginning (20:00 h) to the end of experiment (04:00 h), mean winds during experiment and estimated transfer velocity during study period.

Station	Date	Diff. $^{17}\Delta^*$ (per meg)	U_{10} (m s^{-1})	k (cm h^{-1})
K2	24–25 Jun 06	42	17.3 ± 3.3	125.0 ± 16.2
	01–02 Jul 06	8	10.9 ± 1.8	38.17 ± 17.2
	08–09 Jul 06	12	6.4 ± 0.8	21.65 ± 7.4
	17–18 Jul 06	12	5.4 ± 1.0	19.18 ± 9.5
S3	29–30 Jul 03	13	6.2 ± 1.5	14.52 ± 6.8
	01–02 Jul 04	7	7.0 ± 2.0	16.21 ± 7.1

*Difference in $^{17}\Delta$ anomaly from 20:00 to 04:00 h during experiment.

The influence of horizontal advection on $^{17}\Delta$ is assumed to be negligible as the spatial variations within ~10 km of radius were within measurement error in Sagami Bay (Sarma *et al.*, 2006). By contrast, vertical advection of water would increase the mixed layer $^{17}\Delta$ due to the occurrence of a higher anomaly below the mixed layer (Figs. 2m–p). In order to examine this, changes in the depth of the mixed layer were monitored at 2 h intervals and a significant deepening of the mixed layer depth was found on 24th June 2006, whereas stable mixed layer depths were observed during other study periods. The changes in mixed layer $^{17}\Delta$ due to entrainment of O_2 from deep water were estimated following the method of Sarma *et al.* (2006) and appropriate corrections were made to the data.

Figure 3 shows gas transfer velocity computed from time-series variations of $^{17}\Delta$ using Eq. (7) as a function of wind speed at a height of 10 m (u_{10}) along with other theoretical and experimental results of gas exchange studies at sea (Table 2). The entire data set at station K2 was fitted to a quadratic equation that yielded:

$$k_{660} = 0.41u_{10}^2, \quad (8)$$

for short-term or instantaneous winds. The k_{660} is gas transfer velocity at a Schmidt number of 660 (cm h^{-1}).

Our k_{660} values obtained from $^{17}\Delta$ are 30–40% higher than the previous estimates based on several tracers (Wanninkhof *et al.*, 1985; Watson *et al.*, 1991; Wanninkhof, 1992; Nightingale *et al.*, 2000) at smooth surface regime ($<8 \text{ m s}^{-1}$), whereas they closely follow McGillis *et al.* (2001) in the breakingwave regime, but are 20% lower in the rough-surface regime ($>13 \text{ m s}^{-1}$). On the other hand, k_{660} at station S3 in Sagami Bay displayed relatively lower velocities compared to that at station K2 at 6–7 m s^{-1} wind speeds. Although the differences are within measurement errors, both the points displayed lower velocities at S3 than K2. The low velocities

at S3 could possibly be due to higher DOC concentration ($>100 \mu\text{mol kg}^{-1}$) than at K2 ($40 \mu\text{mol kg}^{-1}$) (Dr. M. Wakita, personal communication, 2007). However, more measurements are required to understand the influence of DOC and other surface conditions on k at different wind speeds. Nevertheless, k estimated by $^{17}\Delta$ is consistent with values reported by McGillis *et al.* (2001) and Ho *et al.* (2006) within the errors associated with these techniques, which measure k directly, whereas our value is higher than that observed on the basis of other techniques. This is expected especially with a k value based on ^{14}C tracer as this method normally averages over a period of several years and might cover a wide wind spectrum, whereas the present estimate is averaged over an ~8 hour period. Sweeney *et al.* (2007) observed that k at the intermediate windspeed of 5 m s^{-1} was about 17 cm h^{-1} based on bomb ^{14}C whereas at the same windspeed the mean k was $20.5 \pm 8 \text{ cm h}^{-1}$ at station K2, which is quite close to the global mean, within the errors involved in the estimations.

The estimation of k involves significant sources of error, mainly from the measurement error on the $^{17}\Delta$ anomaly estimation of 5 per meg, which gives an error in k of 7.6 to 16.4 cm h^{-1} , and which is larger at lower anomaly. The uncertainty of ratio of the mass-dependent isotope fractionation factor (λ), which is reported to lie between 0.516 and 0.521 (Luz *et al.*, 1999; Luz and Barkan, 2005), may possibly introduce further uncertainty in estimating k . However, the sensitivity of λ changes contributes only up to 0.6 cm h^{-1} to the estimation of k , so it can be said that λ plays a minor role in the entire error estimation. Additionally, a smaller less error of 0.1 cm h^{-1} can come from oxygen concentration analysis by Winkler titration, which has an uncertainty of 0.1%. Therefore, the total error in k may vary from 18 to 50% depending on the wind speed conditions and productivity of the waters. The errors are relatively lower in high productivity waters, where high anomalies are expected, than in oligotrophic waters.

Finally, the response time of the gas transfer, i.e., the residence time of the mixed layer dissolved oxygen, is estimated for K2 results. The depths of mixed layer for each observation are 20, 15, 7 and 7 m, respectively for 24–26 June, 01–02 July, 08–09 July and 17–18 July 2006. Therefore, the response time (mixed layer depth/gas transfer velocity) should be 16, 39, 32, 36 hours for each. In the highest wind field, most of the mixed layer O₂ was replaced during the night; on the other hand, it took almost one and a half days (39 hours) in the intermediate wind field and mixed layer depth. It can be said that our sampling interval (2 hours) was suitable for these observations. For the case with shallow mixed-layer depth and/or higher wind speed, a shorter sampling interval should be considered.

This study clearly establishes that naturally occurring triple oxygen isotopes can be effectively used to derive gas transfer velocities at air-water interfaces, and the method is free from the operational constraints of artificial tracers. The major advantage of our method is that: (1) it can be applied to any aquatic environments, such as lakes, coastal regions, and the open ocean; and (2) it does not involve any artificial or radioactive tracers such as SF₆, ³He, and ¹⁴C. The present method is more robust and provides an easy estimate of *k* in any region. In the years to come, measurements of oxygen isotopes are expected to occur on a routine basis under ongoing or planned international projects, such as the Surface Ocean Lower Atmosphere Study (SOLAS), Integrated Marine Biogeochemical and Ecosystems Research (IMBER), and International study of the marine Biogeochemical cycles of trace elements and their isotopes (GEOTRACES). This will hopefully facilitate the application of our method on a large scale in order to gain a comprehensive global picture of the transfer of greenhouse gases across the air-water interface, thereby reducing uncertainties in the oceanic sinks/sources of trace gases. Such a picture is now more within reach.

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