GEOPHYSICAL RESEARCH LETTERS, VOL. 33, L16611, doi:10.1029/2006GL026817, 2006

Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations

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Received 5 May 2006; revised 27 June 2006; accepted 7 July 2006; published 25 August 2006.

[1] The SOLAS Air-Sea Gas Exchange (SAGE) Experiment was conducted in the western Pacific sector of the Southern Ocean. During SAGE, gas transfer velocities were determined using the $^3He/SF_6$ dual gas tracer technique, and results were obtained at higher wind speeds (16.0 m s^{-1}) than in previous open ocean dual tracer experiments. The results clearly reveal a quadratic relationship between wind speed and gas transfer velocity rather than a recently proposed cubic relationship. A new parameterization between wind speed and gas transfer velocity is proposed, which is consistent with previous $^3He/SF_6$ dual tracer results from the coastal and open ocean obtained at lower wind speeds. This suggests that factors controlling air-sea gas exchange in this region are similar to those in other parts of the world ocean, and that the parameterization presented here should be applicable to the global ocean. **Citation:** Ho, D. T., C. S. Law, M. J. Smith, P. Schlosser, M. Harvey, and P. Hill (2006), Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations, *Geophys. Res. Lett.*, *33*, L16611, doi:10.1029/2006GL026817.

1. Introduction

[2] Air-sea gas exchange plays an important role in climate regulation by controlling the rate of CO_2 uptake by the ocean. Thus, many experiments have been designed to determine the relationship between environmental variables and the rate of air-sea gas exchange. Globally, the dominant control of air-sea gas exchange is turbulent energy delivered to the air-sea interface by wind. Relationships relating gas transfer velocities to wind as the primary source of energy for the atmospheric and oceanic molecular boundary layers have been derived from SF_6 tracer experiments in lakes, global excess ^{14}C inventories of the ocean, micrometeorological measurements of CO_2 fluxes in the ocean, and $^3He/SF_6$ dual tracer experiments conduced in the coastal ocean [e.g., *Liss and Merlivat*, 1986; *Wanninkhof*, 1992; *Wanninkhof and McGillis*, 1999; *Nightingale et al.*, 2000b]. However, these formulations diverge widely at high wind speeds (>10 m s^{-1}), leading to significant uncertainties in estimates of CO_2 uptake by high wind speed regions of the ocean, such as the Southern Ocean, which is potentially an important CO_2 sink region.

[3] Presently, the $^3He/SF_6$ dual tracer method is considered the most effective approach to integrated measurement of gas transfer velocities in the field. However, although several $^3He/SF_6$ dual tracer experiments have been conducted in the coastal ocean over the last decade, it was not until recently that systematic $^3He/SF_6$ experiments were conducted in the open ocean [*Nightingale et al.*, 2000a; *McGillis et al.*, 2001; *Wanninkhof et al.*, 2004]. So far, there have only been eight measurements from these open ocean experiments, and they cover wind speeds ranging only up to 11.3 m s^{-1}, thus severely limiting the verification of the existing wind speed/gas exchange parameterizations, especially at higher wind speeds.

[4] We report results from an open ocean $^3He/SF_6$ dual tracer release experiment conducted at high wind speeds in the Southern Ocean. The SAGE experiment has more than doubled the number of $^3He/SF_6$-derived gas transfer velocity measurements from the open ocean. It has also greatly increased the number of open ocean gas transfer velocity measurements from high wind periods (above 10 m s^{-1}). In addition to comparing the results with $^3He/SF_6$ measurements obtained previously from the coastal and open ocean, and comparing the results to previously proposed parameterizations, we derive a parameterization between wind speed and gas transfer velocity based on $^3He/SF_6$ data collected from the open ocean during the SAGE experiment, and constrained by a new estimate of global ocean ^{14}C uptake.

2. Method

2.1. Location

[5] The SAGE Experiment was conducted on the edge of a cyclonic eddy at 46.5°S, 172.5°E in the southwest of the Bounty Trough, to the southeast of New Zealand (Figure 1). The measured mixed layer depths were in the range of 60 to 80 m for much of the experiment, based on the temperature criteria of *Kara et al.* [2000]. Sea surface temperature cooled through the experiment from around 11.6 to 10.5 °C. A wide range in wind speed was anticipated and encountered with the regular westerly progression of storms through the ''roaring forties'' of the Southern Ocean.

2.2. $^3He/SF_6$ Dual Tracer Technique

[6] The $^3He/SF_6$ deliberate tracer technique utilizes two inert gases with different Schmidt numbers (*Sc* = kinematic viscosity of water, divided by diffusion coefficient of the gas in water) that are injected at a constant ratio into the

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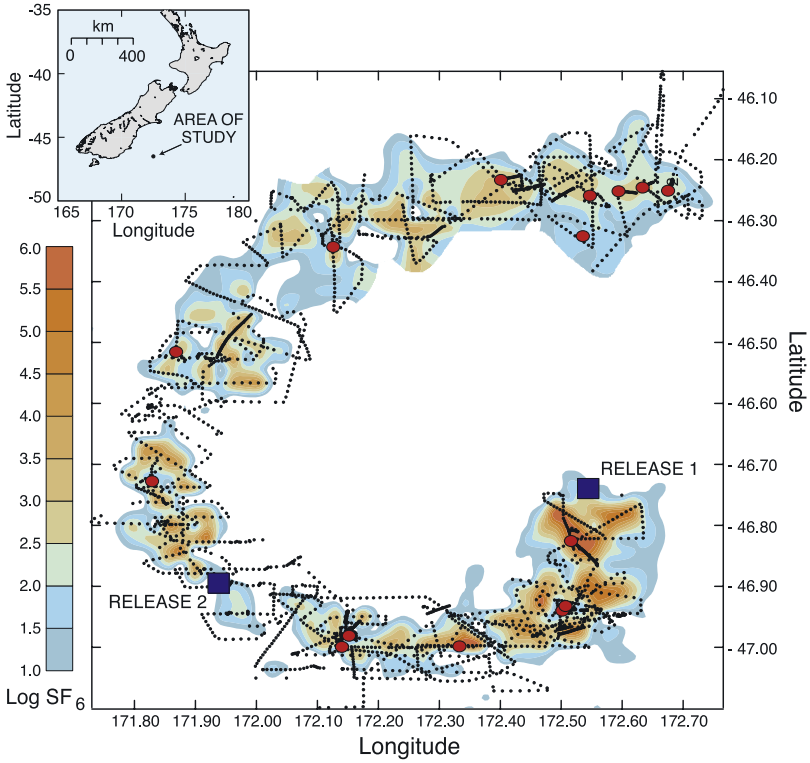

Figure 1. Map of SF_6 tracer patch for the entire SAGE experiment, with the ship track (dots), location of the tracer releases (squares), and stations from where $^3He/SF_6$ samples were taken to calculate $k(600)$ (circles).

mixed layer. Gas transfer velocities are determined from the change in the $^3He/SF_6$ ratio over time, assuming that advection and dispersion are first order processes that do not alter the $^3He/SF_6$ ratio. $k_{3_{He}}$ can be determined as follows [*Wanninkhof et al.*, 1993]:

$$k_{3_{He}} = h\frac{d}{dt}\left(\ln\left({}^3He_{exc}/SF_6\right)\Big/\left(1-\left(Sc_{SF_6}/Sc_{3_{He}}\right)^{-1/2}\right)\right) \quad (1)$$

where h is the tracer mixed layer depth, as indicated by the depth at which SF_6 decreased to 50% of the concentration at 15 m [*Nightingale et al.*, 2000a], and SF_6 and $^3He_{exc}$ are the measured SF_6 and excess ^3He concentrations in the mixed layer, respectively. Gas transfer velocities reported here, $k(600)$, were normalized to a Schmidt number for CO_2 in freshwater at 20 °C (Sc = 600).

2.3. Tracer Injection, Sampling, and Measurement

[7] ^3He and SF_6 were added to approximately 8000 L of seawater (in two 4000 L containers) and injected into the surface ocean in a manner similar to that of previous experiments [*Upstill-Goddard et al.*, 1991]. Two $^3He/SF_6$ releases were conducted during SAGE (Figure 1), and the initial size of the tracer patch was ca. 40 km^2 after both releases.

[8] Samples for ^3He and SF_6 were collected from a 24-bottle CTD rosette. Typically, duplicate or triplicate Niskin bottles were tripped at each depth, with 6 to 11 depths sampled at each station, spanning the mixed layer, the thermocline, and subthermocline.

[9] ^3He samples were collected in copper tubes mounted in aluminum channels sealed off by stainless steel pinch-off clamps, and shipped back to LDEO, where the gases were extracted into ampoules and measured using a mass spectrometric technique described in detail by *Ludin et al.* [1998]. Samples for SF_6 were collected in duplicate in 500 ml glass bottles with ground glass stoppers and analyzed onboard the ship using a GC/ECD system [*Law et al.*, 1994]. A total of 750 SF_6 and 206 ^3He samples were taken during SAGE.

3. Results and Discussion

3.1. Ship and Satellite-Derived Wind Speeds

[10] Wind speeds for the experiment were derived from anemometer measurements from the ship and satellite measurements from QuikSCAT. The shipboard wind speed measurements were made at 25.2 m height above the sea surface, and corrected to 10 m (u_{10}) accounting for atmospheric stability using the COARE 3.0 algorithms [*Fairall et al.*, 2003]. For QuikSCAT, swath data were selected from within 1° (ca. 80 × 110 km) of the ships mean position for each time interval used to calculate gas transfer velocity.

[11] The agreement between shipboard winds and satellite winds was good considering the spatial separation of ~100 km and the limited temporal coverage of the satellite data. The distribution of the ship winds shows generally greater occurrence of wind speeds in the 10 to 17 m s^{-1} range than the satellite measurements. This may be the result of undersampling of the higher winds by the satellite, but also airflow distortion over the ship can result in an accelerated flow dependent on the orientation of the ship relative to the wind [*Popinet et al.*, 2004]. Shipboard wind speed measurements presented here have not been corrected

Table 1. Summary of Wind Speeds and k(600) Derived From $^3He/SF_6$ During SAGE

Wind speed (u_{10}), m s^{-1}		$\overline{u_{10}^2}/\overline{u_{10}}^2$		Gas transfer velocities k(600), cm h^{-1}	QuikSCAT Enhancement-Corrected k(600), cm h^{-1}	Error k(600), cm h^{-1}	Hours[a]	Measurements[b]	
Ship-Based	QuikSCAT	Ship-Based	QuikSCAT					Ship-Based	QuikSCAT
7.4	7.4	1.13	1.11	17.8	16.0	0.5	23	276	84
9.8	8.9	1.21	1.14	18.3	16.1	10.1	24	232	114
10.5	9.0	1.09	1.15	37.3	32.4	9.0	24	195	114
10.6	7.7	1.22	1.24	14.2	11.4	10.4	24	248	105
10.9	11.3	1.16	1.10	32.8	29.8	17.5	22	248	86
11.3	11.5	1.04	1.03	26.4	25.6	15.7	24	232	106
11.5	10.4	1.02	1.05	32.0	30.4	4.7	24	234	92
12.3	8.7	1.08	1.25	34.9	27.9	5.7	34	358	152
12.9	10.8	1.02	1.04	39.1	37.6	6.6	25	234	102
15.2	15.5	1.05	1.03	55.0	53.4	3.4	50	458	206
16.0	16.0	1.03	1.03	73.6	71.5	4.3	59	574	246

[a]Number of hours covered by the 3 stations used to calculate k(600).
[b]Number of measurements used to calculate the mean wind speed in each interval.

for airflow distortion, but will be addressed in a future contribution.

[12] Shipboard wind speeds ranged from 0.6 to 23.5 m s^{-1}, with a mean of 11.3 m s^{-1}, while QuikSCAT wind speeds ranged from 1.2 to 27.2 m s^{-1}, with a mean of 11.3 m s^{-1}. The accuracies of the shipboard and QuikSCAT wind speed measurements were ±0.4 and ±2 m s^{-1}, respectively. The mean ship-based wind speed for the intervals over which k(600) was calculated ranged from 7.5 to 16.1 m s^{-1}, while the QuikSCAT winds ranged from 7.4 to 16.0 m s^{-1} (Table 1). There were two periods when QuikSCAT and ship winds differed by $\geq$3 m s^{-1}. During these periods, the variance in the QuikSCAT data was ca. 25%, suggesting greater spatial variability in wind speeds than what was captured by measurements from the ship. In order to ensure consistency with previous and future experiments, data from QuikSCAT were used to derive the relationship between wind speed and gas transfer velocity described below.

3.2. Gas Transfer Velocity

[13] Samples of ^3He and SF_6 used to derive k(600) were taken about every 12 hours. For each station, there were typically 6 to 11 $^3He/SF_6$ pairs, and the averaged $^3He/SF_6$ ratios in the mixed layer of three consecutive stations were used to calculate k(600), and the associated error. Errors in k(600) were derived by propagating the standard deviations in $^3He/SF_6$ ratios from each profile. Three consecutive stations typically span a period of 24 h, although in three cases the time period covered 34, 50, and 59 h. A total of 159 $^3He/SF_6$ pairs were evaluated, consisting of 31 stations. Some of the stations were background stations taken before the tracer injection, and others were outside the tracer patch during the experiment. Overall 11 estimates of k(600) were obtained (Table 1 and Figure 2).

[14] k(600) derived from the $^3He/SF_6$ dual tracer technique during SAGE ranged from 17.8 to 73.6 cm h^{-1}, and correlated well with wind speed (Figure 2). They represent gas transfer velocities for the highest wind speed measured during a $^3He/SF_6$ tracer release experiment, and nearly triple the number of $^3He/SF_6$-derived gas transfer velocity measurements from a single site in the open ocean. This experiment has demonstrated the utility of the $^3He/SF_6$ dual tracer technique, if the sample frequency (i.e., number of stations and samples) is adequate and the experiment is conducted in the right environment (i.e., area with a range of wind speeds, including high wind speeds).

[15] It has been pointed out that the differences in net global CO_2 fluxes calculated from the different wind speed/gas exchange parameterizations are mainly due to wind speed differences in the range of 4 to 17 m s^{-1} [*Boutin et al.*, 2002]. The data from SAGE fall exactly in this range, which allows these parameterizations to be constrained.

[16] A comparison of the SAGE data with existing parameterizations between wind speed and gas exchange indicate that gas transfer velocities at high wind speeds are significantly lower than predicted by the cubic parameterization of *Wanninkhof and McGillis* [1999] but higher than the piecewise linear one of *Liss and Merlivat* [1986]. The SAGE $^3He/SF_6$ data are best described by the *Nightingale et al.* [2000b, hereinafter referred to as N2000] and *Wanninkhof* [1992, hereinafter referred to as W92] relationships (Figure 2).

3.3. Parameterization Between Wind Speed and Gas Exchange

[17] Both N2000 and W92 have potential shortcomings. N2000 was based on $^3He/SF_6$ data collected in the coastal ocean, which may experience a different relationship between wind speed and gas transfer velocity due to factors such as less developed wind fields and higher occurrence of surfactants. N2000 also has no explicit consideration for global excess ^{14}C inventory, while W92 was based on excess ^{14}C inventory of the global ocean that is likely an overestimate [e.g., *Hesshaimer et al.*, 1994; *Peacock*, 2004]. Hence, the SAGE $^3He/SF_6$ data were used to produce a new parameterization between wind speed and gas transfer velocity for the open ocean.

[18] In order to derive a relationship between short-term (steady) winds and gas transfer velocity, the wind variability needs to be evaluated. This was accomplished by examining the second moment of the wind velocity and deriving an enhancement factor $\varepsilon = \overline{u_{10}^2}/\overline{u_{10}}^2$ [*Wanninkhof et al.*, 2004].* Using the enhancement factor, the k(600) was corrected accordingly and a fit was made to the corrected data to derive a relationship between steady wind speed and gas transfer velocity. Furthermore, the relationship derived here was constrained by a new estimate of global ocean excess ^{14}C uptake [*Key et al.*, 2004; *Peacock*, 2004; *Naegler et al.*,

*The equation is correct here. The article as originally published is online.

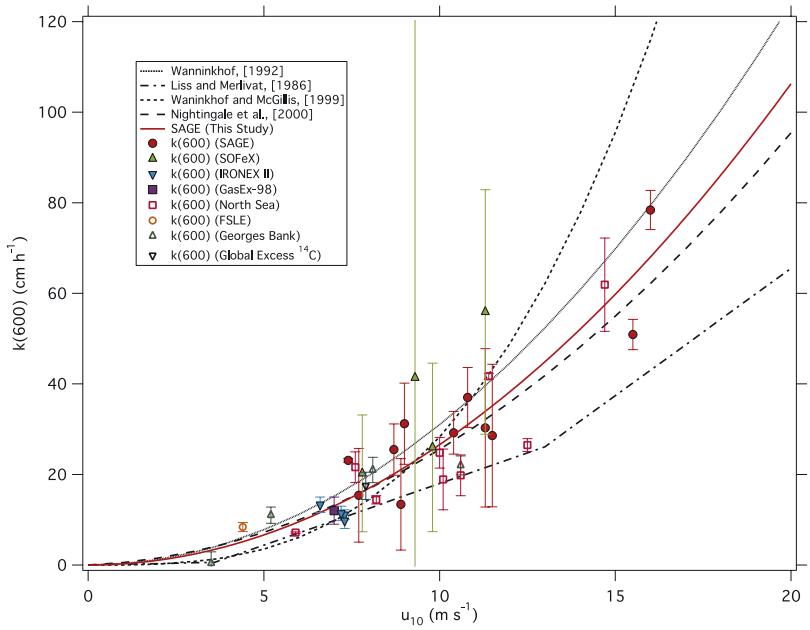

Figure 2. Commonly used short-term wind speed/gas exchange parameterizations, plotted along with $^3He/SF_6$ data points from the coastal (open symbols) and open ocean (solid symbols). The new wind speed/gas exchange parameterization proposed here is shown as a solid line. The North sea data are from *Nightingale et al.* [2000b], FSLE data from *Wanninkhof et al.* [1997], GasEx-98 data from *McGillis et al.* [2001], Georges Bank data are from *Wanninkhof et al.* [1993], and reanalyzed by *Asher and Wanninkhof* [1998], IRONEX data are from *Nightingale et al.* [2000a], and SOFeX data are from *Wanninkhof et al.* [2004]. The global excess ^{14}C point is from *Naegler et al.* [2006]. The SAGE and SOFeX data have been corrected for wind speed enhancement, assuming a quadratic relationship.

2006]. The wind speed/gas exchange relationship proposed here for short-term steady winds is intermediate between those of N2000 and W92: $k(600) = (0.266 \pm 0.019)u_{10}^2$ (Figure 2).

3.4. Air-Sea Gas Exchange in the Southern Ocean

[19] It has been postulated that wind has a larger effect on air-sea gas exchange in the Southern Ocean than elsewhere in the ocean due to larger fetch and hence more fully developed wave fields [*Nightingale et al.*, 2000a]. Next to the SAGE experiment, the location with the most number of $^3He/SF_6$ derived $k(600)$ measurements is the coastal site in the southern North Sea, with data collected from four separate experiments over a period of four years [*Nightingale et al.*, 2000b]. To compare the two data sets, a certain functionality could be assumed for the relationship between wind speed and $k(600)$ (i.e., a quadratic). The coefficient for the fit to the SAGE data (0.266 ± 0.019; $r^2 = 0.84$) is slightly higher than that for the North Sea data (0.246 ± 0.021; $r^2 = 0.78$). The North Sea data have not been corrected for wind speed enhancement (i.e., ε) and the difference is likely to be greater, but at present the difference is not significant. It is remarkable that the difference between the Southern Ocean and the coastal North Sea is not larger, given the contrast in the two physical environments. It is possible that coastal waters, due to smaller fetch, have 'younger' waves that are steeper and therefore more prone to breaking than fully developed waves. Also, because of its shallow depth, coastal areas such as the southern North Sea may have bathymetry-induced wave breaking. Currently, there is insufficient data from other areas of the open ocean to evaluate systematic differences between these regions and the Southern Ocean.

[20] Within the errors, the gas transfer velocities measured during the SAGE experiment are consistent with previous measurements made in the coastal and open ocean (Figure 2), and there is no evidence that wind has a larger effect on air-sea gas exchange in the Southern Ocean than anywhere else in the open or coastal ocean (Figure 2). SAGE was conducted a few hundred km from the coast of New Zealand, and it is possible that in other areas of the Southern Ocean with greater fetch, the wave fields are more developed and the relationship between wind speed and gas exchange is different. However, the high wind speeds measured during SAGE were south-westerly/southerly winds that were not obstructed by land. A detailed analysis of wind speeds and waves fields is beyond the scope of this contribution and will be forthcoming elsewhere.

[21] It is worth noting that the $^3He/SF_6$-derived gas transfer velocities from SOFeX [*Wanninkhof et al.*, 2004] are markedly different than those from SAGE (Figure 2), even though both experiments were conducted in the Southern Ocean. However, given the large errors associated with the SOFeX data, it is not possible to determine if the difference between SOFeX and other data is representative of a different gas exchange regime in the Southern Ocean.

3.5. Implications for Global and Regional CO_2 Uptake by the Ocean

[22] Using the new wind speed/gas exchange relationship proposed here, the global mean ocean CO_2 uptake for 1995, calculated from the surface ocean pCO_2 climatology of *Takahashi et al.* [2002], NCEP 41-year analysis winds with

Table 2. Selected Estimates of Global and Southern Ocean CO_2 Uptake

		Net CO_2 Uptake, pgC y^{-1}		
	Method	Global		Southern Ocean (> 46 °S)
Air-sea pCO_2 disequilibrium	SAGE (this study)	1.3 ± 0.3[a]		0.53 ± 0.11
	Liss and Merlivat [1986]	0.9 ± 0.2[a]		0.36 ± 0.07
	Wanninkhof [1992]	1.6 ± 0.3[a]		0.65 ± 0.13
	Wanninkhof and McGillis [1999]	1.9 ± 0.4[a]		0.69 ± 0.14
	Nightingale et al. [2000b]	1.2 ± 0.2[a]		0.52 ± 0.10
Model-based	OGCMs [*Matsumoto et al.*, 2004; A. R. Jacobson et al., A joint atmosphere-ocean inversion for surface fluxes of carbon dioxide: 1. Methods and global-scale fluxes, submitted to *Global Biogeochemical Cycles,* 2006a, hereinafter referred to as Jacobson et al., submitted manuscript, 2006a]	1.7 ± 0.2	(2.2 ± 0.2)[b]	0.59 ± 0.14
	Atmospheric Inversion [*Gurney et al.*, 2004]	1.3 ± 1.0		0.55 ± 0.37
	Joint Inversion (A. R. Jacobson et al., A joint atmosphere-ocean inversion for surface fluxes of carbon dioxide: 2. Regional results, submitted to *Global Biogeochemical Cycles*, 2006b)	1.7 ± 0.2		0.15 ± 0.07
Data-based	Ocean Inventory [*McNeil et al.*, 2003]	1.5 ± 0.4	(2.0 ± 0.4)[b]	-
	O_2/N_2 [*Bender et al.*, 2005]	1.2 ± 0.5	(1.7 ± 0.5)[b]	-

[a]Delta pCO_2 data used for air-sea pCO_2 disequilibrium calculations are from *Takahashi et al.* [2002].
[b]Ocean CO_2 uptake estimates based on atmospheric O_2/N_2, ocean CO_2 inventories, and OGCM yield gross fluxes (in parenthesis), and in order to compare with net estimates using air-sea pCO_2 disequilibrium, ca. 0.5 pgC y^{-1} needs to be subtracted from the gross fluxes to account for oxidation and outgassing of riverine carbon and $CaCO_3$ [*Sarmiento and Sundquist*, 1992; Jacobson et al., submitted manuscript, 2006a].

the appropriate enhancement factor applied, and Levitus SST fields, is 1.3 ± 0.3 pgC y^{-1}, which is intermediate between the various wind speed/gas exchange parameterizations mentioned above. A comparison with other estimates of global CO_2 uptake is presented in Table 2, and within the errors, estimates derived using the various methods are in agreement.

[23] The Southern Ocean represents a major uncertainty in other estimates of global ocean CO_2 uptake. Using the proposed SAGE relationship, the estimate for CO_2 uptake in the Southern Ocean (>46 °S) is 0.53 ± 0.11 pgC y^{-1}, which is in agreement with estimates from atmospheric inversion and OGCM, but in conflict with the joint atmosphere/ocean inversion (Table 2).

[24] As $^3He/SF_6$ dual tracer results from experiments conducted in different parts of the (coastal and open) ocean are in general agreement, and the resulting air-sea pCO_2 disequilibrium estimates agree with other studies, it suggests that enhanced air-sea gas exchange in the Southern Ocean cannot account for the discrepancies between different methods of estimating oceanic CO_2 uptake. It is possible that given the dynamical nature of surface ocean pCO_2, a climatological surface ocean pCO_2 map cannot capture all the variability and could lead to inaccurate results when used to calculate global or even regional CO_2 fluxes, but the agreement with other estimates of oceanic CO_2 uptake suggests that this variability has negligible impact.

4. Conclusions

[25] As part of the SOLAS Air-Sea Gas Exchange (SAGE) experiment, a $^3He/SF_6$ dual tracer experiment was conducted in the Southern Ocean. The experiment yielded the most number of $^3He/SF_6$ derived gas transfer velocity measurements from a single site in the open ocean, and showed that with adequate design, (i.e., enough stations and samples at each station) and environmental conditions (i.e., high wind speed and variability), the $^3He/SF_6$ dual tracer technique is a powerful way to measure gas transfer velocities in the open ocean.

[26] For the first time, gas transfer velocity measurements were obtained using the $^3He/SF_6$ dual tracer technique at high wind speeds (>15 m s^{-1}). The results from SAGE show that two of the commonly used parameterizations between wind speed and gas exchange, the piecewise linear relationship of *Liss and Merlivat* [1986] and the cubic relationship of *Wanninkhof and McGillis* [1999], are inconsistent with measurements of gas transfer velocities at high wind speeds from the open ocean.

[27] A new relationship between wind speed and gas transfer velocity was derived using the SAGE data: $k(600) = (0.266 \pm 0.019)u_{10}^2$. Predictions of global and regional ocean CO_2 uptake made using this new relationship are generally consistent with other independent estimates, but some discrepancies still exist between various methods to estimate this important parameter.

[28] Finally, the relationship between wind speed and gas transfer velocities from SAGE are generally consistent with previous experiments conducted in the coastal and open ocean, with no indication of differences due to regional variability in physical processes at the air-sea interface. Factors influencing air-sea gas exchange in the Southern Ocean should be the subject of future investigations, in regions with climatologically greater significant wave heights. Also, systematic measurements of gas transfer velocities with $^3He/SF_6$ should be made in other regions of the open ocean.

[29] **Acknowledgments.** We thank E. Abraham for assistance in site selection, patch release and mapping, A. Marriner for assistance with tracer infusion, C. McNally for ^3He extraction, B. Turrin for ^3He measurements, J. Trinanes for providing the QuikSCAT data, C. Sweeney, and R. Wanninkhof for helpful discussions, and the crew of the R/V TANGAROA for their invaluable assistance during SAGE. Funding was provided by the US National Science Foundation through OCE-0327779, and by the New Zealand Foundation for Research, Science and Technology through CO1X0204. LDEO contribution 6921.

References

Asher, W. E., and R. Wanninkhof (1998), The effect of bubble-mediated gas transfer on purposeful dual-gaseous tracer experiments, *J. Geophys. Res.*, *103*, 10,555–10,560.

Bender, M. L., D. T. Ho, M. B. Hendricks, R. Mika, M. O. Battle, P. P. Tans, T. J. Conway, B. Sturtevant, and N. Cassar (2005), Atmospheric O_2/N_2 changes, 1993–2002: Implications for the partitioning of fossil fuel CO_2 sequestration, *Global Biogeochem. Cycles*, *19*, GB4017, doi:10.1029/2004GB002410.

Boutin, J., J. Etcheto, L. Merlivat, and Y. Rangama (2002), Influence of gas exchange coefficient parameterisation on seasonal and regional variability of CO_2 air-sea fluxes, *Geophys. Res. Lett.*, *29*(8), 1182, doi:10.1029/2001GL013872.

Fairall, C. W., E. F. Bradley, J. E. Hare, A. A. Grachev, and J. B. Edson (2003), Bulk parameterization of air-sea fluxes: Updates and verification for the COARE algorithm, *J. Clim.*, *16*, 571–591.

Gurney, K., et al. (2004), Transcom 3 inversion intercomparison: Model mean results for the estimation of seasonal carbon sources and sinks, *Global Biogeochem. Cycles*, *18*, GB1010, doi:10.1029/2003GB002111.

Hesshaimer, V., M. Heimann, and I. Levin (1994), Radiocarbon evidence for a smaller oceanic carbon dioxide sink than previously believed, *Nature*, *370*, 201–203.

Kara, A. B., P. A. Rochford, and H. E. Hurlburt (2000), An optimal definition for ocean mixed layer depth, *J. Geophys. Res.*, *105*, 16,803–16,821.

Key, R. M., A. Kozyr, C. L. Sabine, K. Lee, R. Wanninkhof, J. L. Bullister, R. A. Feely, F. J. Millero, C. Mordy, and T.-H. Peng (2004), A global ocean carbon climatology: Results from Global Data Analysis Project (GLODAP), *Global Biogeochem. Cycles*, *18*, GB4031, doi:10.1029/2004GB002247.

Law, C. S., A. J. Watson, and M. I. Liddicoat (1994), Automated vacuum analysis of sulfur hexafluoride in seawater: Derivation of the atmospheric trend (1970–1993) and potential as a transient tracer, *Mar. Chem.*, *48*, 57–69.

Liss, P. S., and L. Merlivat (1986), Air–sea gas exchange rates: Introduction and synthesis, in *The Role of Air–Sea Exchange in Geochemical Cycling*, edited by P. Buat-Ménard, pp. 113–127, Springer, New York.

Ludin, A., R. Weppernig, G. Bönisch, and P. Schlosser (1998), Mass spectrometric measurement of helium isotopes and tritium in water samples, technical report, 42 pp., Lamont-Doherty Earth Obs., Palisades, N. Y.

Matsumoto, K., et al. (2004), Evaluation of ocean carbon cycle models with data-based metrics, *Geophys. Res. Lett.*, *31*, L07303, doi:10.1029/2003GL018970.

McGillis, W. R., J. B. Edson, J. D. Ware, J. W. H. Dacey, J. E. Hare, C. W. Fairall, and R. Wanninkhof (2001), Carbon dioxide flux techniques performed during GasEx 98, *Mar. Chem.*, *75*, 267–280.

McNeil, B. I., R. J. Matear, R. M. Key, J. L. Bullister, and J. L. Sarmiento (2003), Anthropogenic CO_2 uptake by the ocean using the global chlorofluorocarbon dataset, *Science*, *299*, 235–239.

Naegler, T., P. Ciais, K. Rodgers, and I. Levin (2006), Excess radiocarbon constraints on air-sea gas exchange and the uptake of CO_2 by the oceans, *Geophys. Res. Lett.*, *33*, L11802, doi:10.1029/2005GL025408.

Nightingale, P. D., P. S. Liss, and P. Schlosser (2000a), Measurements of air-sea gas transfer during an open ocean algal bloom, *Geophys. Res. Lett.*, *27*, 2117–2120.

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000b), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, *14*, 373–387.

Peacock, S. (2004), Debate over the ocean bomb radiocarbon sink: Closing the gap, *Global Biogeochem. Cycles*, *18*, GB2022, doi:10.1029/2003GB002211.

Popinet, S., M. Smith, and C. Stevens (2004), Experimental and numerical study of the turbulence characteristics of airflow around a research vessel, *J. Atmos. Oceanic Technol.*, *21*, 1575–1589.

Sarmiento, J. L., and E. T. Sundquist (1992), Revised budget for the oceanic uptake of anthropogenic carbon dioxide, *Nature*, *356*, 589–593.

Takahashi, T., et al. (2002), Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects, *Deep Sea Res., Part II*, *49*, 1601–1622.

Upstill-Goddard, R. C., A. J. Watson, J. Wood, and M. I. Liddicoat (1991), Sulphur hexafluoride and Helium-3 as sea-water tracers: Deployment techniques and continuous underway analysis for sulphur hexafluoride, *Anal. Chim. Acta*, *249*, 555–562.

Wanninkhof, R. (1992), Relationship between gas exchange and wind speed over the ocean, *J. Geophys. Res.*, *97*, 7373–7381.

Wanninkhof, R., and W. R. McGillis (1999), A cubic relationship between air-sea CO_2 exchange and wind speed, *Geophys. Res. Lett.*, *26*(13), 1889–1892.

Wanninkhof, R., W. Asher, R. Weppernig, H. Chen, P. Schlosser, C. Langdon, and R. Sambrotto (1993), Gas transfer experiment on Georges Bank using two volatile deliberate tracers, *J. Geophys. Res.*, *98*, 20,237–20,248.

Wanninkhof, R., et al. (1997), Gas exchange, dispersion, and biological productivity on the west Florida shelf: Results from a Lagrangian tracer study, *Geophys. Res. Lett.*, *24*(14), 1767–1770.

Wanninkhof, R., K. F. Sullivan, and Z. Top (2004), Air-sea gas transfer in the Southern Ocean, *J. Geophys. Res.*, *109*, C08S19, doi:10.1029/2003JC001767.

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