Toward a universal relationship between wind speed and gas exchange: Gas transfer velocities measured with $^3$He/SF$_6$ during the Southern Ocean Gas Exchange Experiment

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Two $^3$He/SF$_6$ dual–gas tracer injections were conducted during the Southern Ocean Gas Exchange Experiment (SO GasEx) to determine gas transfer velocities. During the experiment, wind speeds of up to 16.4 m s$^{-1}$ were encountered. A total of 360 $^3$He and 598 SF$_6$ samples were collected at 40 conductivity-temperature-depth (CTD) rosette casts and two pumped stations. The gas transfer velocity $k$ was calculated from the decrease in the observed $^3$He/SF$_6$ ratio using three different approaches. Discrete points of wind speed and corresponding $k$ were obtained from the change in $^3$He/SF$_6$ ratio over three time intervals. The results were also evaluated using an analytical model and a 1-D numerical model. The results from the three approaches agreed within the error of the estimates of about ±13%–15% for Patch 1 and ±4% for Patch 2. Moreover, $^3$He/SF$_6$ dual-tracer results from SO GasEx are similar to those from other areas in both the coastal and open ocean and are in agreement with existing parameterizations between wind speed and gas exchange. This suggests that wind forcing is the major driver of gas exchange for slightly soluble gases in the ocean and that other known impacts are either intrinsically related to wind or have a small effect (<20% on average) on time scales of the order of days to weeks. The functionality of the wind speed dependence (quadratic or cubic) cannot be unequivocally determined from SO GasEx results.


1. Introduction

In order to constrain the magnitude and variability of natural and anthropogenic CO$_2$ uptake by the ocean, and to determine the air–sea fluxes of other climate relevant gases such as DMS, it is essential to quantify gas transfer velocities ($k$) and relate them to environmental forcing. Considerable effort has been spent on determining empirical relationships between $k$ and wind speed ($u_{10}$) [Liss and Merlivat, 1986; Wanninkhof, 1992; Wanninkhof and McGillis, 1999; Nightingale et al., 2000b; Ho et al., 2006] since wind plays a central role in the generation of turbulence through the transfer of momentum to waves and currents at the water surface, and wind speed is widely measured. Relationships between $k$ and $u_{10}$ are used extensively in numerical models aimed at improving our understanding of the carbon cycle, and they are also used in combination with climatologies of surface ocean pCO$_2$, wind speed, and sea surface temperature to determine CO$_2$ uptake by the ocean [e.g., Takahashi et al., 2009].

Over the years, different methods have been employed to determine gas transfer velocities in the ocean, including the use of opportunistic tracers such as the $^{222}$Rn deficit method [e.g., Peng et al., 1979; Roether and Kromer, 1984; Bender et al., 2011], natural and bomb $^{14}$C [e.g., Wanninkhof, 1992; Naegler et al., 2006; Sweeney et al., 2007], deliberate tracers such as $^3$He/SF$_6$ [e.g., Watson et al., 1991], and micrometeorological techniques like eddy covariance, eddy accumulation, and gradient flux techniques [e.g., McGillis et al., 2001b; Huebert et al., 2004]. Each of the methods has characteristic time and space scales associated with it, and has unique attributes and shortcomings [Wanninkhof et al., 2009]. For experiments on time scales of hours to
days, $\text{He}/\text{SF}_6$ and eddy covariance have emerged as prevalent methods for measuring gas exchange over the ocean. [1] During the Southern Ocean Gas Exchange Experiment (SO GasEx) [Ho et al., 2011], gas transfer velocities were measured with $\text{He}/\text{SF}_6$, and also determined from eddy covariance of CO$_2$ (J. B. Edson et al., Eddy-covariance measurement of CO$_2$ gas transfer velocity during the Southern Ocean Gas Exchange Experiment (SO GasEx): Wind speed dependency, submitted to Journal of Geophysical Research, 2011) and DMS [Yang et al., 2011]. In this contribution, we focus on the $\text{He}/\text{SF}_6$ component, as it provides integrated measurements of gas exchange over a period of a day or more, and spatial scales of a few tens of kilometers. In contrast, eddy covariance provides measurements on time scales of 20–30 min and spatial scales of a few kilometers. However, since the signal to noise of individual measurements is low, averaging techniques (such a bin averaging over discrete wind speed intervals) are frequently employed. [5] One observation of note from previous $\text{He}/\text{SF}_6$ experiments is that the two most complete data sets are from two different environments, that is, a composite data set from the coastal ocean (North Sea) [Nightingale et al., 2000b] and a single study over the open ocean (Southern Ocean) [Ho et al., 2006]. Yet, the relationships between wind speed and gas exchange from those two areas are similar. Furthermore, two Southern Ocean $\text{He}/\text{SF}_6$ experiments, SAGE [Ho et al., 2006] and SOFeX [Wanninkhof et al., 2004] show some differences. Because the large experimental uncertainties in the SOFeX data preclude development of a robust relationship with wind, data from SO GasEx are critical to explore if the SAGE results taken near New Zealand are representative for different sectors of the Southern Ocean, or if the appreciable differences between SOFeX and SAGE are caused by effects that are not directly quantifiable by relating gas transfer velocity to wind speed (e.g., fetch).

2. Methods

2.1. Study Site

[6] The $\text{He}/\text{SF}_6$ dual-tracer experiment was conducted as part of SO GasEx, which took place in the southwest Atlantic sector of the Southern Ocean (nominally at 50°S, 40°W), near South Georgia Island from 29 February to 12 April 2008. For more information about the study site, see the work of Ho et al. [2011].

2.2. Wind Speeds

[7] Two sets of wind speed measurements are compared: one from a satellite, QuikSCAT, and the other from the ship. The ship-based wind speeds and directions were constructed from three sonic anemometers installed on the foremost of the ship. The relative wind direction was used to select the sonic anemometer(s) expected to be least affected by flow distortion, and the measurements were corrected for both the motion of the ship [Edson et al., 1998], and for flow distortion using an empirical correction. For more details on the wind speed measurements made from the ship during SO GasEx, see the work of Ho et al. [2011]. The colocated satellite winds were selected using QuikSCAT Level 2B 12.5 km data within ±0.5 degrees and 1 h of the ship location for each overpass (12.5 km swath). Rain flagged data were omitted from the analysis. Details on the retrieval of the vector winds at 10 m reference height $u_{10}$ can be found in the QuikSCAT Science Data Product User Manual (ftp://podaac.jpl.nasa.gov/ocean_wind/quickscat/l2b/doc/QSUG_v3.pdf). The comparison between ship and QuikSCAT wind speeds was performed to confirm that there are no significant biases between the wind speed products, so that the gas exchange/wind speed relationships determined in this study can be applied to other regions using the (global) QuikSCAT product.

2.3. The $\text{He}/\text{SF}_6$ Technique

[8] The $\text{He}/\text{SF}_6$ dual-tracer technique has been employed in coastal and open ocean experiments during the past two decades to obtain integrated measurements of gas transfer velocities [e.g., Watson et al., 1991; Wanninkhof et al., 1993, 1997, 2004; Nightingale et al., 2000a, 2000b; Ho et al., 2006]. $\text{He}$ and SF$_6$, two inert gases with different Schmidt numbers ($Sc =$ kinematic viscosity of water divided by diffusion coefficient of the gas in water), are injected together into the mixed layer at a constant ratio, and the $\text{He}/\text{SF}_6$ ratio is monitored over time. The assumption is made that patch dilution (e.g., horizontal mixing) is the dominant process that affects the individual tracer concentrations but this process does not alter the $\text{He}/\text{SF}_6$ ratio. The ratio of $k$ for $\text{He}$ and SF$_6$ can be expressed as

$$k_{\text{He}}/k_{\text{SF}_6} = \left( \frac{Sc_{\text{He}}}{Sc_{\text{SF}_6}} \right)^{-1/2},$$

where $k_{\text{SF}_6}$ and $k_{\text{He}}$ are the gas transfer velocities and $Sc_{\text{SF}_6}$ and $Sc_{\text{He}}$ are the Schmidt numbers for SF$_6$ and $\text{He}$, respectively. $Sc_{\text{SF}_6}$ and $Sc_{\text{He}}$ were determined from the measurements of King and Saltzman [1995] for SF$_6$, and Jähne et al. [1987] for $\text{He}$, which can be used to calculate $Sc_{\text{He}}$ if the fractionation between $\text{He}$ and $\text{He}$ is known. Jähne et al. [1987] determined the fractionation to be 15 ± 3%, which agrees with the ratio of the reduced masses (12.8%). A more recent result based on molecular dynamics simulations suggests the number to be 4.96 ± 0.83% [Bourg and Sposito, 2008]. It is possible that because the molecular dynamics simulations neglect quantum isotope effects, the fractionation could be higher than that based on these simulations. Further laboratory measurements or molecular dynamics simulations including quantum isotope effects will be necessary to determine the exact fractionation. Here, we use a fractionation of 12.8% (based on the ratio of the reduced masses) to be consistent with Wanninkhof et al. [1993, 1997, 2004] and Nightingale et al. [2000b]. K(600), the gas transfer velocity at a Sc number of 600, would be about 11% higher if no correction for the difference in diffusivity between $\text{He}$ and $\text{He}$ is applied [e.g., Ho et al., 2006] (see equation (2) below). Likewise, if $Sc_{\text{SF}_6}$, from Wanninkhof [1992] were used instead of values from King and Saltzman [1995], K(600) would be about 3% lower at the sea surface temperatures of ca. 5–6°C for SO GasEx. This analysis illustrates the level of uncertainty in the gas transfer velocity due to lack of accurate basic physical data for $\text{He}$ and SF$_6$. [9] The gas transfer velocity for $\text{He}$ $k_{\text{He}}$ can be determined by combining the advection-diffusion equations for
\( ^3\text{He} \) and SF\(_6\), vertically averaged over the mixed layer, and equation (1) [Wanninkhof et al., 1993]:

\[
k_{\text{mix}} = -\frac{d}{dt} \left( \frac{\ln (\text{He}_{\text{exc}}/\text{SF}_6)}{1 - (\text{Sc}_{\text{He}}/\text{Sc}_{\text{mix}})^{1/2}} \right),
\]

where \( h \) is the characteristic gas exchange depth, which is the depth where the \( ^3\text{He}_{\text{exc}}/\text{SF}_6 \) ratio changes appreciably from the constant values above. This depth corresponds closely to the depth where SF\(_6\) reaches 50\% of its averaged concentration in the top 20 m. SF\(_6\) and \( ^3\text{He}_{\text{exc}} \) are the SF\(_6\) and excess \( ^3\text{He} \) concentrations (i.e., \( ^3\text{He} \) in excess of solubility equilibrium) in the mixed layer, respectively. In this contribution, the terms \( ^3\text{He}_{\text{exc}} \) and \( ^3\text{He} \) will be used interchangeably. The characteristic gas exchange depth during SO GasEx, referred to as mixed-layer depth below, is generally somewhat deeper than the mixed-layer depth defined by density, particularly during periods of rapid shoaling of the density-defined mixed layer as will be seen to occur during the periods of both tracer patches. The gas transfer velocities measured during SO GasEx are normalized to \( k(600) \), where 600 corresponds to \( \text{Sc} \) of CO\(_2\) in freshwater at 20°C:

\[
k(600) = k_{\text{mix}} \left( \frac{600}{\text{Sc}_{\text{He}}} \right)^{-1/2}.
\]

\subsection{2.4. Tracer Injection}

[10] The \( ^3\text{He} \) and SF\(_6\) injection was achieved in a similar way to previous tracer release experiments [Upstill-Goddard et al., 1991]. On the aft deck of the ship, a large 4800 L steel tank was filled with seawater and infused with SF\(_6\) and \( ^3\text{He} \) prior to injection into the surface mixed layer. After the tank was filled with seawater, a 1 L headspace was created and flushed continuously with SF\(_6\). The SF\(_6\) was circulated through the water via a length of diffuser tubing using a pump until SF\(_6\) in the water reached the desired concentration. A few hours before injection, a 1 L \( ^3\text{He} \) headspace was created and circulated with a pump through the water until the gas dissolved. This was repeated until the desired amount of \( ^3\text{He} \) was infused into the tank (ca. 10 L at STP for each patch). During tracer injection, the top of the tank was fitted with a weather balloon. As water was pumped out of the tank with a peristaltic pump, the weather balloon was gravity fed with seawater from a header tank to ensure that no headspace developed, thus preventing \( ^3\text{He} \) and SF\(_6\) from exchanging with the headspace and altering the \( ^3\text{He}/\text{SF}_6 \) ratio.

[11] The tracer release was completed in a hexagonal pattern within a Lagrangian framework, achieved by following a central GPS-enabled drifter with a line-of-sight VHF transmitter to adjust the ships track for surface water advection during the release. The drifter marked the center of the water parcel and the ship followed a track marked by waypoints at the vertices of expanding hexagons, each centered on an up-to-date position of the GPS drifter.

[12] The ship speed during the injections was ca. 7.5 km h\(^{-1}\). The first injection took place on 8 March 2008 (yearday 68), and lasted 13.5 h at a flow rate of 6 L min\(^{-1}\), creating a patch with an area of ca. 50 km\(^2\). The second injection, in a different water parcel, was on 21 March 2008 (yearday 81), and lasted 6.5 h at a flow rate of 10.2 L min\(^{-1}\), creating a patch with an area of ca. 12.5 km\(^2\). Nominal injection depth for both patches was about 5–6 m.

[13] Because the volume of SF\(_6\) and \( ^3\text{He} \) infused water injected was the same for both patches and Patch 2 was smaller, it had higher SF\(_6\) and \( ^3\text{He} \) concentrations. Thus, it was easier to survey and could be followed for a longer period.

\subsection{2.5. Underway SF\(_6\) Measurements}

[14] An underway SF\(_6\) system, described in detail by Ho et al. [2002] was used to monitor the advection and dispersion of the tracer patch. In addition to determining the boundaries of the water parcel for the Lagrangian experiment, the system was used to determine the center of the patch (i.e., the area of maximum tracer concentration) for the twice-daily conductivity-temperature-depth (CTD) casts. For more information about underway SF\(_6\) measurements made during SO GasEx, see the work of Ho et al. [2011].

\subsection{2.6. The \( ^3\text{He} \) Samples}

[15] \( ^3\text{He} \) samples (ca. 40 mL each) were drawn from 40 CTD casts and 2 submersible pump stations to be used in conjunction with SF\(_6\) to calculate the gas transfer velocity and to determine the extent of horizontal and vertical mixing. Typically, 8 to 10 depths per station were sampled, covering the mixed layer, thermocline, and deeper water below. The samples were stored in copper tubes closed at both ends by means of stainless steel pinch-off clamps. The \( ^3\text{He} \) measurements were performed in the Lamont-Doherty Earth Observatory noble gas laboratory. \( ^3\text{He} \) and other gases were extracted from the copper tubes and transferred to flame-sealed glass ampoules with low helium permeability containing activated charcoal using a vacuum extraction system [Ludin et al., 1998]. The \( ^4\text{He} \) concentration and the \( ^3\text{He}\!/^4\text{He} \) ratio were measured on a dedicated VG-5400 He isotope mass spectrometer. Prior to introduction into the mass spectrometer, He was separated from all other gases by a series of cold traps. He was measured using a Faraday Cup and \( ^4\text{He} \) was measured using a channel electron multiplier (Channeltron). Neon was measured in parallel on a quadrupole mass spectrometer [Ludin et al., 1998]. Precision was about 0.5\% in \( ^3\text{He} \) for samples with very high \( ^3\text{He} \) excesses (100\% < \( ^3\text{He} < 1000\% \)), and 0.2 to 0.5\% for samples with lower \( ^3\text{He} \) excesses (−1.7\% < \( ^3\text{He} < 100\%) \). Precision of the \( ^4\text{He} \) and Ne measurements was about 0.2 to 0.5, and 0.5 to 1\%, respectively. 35 samples were lost during extraction or measurement, and 111 samples had anomalous \( ^3\text{He} \) and Ne concentrations suggesting excess air in the samples or fractionation during measurement. These samples were not used in the interpretation.

\subsection{2.7. Discrete SF\(_6\) Samples}

[16] Discrete SF\(_6\) samples were collected in 550 mL borosilicate bottles with ground glass stoppers for shipboard analysis. 598 samples were collected during 40 CTD casts, 56 samples were collected from the underway seawater line at 19 locations, and 11 samples were collected at the 2 submersible pump stations. Over 40 pairs of duplicate samples were drawn at various times from the same Niskin.
and the agreement between these duplicates was typically better than 2%. The SF$_6$ (and $^3$He) samples from the two pumped stations were contaminated with ambient air and are not used in the analysis here.

[17] An analytical system patterned after Law et al. [1998], consisting of a purge-and-trap inlet coupled to a GC-ECD, was used to quantify the vertical SF$_6$ distribution. The dissolved gases in 269 mL of water sample were purged with UHP N$_2$ and then trapped on a Carboxen 1000 trap held at −68°C. After several minutes of purging, the trap was isolated and heated to 150°C. The purged gases were swept onto a molecular sieve 5A column where the SF$_6$ was separated from other gases. SF$_6$ was measured with a GC-ECD. The detector was calibrated using six standards with concentrations of 5.7, 55.1, 112, 167, 345, and 1109 ppt. Custom software (LabVIEW) was used for instrument control, acquisition of the ECD output, and reintegration of the chromatographic peaks. 56 discrete samples were taken from the uncontaminated seawater line and used to adjust the final calibration of the underway SF$_6$ system.

2.8. Models of $^3$He/SF$_6$

[18] The temporal change in SF$_6$ and $^3$He in response to vertical mixing and air-sea gas exchange during SO GasEx can be examined by (1) looking at the differences in mixed layer averaged $^3$He/SF$_6$ profiles from each CTD station or (2) considering all the $^3$He/SF$_6$ pairs measured together. We do both here by using an analytical model to examine the former, and a 1-D numerical model to examine the latter. The objective of both is to compare the model-predicted tracer ratio ($^3$He/SF$_6$) to the observations in order to determine the optimal relationship between $k(600)$ and 10 m (neutral stability) winds ($u_{10N}$).

2.9. Analytical Model

[19] Using the assumption that air-sea gas exchange is the only process that alters the $^3$He/SF$_6$ ratio in the mixed layer, the change in $^3$He/SF$_6$ ratio during SO GasEx can be modeled by an analytical solution to equation (2):

$$\frac{[^3\text{He}_{mix}/\text{SF}_6]}{[^3\text{He}_{mix}/\text{SF}_6]_{t-1}} = \exp\left(-\frac{k_{10N} \Delta t}{h} \left(1 - \frac{S_{\text{SF}_6}}{S_{\text{Cl}_{\text{mix}}}}\right)^{-1/2}\right), \quad (4)$$

where $[^3\text{He}_{mix}/\text{SF}_6]$ is the $^3$He to SF$_6$ ratio at time $t$ and $[^3\text{He}_{mix}/\text{SF}_6]_{t-1}$ is the tracer ratio at the previous time step. $k_{10N}$ is prescribed from wind speeds measured during SO GasEx and existing parameterizations between $u_{10N}$ and $k(600)$. The 10 min averaged wind speeds from the ship are used, so that each time step is 10 min. By using the average of all $^3$He/SF$_6$ points in the mixed layer at each time step and using equation (4), we are assuming that the average ratios represent the mixed-layer profiles. While inspection of the profiles suggests that this is a reasonable assumption, there are periods where the $^3$He/SF$_6$ ratio at the surface is lower and this approach will lead to an anomalously low $k$. [20] The ability of commonly used parameterizations, including the piecewise linear parameterizations of Liss and Merlivat [1986], quadratic relationships of Wanninkhof [1992], Nightingale et al. [2000b], and Ho et al. [2006], cubic relationship of Wanninkhof and McGillis [1999], and the hybrid parameterization of Wanninkhof et al. [2009], to predict the $^3$He/SF$_6$ measured during SO GasEx could be evaluated by examining the relative root mean square error (rRMSE) between the observed and modeled $^3$He/SF$_6$ ratios:

$$r\text{RMSE} = \sqrt{\frac{\sum_{n=1}^{N} \left(\frac{R_{\text{obs}} - R_{\text{mod}}}{R_{\text{obs}}}\right)^2}{N}}, \quad (5)$$

where $R_{\text{obs}}$ and $R_{\text{mod}}$ are the observed and modeled $^3$He/SF$_6$ tracer ratios, respectively, $N$ is the number of stations sampled, and the summation is over the averaged $^3$He/SF$_6$ ratios in the mixed layer for each station.

$[21]$ The data are also used to determine the optimal coefficients ($a_2$ and $a_3$) for a quadratic ($k = a_2u_{10N}^2$) and cubic ($k = a_3u_{10N}^3$) parameterization for each patch, by minimizing the rRMSE.

2.10. One-Dimensional Numerical Model

$[22]$ The one-dimensional generalized ocean turbulence model (GOTM) was forced with surface fluxes estimated from shipboard meteorological measurements and was nudged to the observations of temperature and salinity from CTD casts and velocity from the shipboard ADCP. Further details of the GOTM implementation can be found in the work of Ho et al. [2011]. Separate runs were carried out for the time periods of the two tracer patches. The vertical diffusivity field (a function of time and depth) from these runs was saved every hour and used to solve the vertical tracer evolution equation.

$[23]$ For each patch, tracer concentrations were initialized to be vertically uniform over the model density-based mixed layer (the portion of the water column where $\rho(z) - \rho(5 \text{ dbar}) \leq 0.01 \text{ kg m}^{-3}$) at the time of the first CTD cast after the tracer injection. The time interval between the end of tracer injection and the first CTD cast was approximately 39 h for Patch 1 and 15 h for Patch 2. Model $^3$He and SF$_6$ concentrations were initialized to their mixed-layer values from water samples taken during the first postinjection CTD cast.

$[24]$ Surface gas fluxes in the model were parameterized using a gas transfer velocity that was a function of $u_{10N}$, assuming zero atmospheric gas concentrations. We tested two functional forms (quadratic and cubic) for the $^3$He gas transfer velocity as in the analytical model. $k(600)$ was derived from $k_{10N}$ using a $S^{-1/2}$ dependency (equation (1)). The optimal coefficients, $a_2$ or $a_3$ for ($k = a_2u_{10N}^2$) and ($k = a_3u_{10N}^3$), were obtained by fitting the model to the observations by minimizing the cost function:

$$F = \sum_{n=1}^{N} \left(\frac{R_{\text{obs}} - R_{\text{mod}}}{R_{\text{obs}}}\right)^2, \quad (6)$$

where the summation is over all observations within the model mixed layer (determined as the depth $z$ at which $\rho(z) - \rho(5 \text{ dbar}) > 0.01 \text{ kg m}^{-3}$). Note that the cost function defined by equation (6) is formally equivalent to the definition in equation (5) (i.e., $F = N \times r\text{RMSE}^2$). As discussed previously, the uncertainties in the measured gas concentrations are expressed as relative errors, so that the uncertainty in the observed tracer ratio is proportional to its magnitude. Therefore, normalization of the differences
in the numerator of equation (6) by the observed ratio is equivalent to weighting by the inverse of the observational errors, known as chi-square fitting [Press et al., 1992]. The cost function (equation (6)) was minimized using a simplex direct search method (Nelder-Mead) [Press et al., 1992].

3. Results and Discussion

3.1. Wind Speed

[25] Ship wind speed during Patch 1, which consists of 555 measurements of 10 min averaged winds, ranged from 3.9 to 14.3 m s$^{-1}$, with a mean of 8.9 m s$^{-1}$ and a standard deviation of 1.7 m s$^{-1}$. Wind speeds during Patch 2, consisting of 2003 measurements, ranged from 1.5 to 16.4 m s$^{-1}$, with a mean of 9.2 m s$^{-1}$ and a standard deviation of 3.1 m s$^{-1}$ (Table 1 and Figure 1). The corresponding QuikSCAT wind speeds for Patch 1 from 502 measurements ranged from 2.4 to 14.5 m s$^{-1}$, and had a mean of 8.7 m s$^{-1}$ and a standard deviation of 2.1 m s$^{-1}$. Patch 2 ranged from 1.4 to 20.8 m s$^{-1}$, with a mean of 9.4 m s$^{-1}$ and a standard deviation of 3.7 m s$^{-1}$. The QuikSCAT and ship wind speeds averaged between CTD stations (ca. every 12 h) compared well ($R^2 = 0.84$), with QuikSCAT winds being higher than ship winds by up to 2 m s$^{-1}$ at $u_{10} > 12$ m s$^{-1}$ (Figure 2). However, considering that the QuikSCAT winds cover a larger region and are based on 2–4 overpasses per day rather than continuous measurements, and because the ship winds are averaged over ca. 12 h, this should be considered a good agreement. The ship winds are thus assumed to be representative over the entire patch.

3.2. SF$_6$ Patch

[26] The center of the tracer patch at the completion of the first injection on 9 March 2008 (yearday 69) was at 50.6042°S, 38.6308°W. SF$_6$ concentrations as high as 440 fmol L$^{-1}$ were measured during the initial survey following tracer injection. The final CTD performed before leaving the study area for the vicinity of South Georgia Island was Station 10 on 14 March 2008 (yearday 74) at 50.8620°S, 38.2394°W, and the surface SF$_6$ concentration at this location was 29 fmol L$^{-1}$. The tracer patch advected approximately 40 km over the six days of the survey [see Ho et al., 2011, Figures 16 and 17].

[27] After 4 days at South Georgia Island, the ship returned to survey in the vicinity of the MAPCO$_2$ buoy that was deployed in the tracer patch. Low SF$_6$ concentrations of 10 fmol L$^{-1}$ were detected near the buoy. A CTD station was conducted at the approximate center of the residual patch at 51.0401°S, 37.6988°W before moving on to locate a site for a second tracer injection. Because there were no high temporal resolution wind speed measurements made at the patch location when the ship was at South Georgia Island, the change in $^{3}$He/SF$_6$ during this period was not used in the analysis here.

Figure 1. Histograms of wind speeds encountered during SO GasEx for (a) Patch 1 and (b) Patch 2.
The second tracer patch, created on 21 March 2008 (yearday 81) was centered on 51.1442°S, 38.4042°W. The maximum SF$_6$ concentration following the injection was 999 fmol L$^{-1}$. The final CTD performed in Patch 2 was on 5 April 2008 (yearday 96) and located at 51.4650°S, 37.4072°W. The surface SF$_6$ concentrations located at this location were $\sim$6 fmol L$^{-1}$. The second patch advected approximately 78 km over the 15 days after the second injection.

3.3. The $^3$He and SF$_6$

For the CTD casts in the tracer patches, the SF$_6$ concentrations were mostly uniform throughout the mixed layer (Figure 3). For a few of the casts, the surface concentrations were lower than the mixed-layer average, but still well above background SF$_6$ concentration. Over the 10.5 days during which CTD casts were done in the first tracer patch (which includes time away at South Georgia Island), the SF$_6$ in the mixed layer in the center of the patch decreased to about 6% of the initial concentration but remained over two times higher than background concentrations.

The initial SF$_6$ concentrations in the second patch were more than 4 times greater than the first patch. Over the 14 days CTD casts were done on the second tracer patch, the mixed-layer SF$_6$ concentrations decreased to less than 2% of the initial concentration but remained over almost three times higher than background concentration.

3.4. SF$_6$ and $^3$He/SF$_6$ Depth Profiles

The large number of samples and duration of the study offers a unique opportunity to further investigate the basic assumptions of the dual gaseous deliberate tracer approach. In particular, we assess the issues of mixed-layer homogeneity and mixed-layer depth, which are both critical for calculating $k_{3He}$. In some previous studies [e.g., Wanninkhof et al., 2004], the mixed-layer depth for gas transfer is assumed to be a classically defined mixed layer based on temperature or density criteria. Here we show that in SO GasEx, the layer exchanging gas with the atmosphere...
as determined from a constant \(^3\)He/SF\(_6\) ratio is often deeper. This is attributed to the longer characteristic time scales of gas transfer, expressed as \(h/k\), of order of a week, compared to the short time scale (<1 day) that it takes the mixed layer to homogenize based on the modeled mixing rates in the GOTM [Ho et al., 2011]. Thermal mixed-layer depth variations can be as short as hours for internal wave motions to several days owing to changes in wind stress and associated turbulence. Figure 3 shows profiles of normalized SF\(_6\), \(^3\)He/SF\(_6\) and temperature for Stations 5 (Patch 1) and 31 (Patch 2). Normalization of SF\(_6\) and \(^3\)He/SF\(_6\) are to mixed-layer concentration and temperature to the difference of the measured \([SF_6]\) = 0. Inspections of all profiles suggest that the depth where SF\(_6\) is half that of the average concentration in the upper 20 m (i.e., \([SF_6]\) = 0.5 × \([SF_6]_{20m}\)) is a reasonable approximation of the depth that exchanges with the atmosphere as this is the depth where \(^3\)He/SF\(_6\) rapidly decreases. Since the time scale of gas transfer is on the order of a week, the average \([SF_6]\) derived mixing depths are used for each patch.

### 3.5. Temporal \(^3\)He/SF\(_6\) Trends

[52] A puzzling aspect of the \(^3\)He/SF\(_6\) trends in several open ocean studies including SO GasEx is that while the ratio shows a strong decrease over the duration of the study, the ratios between some individual sampling points either decrease precipitously or even increase or remain steady (see Figure 4). These changes are greater than can be attributed to instrumental uncertainty and cannot be solely explained by local mixed-layer dynamics. For instance, the observed increases are not always caused by stratification of the mixed layer and outgassing, with a decrease in \(^3\)He/SF\(_6\), followed by reestablishment of a deeper mixed layer causing the isolated waters with high \(^3\)He/SF\(_6\) to increase the \(^3\)He/SF\(_6\) such as shown in Figure 3b. We attribute the nonsystematic changes in \(^3\)He/SF\(_6\) to two factors both related to mixed-layer depth variations.

[33] Several instances show a sharp decrease in \(^3\)He/SF\(_6\) in a transition from light winds to higher winds and deeper mixed layers. This is attributed to enhanced gas transfer due to higher winds preceding mixed-layer deepening such that the gas loss is over a smaller volume.

[34] Another cause for the occasional increases of \(^3\)He/SF\(_6\) is mixed-layer heterogeneity, in particular the variations in depth of water exchanging \(^3\)He and SF\(_6\) with the atmosphere over the tracer patch. The tracers were released in an eddy-like feature that likely has systematic spatial differences in depth. Figure 3b shows an extreme example of variations in SF\(_6\) and \(^3\)He/ SF\(_6\) encountered in the near surface layer.

### 3.6. Gas Transfer Velocities

[35] Because of the variability in \(^3\)He/SF\(_6\) described above, and to decrease some of the experimental uncertainty in order to obtain more accurate measurements of \(k(600)\) from \(^3\)He/SF\(_6\) [e.g., Asher, 2009], we have chosen to derive \(k(600)\) for longer time intervals and use three segments of the experiment, one for Patch 1 and two for Patch 2 (Table 1). Patch 2 was divided on the basis of the change in \(^3\)He/SF\(_6\) at day 86.56 (Figure 4). The \(k(600)\) results shown in Figure 5 have been corrected for wind speed enhancement assuming a quadratic function with wind speed (i.e., \(\varepsilon = \frac{u^2}{10^2} \times 10^{-5}\) [Wanninkhof et al., 2004] by dividing \(k(600)\) by \(\varepsilon\) (Table 1).

### 3.7. Analytical Model

[36] The two patches were considered separately, and the analytical model was initialized with the second mean \(^3\)He/SF\(_6\) profile for each to ensure that the patch was relatively homogeneous. The same was done with the first profile with similar results. Because the wind speed was in the range where many of these wind speed/gas exchange parameterizations are similar, many of them were able to produce the \(^3\)He/SF\(_6\) from SO GasEx to a large extent (Table 1). For example, for Patch 1, the parameterizations of Wanninkhof [1992] and Wanninkhof and McGillis [1999]...
were both able to predict the $^3$He/SF$_6$ well (Figure 4a), even though they have different functional forms and diverge at high wind speeds. For Patch 2, the parameterizations of Nightingale et al. [2000b], Ho et al. [2006], and Wanninkhof et al. [2009] were all similar in terms of performance (Figure 5). This is not surprising given that in the wind speed range encountered, these parameterizations share many features (Figure 5). Table 2 also shows the optimized coefficients for quadratic and cubic parameterizations. For Patch 1, the optimal quadratic coefficient is ca. 8% greater than that proposed by Ho et al. [2006], and the optimal cubic coefficient is identical to that proposed by Wanninkhof and McGillis [1999], with the resulting rRMSE being similar between the optimization and the existing parameterizations. For Patch 2, the parameterizations of Nightingale et al. [2000b], Ho et al. [2006], and Wanninkhof et al. [2009] share similar statistics as the optimization.

**Table 2. Statistics of Comparison Between $^3$He/SF$_6$ Measured During SO GasEx and $^3$He/SF$_6$ Predicted by an Analytical Model Using Various Wind Speed/Gas Exchange Parameterizations**

<table>
<thead>
<tr>
<th>Parameterizations</th>
<th>Patch 1</th>
<th>Patch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>rRMSE (%)</td>
<td>Coefficients</td>
</tr>
<tr>
<td>Liss and Merlivat [1986]</td>
<td>6.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Wanninkhof [1992]</td>
<td>5.5</td>
<td>20.8</td>
</tr>
<tr>
<td>Wanninkhof and McGillis [1999]</td>
<td>4.7</td>
<td>24.3</td>
</tr>
<tr>
<td>Nightingale et al. [2000b]</td>
<td>5.2</td>
<td>7.7</td>
</tr>
<tr>
<td>Ho et al. [2006]</td>
<td>4.9</td>
<td>8.6</td>
</tr>
<tr>
<td>Wanninkhof et al. [2009]</td>
<td>6.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Optimization ($a^2$)</td>
<td>4.6</td>
<td>0.286</td>
</tr>
<tr>
<td>Optimization ($a^3$)</td>
<td>4.7</td>
<td>0.0298</td>
</tr>
</tbody>
</table>

*Also included are optimizations using quadratic and cubic fits. The coefficients are for $Sc = 600.$
3.8. Numerical Model

[37] The $^3$He/SF$_6$ results from the 1-D GOTM were fitted to the observations by varying the coefficients, $a_2$ or $a_3$, (described above). The model fitting procedure was performed using observations from each tracer patch separately as well as for both patches combined. The optimized coefficients and estimates of their uncertainty are given in Table 3. The uncertainties were estimated using a bootstrap technique [Efron and Gong, 1983], whereby a large number (500) of simulated data sets were drawn from the actual data set and each subjected to the model fitting procedure. The uncertainties in Table 3 are the 95% confidence levels of the estimated coefficients.

[38] Using data from both patches, the fit of the model to the observations (the sixth and seventh columns of Table 3) is quite similar for the quadratic and cubic dependencies. RMS normalized differences (sixth column, Table 3) are 7.6% and 8.6% for the quadratic and cubic cases, respectively, and the corresponding $R^2$ values are 0.975 and 0.970. The best fit quadratic and cubic coefficients (for $Sc = 600$) are $0.277 \pm 0.010$ and $0.0241 \pm 0.0010$, respectively, where the former corresponds reasonably well to the coefficient of 0.266 proposed by Ho et al. [2006]. Performing the optimization using data from Patch 1 gives somewhat higher values, $0.310 \pm 0.046$ for the quadratic and $0.0331 \pm 0.0042$ for the cubic coefficients, respectively. Owing to the large estimated uncertainty in the optimized coefficient, the Patch 1 quadratic coefficient is not significantly different from the value estimated using data from both patches. The values estimated for Patch 2 are essentially the same as those derived from both patches, as the major part of the combined data set is composed of Patch 2 data.

[39] Figure 6 shows a comparison of the $^3$He/SF$_6$ ratios from the model and observations for the case of quadratic wind speed dependency. Note that although the model-data differences in Figure 6 are shown for all depths, the model was fit to the data using only observations within the model mixed layer based on density criteria. The modeled tracer ratio below the mixed layer is systematically higher than in the observations. This is likely due to the fact that the model, lacking a realistic internal wavefield, underestimates vertical mixing in the pycnocline below the mixed layer. The individual tracer concentrations in the model below the mixed-layer base are very small, thus the model ratios are not meaningful there. Above the mixed-layer base, model ratios in the Patch 1 simulation are higher than observed in the early portion of the run (i.e., the modeled gas transfer velocity is too low), and lower near the end (Figure 6d). In the Patch 2 simulation, agreement is quite good above the mixed-layer base except for the period of mixed-layer shoaling around yearday 86 when model tracer ratios are lower than observed. This is partly due to the increase in the observed tracer ratio at station 26 (yearday 85.62) compared to the values at station 25 (yearday 85.15), an event that is not consistent with a 1-D model. During this period, however, the model mixed-layer shoals somewhat earlier than the observed mixed layer. This results in a more rapid decrease in the near-surface tracer ratio as the more volatile tracer ($^3$He) is drawn down within the shallower mixed layer and contributes to the model-data misfit near the surface. The fit of the model with gas transfer velocity as a function of the cube of wind speed (not shown) is very similar to the quadratic case shown in Figure 6.

[40] The best fit coefficients $a_2$ and $a_3$ derived with the numerical model are systematically higher (7 to 10%) than the values estimated using the analytical model. These differences could be due to the fact that the analytical model considers the tracer mixed-layer average $^3$He/SF$_6$ from each station, whereas the numerical model uses each individual $^3$He/SF$_6$ measurement within the model mixed layer. Gas exchange in the numerical model is computed as the product of the gas transfer velocities and the surface tracer concentrations, whereas in the analytical model the exchange is based on the mixed-layer average concentrations. Thus, for equal gas exchange in the two models, lower ratios at the surface compared to the mixed-layer average mixed would lead to an anomalously low gas transfer velocity in the analytical model (and the coefficients in the wind speed parameterizations). In the numerical model, the mean value of the ratio of surface $^3$He concentration to (tracer) mixed-layer $^3$He concentration is approximately 0.85, and for SF$_6$, the corresponding ratio is 0.96. This reduction of near-surface tracer concentrations relative to the mixed-layer values in the model is qualitatively consistent with the higher gas transfer velocities estimated from the numerical model. In the data, most of the time, this surface versus mixed-layer difference is small as, for example, the SF$_6$ measured at 5 m is typically within 1–2% of its mixed-layer average. However, there is one occasion during Patch 1 where this difference is almost 20%, and several occasions during Patch 2 where the surface concentration is 13–46% lower (see Figure 3b, for example).

3.9. Relationship Between Wind Speed and Gas Exchange

[41] Within the errors of the optimization (Table 3), the analytical and numerical models show consistent results in their estimates of $a_2$ and $a_3$ for Patches 1 and 2. One

---

<table>
<thead>
<tr>
<th>Data Set</th>
<th>Function</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>N</th>
<th>(F/N)$^{1/2}$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Patch 1</td>
<td>quadratic</td>
<td>0.310 ± 0.046</td>
<td>0.0331 ± 0.0042</td>
<td>23</td>
<td>0.060</td>
<td>0.837</td>
</tr>
<tr>
<td></td>
<td>cubic</td>
<td>0.277 ± 0.011</td>
<td>0.00241 ± 0.0010</td>
<td>61</td>
<td>0.080</td>
<td>0.959</td>
</tr>
<tr>
<td>Patch 2</td>
<td>quadratic</td>
<td>0.277 ± 0.010</td>
<td>0.00241 ± 0.0010</td>
<td>61</td>
<td>0.088</td>
<td>0.950</td>
</tr>
<tr>
<td></td>
<td>cubic</td>
<td>0.277 ± 0.010</td>
<td>0.00241 ± 0.0010</td>
<td>84</td>
<td>0.076</td>
<td>0.975</td>
</tr>
</tbody>
</table>

*The values $a_2$ and $a_3$ are the coefficients of the quadratic and cubic forms, respectively, of $k(600)$ as a function of $u_{100}$. The uncertainties in the best fit coefficients were determined using a bootstrap methodology and represent estimates at the 95% confidence level.
An interesting aspect of the 
$^3$He/SF$_6$ data that shows up in both 
the analytical and numerical models is the difference 
between Patches 1 and 2 (Tables 2 and 3). For instance, in 
the analytical model, while all the parameterizations were 
similar in being able to reproduce $^3$He/SF$_6$ from Patch 1 
(rRMSE between 4.7 and 6.8%; Table 2), Wanninkhof 
[1992] and Wanninkhof and McGillis [1999] fail to simu-
late the data from Patch 2 (rRMSE of 20.8% and 24.3%, 
respectively; Table 2). Part of the explanation lies in the 
wind speeds encountered during the two patches (Figure 1). 
For Patch 1, the wind speeds were mostly in the range 
between 6 and 12 m s$^{-1}$, where the various parameteriza-
tions overlap. For Patch 2, the wind speeds were between 
2 and 16 m s$^{-1}$, where there is considerable divergence 
between the parameterizations. At these higher wind speeds, 
Wanninkhof [1992] and Wanninkhof and McGillis [1999] 
overestimate $k(600)$, whereas Liss and Merlivat [1986] 
underestimate $k(600)$.

The difference between the two patches could also 
indicate that something other than direct wind effects 
influences air–sea gas exchange in the Southern Ocean, but 
these effects are small relative to the dominant effect of 
wind. Both existing parameterizations and the optimizations 
yield similar results in terms of rRMSE (i.e., 5%–9%), 
indicating wind forcing is the major driver of gas exchange 
for slightly soluble gases in the ocean and that other known 
impacts are either intrinsically related to wind or have a 
minor effect on gas exchange time scales of the order of 
days to weeks.

The analytical and numerical models show that to a 
large extent, previously proposed parameterizations rea-
sonably describe the relationship between wind speed and
gas transfer velocity during SO GasEx, and the results from SO GasEx are in accord with global constraints based on ocean bomb $^{14}$C inventories [Naegele et al., 2006; Sweeney et al., 2007]. Furthermore, with the exception of two anomalous points from SOFeX (Figure 5), the parameterizations of Ho et al. [2006], Nightingale et al. [2000b], and Wanninkhof et al. [2009] explain 83%, 82%, and 80% of the variance in all $^{3}$He/$^{36}$He dual-tracer studies conducted in the coastal and open ocean, including SO GasEx. These parameterizations have different functional forms: that of Ho et al. [2006] is quadratic; that of Nightingale et al. [2000b] is a polynomial that includes a linear term and a quadratic term; and that of Wanninkhof et al. [2009] is a polynomial that includes a constant, a linear term, a quadratic term, and a cubic term.

[44] There are three important implications of these findings: (1) Relationships between wind speed and gas exchange determined in one ocean locale can be applied to other regions. In fact, Asher [2009] determined that up to half of the variability in the $^{3}$He/$^{36}$He data sets could be due to experimental variability, so the differences can largely be explained by experimental uncertainties. (2) The functional form of wind speed/gas exchange parameterizations (i.e., quadratic, cubic, or hybrid) cannot be unequivocally determined from field experiments, including SO GasEx. (3) Although it is recognized that wind speed might not be the only correlate for gas exchange, it is a sufficient one. The results suggest that wind forcing is the major driver of gas exchange for slightly soluble gases in the ocean and that other known impacts are either intrinsically related to wind or have a minor effect on gas exchange time scales of the order of days to weeks. There are other parameters to predict gas exchange, such as turbulence dissipation [e.g., Zappa et al., 2007], but those parameters are not routinely measured and are difficult to implement in global biogeochemical models.

[45] The parameterizations of Liss and Merlivat [1986], Wanninkhof [1992], and Wanninkhof and McGillis [1999] can reasonably describe the relationship between wind speed and gas exchange in the 5 to 11 m s$^{-1}$ wind speed range. However, compared to the entire $^{3}$He/$^{36}$He data set (Figure 5), they are only able to explain 53%, 64%, and 2% of the variance, respectively. The cubic relationship of Wanninkhof and McGillis [1999] deviates significantly from the dual-tracer results at high wind speeds (>12 m s$^{-1}$). If the comparison is limited to the wind speed range below 12 m s$^{-1}$, then Wanninkhof and McGillis [1999] are able to explain about 37% of the variance. Like that of Wanninkhof and McGillis [1999], another cubic parameterization derived from eddy covariance CO$_{2}$ measurements during GasEx 98 is that proposed by McGillis et al. [2001a]. This parameterization was derived from the same data set but assumed a nonzero intercept and predicts $k$($600$) that are 10–15% lower than that of Wanninkhof and McGillis [1999] between $u_{10}$ of 12 and 20 m s$^{-1}$. The result is that it is able to explain 48% of the variance in the $^{3}$He/$^{36}$He data set over the entire wind speed range.

3.10. The Future of $^{3}$He/$^{36}$He Dual-Tracer Experiments

[46] One of the reasons that short time scale measurements like eddy covariance measurements of CO$_{2}$ often produce these higher-order dependencies (i.e., cubic versus quadratic) that are not reflected in the $^{3}$He/$^{36}$He data might be because on these time scales (i.e., minutes to hours), the fluxes are indeed very high at the near surface. However, because vertical mixing cannot keep pace with the fluxes, the full water column is not impacted and therefore the higher-order dependence is not reflected in techniques that utilize full water column mass balances. However, the $^{3}$He/$^{36}$He is an integrative approach that yields robust estimates of total gas exchanged in the mixed layer over periods ranging from days to weeks. This is often the relevant parameter in biogeochemical cycling whereas the micro-meteorological techniques are discrete, and sometimes discontinuous, measurements with an appreciable uncertainty in each discrete value. The deviation between $^{3}$He/$^{36}$He dual-tracer and CO$_{2}$ eddy covariance measurements is most pronounced at higher wind speeds (i.e., > 12 m s$^{-1}$) [e.g., Edson et al., submitted manuscript, 2011] where the eddy covariance values are higher. Simultaneous $^{3}$He/$^{36}$He dual-tracer and CO$_{2}$ eddy covariance measurements at high wind speeds, along with natural tracers of gas exchange and surface water residence time such as and $^{22}$Rn and $^{1}$Be [Kadko and Olson, 1996], and detailed physical mixed-layer measurements are expected to help us resolve the conflict between these two leading techniques.

[47] The $^{3}$He/$^{36}$He tracer release experiments conducted in the ocean have demonstrated the power of deliberate tracers to quantify gas exchange over a period of several days or more, and spatial scales of a few tens of kilometers. However, because of the global $^{3}$He shortage [Cho, 2009], future $^{3}$He/$^{36}$He experiments could be jeopardized. At the moment, no alternative tracer with the properties that make $^{3}$He the perfect companion to be used with SF$_{6}$ (i.e., inert, low background, similar solubility, very different diffusivity) has emerged. A concerted effort should be made to obtain $^{3}$He for these experiments, and/or to find alternative deliberate tracers to quantify air-sea gas exchange. Since there is no other volatile tracer with a Schmidt number as low as $^{3}$He and as large a dynamic range over which it can be measured, the likely candidate is a nonvolatile tracer. The innovative application of bacteria spores used by Nightingale et al. [2000b] is an option but has a limited dynamic range for large-scale open ocean experiments. Dyes such as Rhodamine WT measured by HPLC with fluorescence detection [e.g., Hofstraat et al., 1991; Stuijlen et al., 1994] hold some promise, as demonstrated by Upstill-Goddard et al. [2001], but losses due to absorption and photobleaching need to be properly quantified [Smart and Laidlaw, 1977].

4. Conclusions

[48] During the Southern Ocean Gas Exchange Experiment (SO GasEx), two $^{3}$He/$^{36}$He injections were made to quantify gas transfer velocities. The experiment had the largest number of $^{3}$He samples collected during a $^{3}$He/$^{36}$He dual-tracer experiment, and concurrent eddy covariance measurements of CO$_{2}$ and DMS were made [see Yang et al., 2011; Edson et al., submitted manuscript, 2011].

[49] The $^{3}$He/$^{36}$He results from SO GasEx show that the recently proposed parameterizations based on dual-tracer or other water column mass balance approaches reasonably describe the relationship between wind speed and gas transfer velocity, and that results from SO GasEx are similar.
to those from other ocean basins. The important implications of these results are as follows.

50] 1. Within 20%, the wind speed/gas exchange parameterizations obtained in one location can be applied to another, so, for example, the measurements made during SAGE or SO GasEx should be applicable to other parts of the Southern Ocean.

2. Field experiments, like SO GasEx, can produce valuable data for determining the relationship between wind speed and gas exchange and allow us to verify existing parameterizations. However, because of their similarities in results they cannot distinguish the functional form of these parameterizations, since these relationships are empirical and within a certain wind speed range, different functional forms will share similar features.

3. Wind speed, while not the direct mechanism responsible for enhancing gas exchange, is generally recognized to be a major forcing and is perhaps the best correlate to use, considering its wide spread measurement and ease of implementation in both simple calculations and in global biogeochemical models. Furthermore, while the parameterizations of Liss and Merlivat [1986], Wanninkhof [1992], and Wanninkhof and McGillis [1999] can describe the relationship between wind speed and gas exchange in certain wind speed ranges, they fail to predict gas transfer velocities derived from the dual-tracer method over the entire range from 0 to 16 m s⁻¹.

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