Uncertainties in gas exchange parameterization during the SAGE dual-tracer experiment

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A dual tracer experiment was carried out during the SAGE experiment using the inert tracers SF6 and 3He, in order to determine the gas transfer velocity, k, at high wind speeds in the Southern Ocean. Wind speed/gas exchange parameterization is characterised by significant variability and we examine the major measurement uncertainties that contribute to that scatter. Correction for the airflow distortion over the research vessel, as determined by computational fluid dynamics (CFD) modelling, had the effect of increasing the calculated value of k by 30%. On the short time scales of such experiments, the spatial variability of the wind field resulted in differences between ship and satellite QuikSCAT winds, which produced significant differences in transfer velocity. With such variability between wind estimates, the comparison between gas exchange parameterizations from diverse experiments should clearly be made on the basis of the same wind product. Uncertainty in mixed layer depth of ~10% arose from mixed layer deepening at high wind speed and limited resolution of vertical sampling. However the assumption of equal mixing of the two tracers is borne out by the experiment. Two dual tracer releases were carried out during SAGE, and showed no significant difference in transfer velocities using QuikSCAT winds, despite the differences in wind history. In the SAGE experiment, duration limitation on the development of waves was shown to be an important factor for Southern Ocean waves, despite the presence of long fetches.
higher exchange due to the longer fetches for wave development compared with fetch limited sites such as the North Sea.

The uncertainty in wind speed is rarely considered in transfer velocity parameterizations. In reality, wind measurements made from ship-based anemometers suffer from a fundamental problem of flow distortion over the ship’s superstructure. The air flow can be accelerated or decelerated, or flow separation can result in reversal of flow. Normally anemometers are placed in a position to be maximally exposed. The effect of this bias on drag coefficients has been evaluated (Yelland et al., 1998; Dupuis et al., 2003; Yelland et al., 2002) and accounted for. For gas transfer relationships a discrepancy of up to 20% has been reported between ship winds and nearby meteorological buoys (Wanninkhof et al., 1993) or platforms (Nightingale et al., 2000b). When available, these alternate sources have been used, but such data are generally unavailable and reliance must be made on ship measurements or satellite derived wind speeds (Wanninkhof et al., 2004). However, satellite winds can be subject to bias as shown by Boutin et al. (2009), who found that QuickSCAT winds appear to overestimate the wind speed by approximately 5%. Some studies have shown an increase of gas transfer with increase in wave height (Nightingale et al., 2000b), not unexpectedly since stronger winds will in general generate higher waves. An attempt to develop a more causal relationship with whitecap coverage was made by Zhao et al., 2003 with a quasi-Reynolds number breaking parameter representing turbulent intensity.

One of the most effective methods in determining the transfer velocity in the open ocean is the dual tracer technique (Watson et al., 1991; Wanninkhof et al., 1993). The first ocean dual tracer experiments were conducted in shallow coastal seas such as Georges Bank (Wanninkhof et al., 1993) or in the North Sea (Watson et al., 1991; Nightingale et al., 2000b), where the tracer mixing was constrained to the water depth. Only a small number of experiments have been conducted in the open ocean where mixing with depth is constrained by the mixed layer depth (Nightingale et al., 2000a; Wanninkhof et al., 2004).

The SOLAS Air–Sea Gas Exchange (SAGE) experiment was a dual tracer experiment carried out in the Southern Ocean, and one of its goals was to determine the parameterization between wind speed and gas transfer at higher wind speeds (Harvey et al., this issue). The evolution and dilution of the dual tracer patch is discussed by Law et al. (this issue) and the mixed layer depth evolution by Stevens et al. (this issue). In the initial analysis of the SAGE dual tracer results, Ho et al. (2006) found a quadratic wind speed parameterization at wind speeds up to 15 m s⁻¹, largely consistent with previous experiments at lower wind speeds, with no evidence of a regional or Southern Ocean dependence on physical mechanisms despite the highest wind speeds for a dual tracer experiment to date. Further analysis of the SAGE data (Ho et al., 2007) demonstrated that this quadratic fit was statistically more significant than the Wanninkhof and McGillis (1999) cubic relationship.

In the following sections we examine some of the sources of uncertainty contributing to the gas exchange parameterization: air flow distortion over the ship, uncertainties in spatial and temporal coverage of satellite scatterometer data, uncertainties in tracer mixed layer depth, and state of wave development. Radar measurements were also made of seastate. These, together with hindcast wave parameters from the WaveWatch III/NCEP reanalysis data, are discussed in relationship to transfer velocity.

2. Methods

2.1. Dual tracer technique

The SAGE experiment was conducted from R.V. Tangaroa 160 km off the coast of the South Island of New Zealand during March and April 2004 (Harvey et al., this issue). The region is exposed to the storm systems of the Southern Ocean. The aim of the dual tracer experiment during SAGE was to determine the gas transfer velocity, \( k \), and its dependence on wind speed. The inert tracers \(^3\)He and SF\(_6\) were released into the mixed layer at a constant ratio at a depth of ~12–15 m for 5–8 h from 25 March 2004 15:00 (yearday 85.6), as described in more detail by Ho et al. (2006) and Law et al. (this issue). A second release was made on 31 March 2004 starting at 00:00 (yearday 91.0) after the SF\(_6\) and \(^3\)He concentrations of the first release declined to very low values.

The dual tracer experiment takes advantage of the difference in diffusion rate of \(^3\)He and SF\(_6\) into the atmosphere from the ocean, while they are assumed to disperse at the same rate within the water column (Watson et al., 1991; Wanninkhof et al., 1993). Gas transfer velocities were determined from the change in the \(^3\)He/SF\(_6\) ratio over time. The transfer velocity for \(^3\)He, \( k_{\text{He}} \), can be determined from

\[
k_{\text{He}} = \frac{h}{\Delta t} \ln \left( \frac{\text{He}}{\text{SF}_6} \right) / (1 - (\text{SF}_6/\text{He})^n)
\]

(Wanninkhof et al., 1993), where \( h \) is the tracer mixed layer depth, \( \text{SF}_6 \) and \(^3\)He are the measured SF\(_6\) and \(^3\)He concentrations in the mixed layer, respectively, and \( \text{SF}_6 \) and \(^3\)He are the Schmidt numbers for SF\(_6\) and \(^3\)He, respectively. The exponent of the Schmidt number ratio, \( n \), is usually taken as ~0.5 for a free surface, although bubble entrainment can effectively alter the value (Asher and Wanninkhof, 1998). Gas transfer velocities reported here, \( k(600) \), were normalized to a Schmidt number for CO\(_2\) in freshwater at 20 °C (\( Sc = 600 \)).

The tracer patch was mapped daily in order to maintain a Lagrangian frame of reference and locate the patch centre with maximum SF\(_6\) concentration. This mapping was carried out over periods of 10–12 h each day using an underway SF\(_6\) system, aided by drogue buoys (Law et al., this issue). Station sampling was carried out both within and outside the patch. For the purposes of the dual tracer experiment, only stations well within the patch were used in the analysis, in order to avoid edge effects as far as possible. Following a storm early in the experiment, the patch stretched significantly, and a mass balance estimate of flux was not possible. However the dilution of the patch is calculated in Law et al. (this issue).

2.2. Mixed layer depth

One of the key parameters in Eq. (2) is the depth, \( h \), over which gases (\(^3\)He and SF\(_6\)) in the ocean are ventilating to the atmosphere. Here we use the tracer mixed layer depth (TLD) based on the depth at which SF\(_6\) decreases to 50% of the concentration at 15 m, following Nightingale et al. (2000b) and Ho et al. (2006). The resolution of the viable tracer samples from CTD discrete vertical profiling was typically 5–20 m, which limits the precision to which the tracer mixed layer depth can be determined. Alternatively, estimates of MLD from high resolution CTD temperature and salinity profiles can be used. Stevens et al. (this issue) found that a ‘density-gradient-proportional’ estimate, \( z_M \), was the most robust approach at capturing shallower steps in the density profile. This is defined as the depth at which the density between 15 m and the depth of maximum buoyancy frequency first exceeds the mean density (over this depth range) by 25%. The top 15 m is avoided because of artefacts related to ship wake disturbance. The depth of maximum buoyancy frequency, \( z_M \), represents a measure of recent mixing.

2.3. Wind data

Previous dual tracer studies have variously used ship winds (Watson et al., 1991; Wanninkhof et al., 1997), fixed platforms (Wanninkhof et al., 1993; Nightingale et al., 2000a), or satellite
Winds (Wanninkhof et al., 2004; Ho et al., 2006). At the SAGE location, there were no fixed platforms, and so local wind measurements were obtained from an Automatic Weather Station (AWS), maintained and calibrated by the Meteorological Service of New Zealand (MetService). It was located at 25.2 m above sea level, above the crow’s nest and bridge of the Tangaroa, which exposed it to all wind directions, unlike the foremost whose exposure is restricted to winds forward of the beam. The AWS wind data were compensated for ship translational motion and logged at 5 min intervals on the ship’s data acquisition system.

Wind speeds were measured under a range of atmospheric stability conditions but were corrected to neutral stability and to 10 m equivalent height ($U_{10}$) using the COARE 3.0a algorithms (Fairall et al., 2003). This calculation incorporated an atmospheric stability correction using air and sea temperatures, and measured solar and infrared fluxes. COARE3 provides the option of making an empirical correction for sea-surface skin temperature, but we were able to use the directly measured radiometric skin temperature from M-AERI (Minnett et al., this issue). The disadvantage of ship measurements is that they are subject to flow acceleration over the superstructure (Yelland et al., 1998) and possibly also pumped due to vessel pitch and roll.

Satellite winds from the QuikSCAT satellite swath data were also used. Swath data is available at a 25 km spatial resolution for a reference height of 10 m, with approximately two passes over the experiment site per day. Thus the spatial resolution is excellent, but limited to ~12 h intervals. A further source of wind data was from a reanalysis of meteorological conditions from the United States National Center for Environmental Prediction (NCEP). These data are based on a 1.875 × 1.875° grid at 6 h intervals and also referenced to a 10 m height.

2.4. Seastate data

Wave height and peak wave period data calculated by the WaveWatch III model, based on NCEP wind data input, were available for the SAGE period at 3 h intervals. The closest grid point to the SAGE site was used. An S-band microwave radar was also operated from the Tangaroa during the SAGE experiment. The radar uses the Doppler velocity of backscatter from the sea surface to derive wave height (Poulter et al., 1995). In normal conditions, the effects of ship roll appeared as a uniform variation of Doppler speed simultaneous to all ranges, and this was effectively removed. While this correction was adequate in moderate wave conditions, the data were unreliable at the height of the storm in wind speeds exceeding 15 m s$^{-1}$ due to ship roll, and so these data were not used in the analysis. While on-station, the radar antenna was automatically steered to maintain a constant azimuth looking into the waves, despite the yawing of the ship. Data for determining wave height were limited to grazing angles from 10° to 15° to avoid the effects of geometric shadowing by wave crests.

3. Ship wind data and air flow distortion

A ship is a difficult platform for measuring wind speed at sea due to the significant air-flow distortion by the vessel’s superstructure (Yelland et al., 1998). A study of the airflow over the Tangaroa was made by Popinet et al. (2004) combining computational fluid dynamics (CFD) modelling (Popinet, 2003) with an array of anemometer measurements. The experimental results showed that the flow distortion relative to a reference site on a foredecks mast was largely independent of wind speed, making the use of computationally intensive modelling practicable. The Gerris model representation of the flow distortion, including flow separation, agreed well with measurements, and has subsequently been used in modelling air flow over other vessels.

The location of the principal anemometer on the Tangaroa (above the crow’s nest above the bridge) was originally designed to give unobstructed exposure over all directions, but the numerical results show that it is also at the site of significant flow acceleration (Fig. 1). The modelling results have been used to obtain a wind speed correction curve at 2 key sites: AWS (the main anemometer above the crow’s nest) and the foremost (Fig. 2).

![Fig. 1. Air flow distortion over the Tangaroa modelled by Gerris with the wind incident at 90° to the bow. Wind is coloured according to the norm of the local wind velocity; a factor of 1 (i.e. unchanged) is shown by green, 1.3 by dark red, and 0 by blue. Acceleration over the superstructure near the automatic weather station (AWS) is evident.](image-url)
The modelled points at \(\sim 15^\circ\) azimuth intervals have been fitted with a polynomial shown by the dotted curve to facilitate correction of experimental data. The foremost shows clearly the blockage of flow by the superstructure in winds from the aft, but otherwise the flow acceleration there is less than at the AWS location. The artefactual increase in wind speed at the AWS location ranges between 10%, for winds from the forward direction, and 20%, when winds approach from 65\(^\circ\) of the forward direction. The bias at the foremost is smaller (\(\sim 10\%\)) but distortion is obviously extremely severe when the wind is from over the stern.

This airflow correction (AFC) has been applied to the time series of wind speed during the SAGE experiment as shown by blue points in Fig. 3. The net reduction in wind speed over the length of the experiment was 15%. For gas exchange parameterizations that have a quadratic wind speed dependence, the air flow distortion will therefore contribute up to 30% bias in transfer velocity when ship winds are used. Also shown in Fig. 3 (red points) are the wind speeds translated to a standard 10 m height after correcting for atmospheric stability using the COARE3 algorithms. This correction produces a further 8% average reduction in wind speed over the ship measurement.

4. Comparison of ship, satellite and reanalysis wind speeds

For any parameterization of gas transfer velocity versus wind speed, a number of sources of wind speed data are available. Ship-based measurements are the most direct, as they are local and usually of the highest temporal density. However, as seen in the previous section, these must be subject to a number of corrections. Satellite scatterometer winds from QuikSCAT have good spatial coverage but are limited in temporal coverage to approximately 12 h intervals. The NCEP reanalysis winds are more frequent but with much coarser spatial resolution. In this section we consider the variance in transfer velocity resulting from the use of these different sources.

Most of the severe weather at these latitudes emanates from the Southern Ocean, with an accompanying potential for very long fetch. Before looking at the wind record in detail, we consider the origin and fetch of the wind field during the two releases. For the strong winds during the first release, the 4-day wind back-trajectory generated from NCEP data shows a fetch extending well to the south of New Zealand in the Southern Ocean (Fig. 4A) with a consequential potential for extremely high seastate. Strong wind speeds from the south-west persisted through to yearday 90 (30 March). A reinjection of tracers was made on yearday 91, and analysis of tracer ratios for this injection commenced on yearday 93 (2 April). The wind built to above 15 m s\(^{-1}\), but at this time there was a strong westerly component. The trajectories (Fig. 4B) cross the landmass of the South Island, thus limiting the fetch to 160–200 km till yearday 97.

Fig. 5 shows the wind speed variation over the course of the SAGE experiment using ship-based \(U_{10}\) and QuikSCAT winds. The tracer injection was completed by the start of yearday 86 (26 March), while winds were light. The wind then increased strongly to over 20 m s\(^{-1}\) during the next few days. At the height of the storm, CTD operations had to be suspended. The ship winds and QuikSCAT winds can be compared in Fig. 5. The ship data (blue) have high temporal sampling at 10 min, while the QuikSCAT data
are only available at 12 h intervals but over a range of different locations at each temporal snapshot. A selection of satellite winds within 1° of the moving ship position has been used. Fig. 5 shows that when the QuikSCAT temporal coverage coincides with the ship, the spatial distribution of QuikSCAT winds covers the ship winds well. However there are occasions such as yearday 94.0 and 95.0 when the local winds experience a temporary increase in speed that is not sampled by the satellite. In order to gauge the impact on the parameterization, the wind speeds from both sources have been averaged over the sampling intervals used for the $^3$He/$SF_6$ ratios (shown as horizontal black bars), the choice of these intervals related to acquiring a statistical significant decrease in the tracer ratio due to air–sea gas exchange. The averages and error bars for one standard deviation are shown in light blue and pink for the ship and QuikSCAT winds, respectively.

In the early part of the experiment (yearday 87–89), average QuikSCAT winds generally exceeded the ship winds, at times by as much as 2.1 m s$^{-1}$. This is partly due to the incomplete temporal satellite sampling of the minimums in wind such as on yearday 89. In contrast, during the second tracer release, the incomplete sampling of local maxima at yearday 94 resulted in lower satellite mean wind than ship wind.

This variability can be better understood by examining the spatial variability of winds, in addition to the temporal variability. The snapshots captured by QuikSCAT cover a wide spatial area as shown in Fig. 6 for 2 satellite passes. Here the ship position over the 24 h is shown by the white track. Within a bound of a $+0.5°$ square centred on the ship, shown by the dashed box, the wind field is relatively uniform. When extended to $+1.0°$, shown by the dotted box, significant variability is encompassed by the satellite measurement, increasing the discrepancy between ship and satellite measurements. The water mass sampling from the Tangaroa was in a Lagrangian frame moving with the ocean currents, and therefore the local wind speed is the most relevant one. To the extent that the wind field is an advected 'frozen field', it can be argued that increase in the spatial coverage can compensate for the lack of temporal coverage (Wanninkhof et al., 2004). However, the example in Fig. 6 shows that in cases of spatial inhomogeneity, this approach is not optimal. In strong wind conditions the extent should clearly be large, but ideally along the trajectory of the wind, since a blanket average will incorporate unrepresentative wind speeds. Fig. 6 suggests that a $+0.5°$ window is appropriate.

The spatially coarser NCEP reanalysis data are shown in Fig. 7 over the course of the experiment for the grid point closest to the SAGE experiment. The values generally agree well with the ship airflow corrected data, but again there are periods when NCEP is larger during lulls in wind experienced on the ship (e.g. at yearday 94.5 (4 April). The QuikSCAT values (Fig. 7A) are the averaged values over a $+0.5°$ square centred on the ship position. When the low wind speed periods are ignored, a regression between individual wind measurements from QuikSCAT and the ship gives a good agreement (slope 1.01, intercept $0.5$ m s$^{-1}$), but a poorer agreement between NCEP and the ship (slope 0.79, intercept $2.6$ m s$^{-1}$). However, as indicated above, during the limited sampling intervals required for the dual tracer experiment, the

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**Fig. 5.** Wind speed temporal variation over the SAGE experiment. Ship based winds from the AWS are shown in blue, with means and standard deviations (cyan). QuikSCAT data is in red, with means and standard deviations (light red). The numbered horizontal bars show averaging periods for the dual tracer calculations.

**Fig. 6.** Wind speed spatial variability at time of peak winds over a 24 h interval. Ship track is in white. The dots with arrows are the QuikSCAT wind vectors, also contoured in colour. The dashed box shows the coverage of a $+0.5°$ bound, and the dotted box a $+1.0°$ bound.
QuikSCAT winds can either exceed the ship values (as during release 1), or lie below ship winds (as during release 2).

5. Gas transfer parameterization

The decrease in the ratio of $^3$He to $SF_6$ due to the faster evasion rate of $^3$He across the air–sea interface has been used to calculate the gas transfer velocity, $k$. The integration intervals indicated in Fig. 5 were determined by the sampling regime and the requirement to have a significant change in ratio (see Ho et al., 2006). These intervals were also used to determine the mean mixed layer depth, $h$, in Eq. (2). As seen in Fig. 5, the wind speed varied across each integration interval. Due to the nonlinearity of the parameterization, this will enhance the exchange coefficient. Therefore, following Wanninkhof et al. (2004) we have used the second moment of the wind speed to adjust for this enhancement in order to produce a wind speed parameterization appropriate to steady wind conditions.

The variation of $k$ versus wind speed during SAGE is shown in Fig. 8, using 3 sources of wind speed. First the red points used the QuikSCAT wind field, as in Ho et al. (2006). The values are tabulated in Table 1 (and also Ho et al., 2007), together with wind speeds and seastate parameters. The error bars on $k$ were obtained from propagating the standard deviation of the $^3$He/$SF_6$ ratios contributing to the points. The red line is the least squares best fit of a quadratic to these data, giving

$$k(600) = 0.266(\pm 0.019)U_{10}^2$$

(3)

Wind speed directly measured by the ship and adjusted to 10 m height with neutral stability is shown as open diamonds, with a least squares fit given by the black line. This is almost identical to the Nightingale et al. (2000a) parameterization. When the airflow correction (AFC) is applied to the ship data (filled diamonds), the parameterization is significantly steeper (blue curve) and is very close to Wanninkhof (1992). These parameterization values are summarized in Table 2. The table also includes a parameterization using the QuikSCAT winds adjusted 5% lower as suggested by Boutin et al. (2009). Also shown in Fig. 8 are the cubic parameterization of Wanninkhof and McGillis (1999) and the piecewise linear relationship of Liss and Merlivat (1986), neither of which fit the present data as well. For example this cubic fit has higher residual ($\chi^2$), $\chi^2=7050$, than the quadratic ($a_2=0.266$); $\chi^2=622$ (see also Ho et al., 2007).

Fig. 7. (A) QuikSCAT data averaged over a ± 0.5° square compared with ship-based wind, corrected for airflow distortion and atmospheric stability adjusted to 10 m height. (B) NCEP reanalysis winds at the closest grid point to the ship compared with ship-based wind, corrected for airflow distortion and atmospheric stability adjusted to 10 m height.

Fig. 8. Gas exchange coefficients measured during SAGE using three wind speed products: QuikSCAT satellite data (red circles), ship wind data adjusted to 10 m height and neutral stability (black open diamonds), and ship wind data corrected for air flow distortion and similarly adjusted to 10 m height and neutral stability (blue filled diamonds). The quadratic fits to these data are the red, black, and blue solid lines, respectively. $k$ has been adjusted for enhancement by wind speed variability assuming a square law dependence on wind speed. The other parameterization curves are from: Wanninkhof and McGillis (1999), Wanninkhof (1992), Nightingale et al. (2000a) and Liss and Merlivat (1986).
shallow coastal sea where the mixing extends to the seabed is straightforward, whereas in the open, deep ocean, significant uncertainty in determining \( h \) can exist. Some workers have used the hydrographic mixed layer depth to define the mixing depth, e.g. Wanninkhof et al. (2004), while others have used the SF6 tracer to define the depth, e.g. Nightingale et al. (2000a).

Fig. 9A shows a contour of SF6 concentration and tracer ratio, \( ^3\text{He}/\text{SF}_6 \) after the initial release, which experienced the highest wind speeds. Three variants of mixed layer depth are shown. For the purposes of determining the depth to which the tracer has mixed, the tracer mixed layer depth (TLD) is the most direct (black line) but is limited in resolution by the CTD bottle sampling interval. \( z_p \) (green line) and the depth of the maximum buoyancy frequency (white line) are also shown.

It can be seen that the MLD was quite variable over the initial few days. Later, as well as vertical mixing, was evident (Law et al., this issue). The mixed layer depth varied significantly over the dual tracer averaging periods of 24–59 h due to both variable wind forcing and water mass intrusions. At this time, small steps in the density profile were evident. It is likely that the steps were spatially variable, so that when the CTD sampled in disparate areas, differing MLDs were observed, despite the efforts to stay near the centre of the patch by mapping underway SF6. It is noticeable that the SF6 concentration on yearday 87.3 was lower than adjacent samples. At this time a “fresh” lens of water was present constraining tracer to less than 10 m depth. This may reflect sampling closer to the edge of the patch. At yearday 88 when winds increased above 15 m s\(^{-1} \), the mixed layer rapidly deepened to 40 m, and then 65 m by yearday 89.4. During this very active mixing period the three estimates of mixed layer depth showed much better agreement as increased vertical mixing eroded small scale density steps.

Turning to the contour of concentration ratio \( ^3\text{He}/\text{SF}_6 \), a more uniform decrease with time is seen. In particular, when the TLD was shallow at 25 m, the ratio was still constant to 40 m. This suggests that when the local SF6 concentration was lower, the ratio, which reflects the escape to the atmosphere, had continued to decrease in the same ratio as the higher concentration patch centre. The second release (Fig. 9B) similarly showed a more uniform ratio with depth, when the absolute SF6 concentration was diluted. In the second release, the depth of maximum buoyancy frequency was below the minimum of the plot. The spatial variability of SF6 concentration is illustrated in more detail in Law et al. (this issue).

The individual profiles of tracer concentration and concentration ratio show these effects in more detail (Fig. 10). The first profile at yearday/DOY 86.2 showed a significantly lower \(^3\text{He}\) concentration at the surface, suggesting ventilation to the atmosphere was occurring.

### Table 1

Summary of wind speeds and seastate parameters averaged over the dual tracer sampling intervals. The day of year (DOY) is the centre of the sampling intervals, \( sd \) are the standard deviations of the preceding columns, QS is QuikSCAT winds, \( H_f/\text{TLD} \) is the enhancement of gas transfer by wind variability in a quadratic relation, \( H_i \) is the significant wave height, \( T_p \) the spectral peak wave period, and WA the wave age, averaged over the dual tracer sampling intervals. The seastate parameters are derived from WaveWatch III data.

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<th>Longitude</th>
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<td>97.32</td>
<td>-46.277</td>
<td>172.629</td>
<td>35.9</td>
<td>10.5 3.2 9.0 2.8 9.0 3.5 1.15 4.7 12.9 2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Table 2

Parameters for a quadratic gas exchange parameterization of the form: \( k(600)=a_2U_{10}/H_i \), derived from wind speed products. \( a_2 \) is the quadratic coefficient; \( r^2 \) is the sum of the squares of residuals, and \( r^2 \) the correlation of fit. Correction has been made for enhancement of \( k \) due to wind speed variability to give short-term parameterizations.

<table>
<thead>
<tr>
<th></th>
<th>( a_2 )</th>
<th>( \chi^2 )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>QS</td>
<td>0.266</td>
<td>623</td>
<td>0.81</td>
</tr>
<tr>
<td>QS−5%</td>
<td>0.294</td>
<td>623</td>
<td>0.81</td>
</tr>
<tr>
<td>U_{10}</td>
<td>0.241</td>
<td>747</td>
<td>0.77</td>
</tr>
<tr>
<td>U_{10} AFC</td>
<td>0.314</td>
<td>777</td>
<td>0.76</td>
</tr>
</tbody>
</table>

### Table 3

Comparison of two tracer releases. Parameters for a quadratic gas exchange parameterization of the form: \( k(600)=a_2U_{10}/H_i \), \( a_2 \) is the quadratic coefficient, and \( r^2 \) the correlation of fit. Correction has been made for enhancement of \( k \) due to wind speed variability to give short-term parameterizations.

<table>
<thead>
<tr>
<th></th>
<th>1st Release</th>
<th>2nd Release</th>
<th>Combined</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_2 ) Using QS wind</td>
<td>0.263</td>
<td>0.273</td>
<td>0.266</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>0.80</td>
<td>0.41</td>
<td>0.81</td>
</tr>
<tr>
<td>Mean QS wind (m s(^{-1} ))</td>
<td>12.6</td>
<td>9.6</td>
<td>11.8</td>
</tr>
<tr>
<td>( a_2 ) Using ship wind</td>
<td>0.344</td>
<td>0.278</td>
<td>0.314</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>0.81</td>
<td>0.48</td>
<td>0.76</td>
</tr>
<tr>
<td>Mean ship wind (m s(^{-1} ))</td>
<td>10.9</td>
<td>9.8</td>
<td>10.2</td>
</tr>
</tbody>
</table>

Fig. 8 combines data from 2 tracer releases. The wind and fetch characteristics differed between them, so it is of interest to compare the transfer coefficient derived from each release separately. There were 4 data points available from the first release and 7 points from the second release. This breakdown is shown in Table 3. Using the QuikSCAT (QS) winds averaged over a ±0.5° square, \( k \) from the separate releases agree well within the statistical significance of the least squares fit. However the narrower range of wind speeds during the second release \( (9.8 \pm 1.4 \text{ m s}^{-1}) \) contributed to a much lower \( r^2 \) value for the fit, despite a greater number of points than the first release. The airflow corrected ship winds were less consistent. Due to the lower mean wind than QuikSCAT during the first release, the ship winds gave a higher value for \( a_2 \).

### 6. Tracer mixed layer depth

The gas transfer velocity, \( k \), depends directly on the depth over which the tracer is mixed, \( h \), in Eq. (2). Evaluation of \( h \) in a
faster than vertical mixing. This is to be expected immediately after tracer injection. None of the other profiles showed a significant decrease in the ratio closer to the surface. The concentrations rapidly declined after yearday 88 when winds exceeded 20 m s\(^{-1}\), due to dilution as the mixing layer deepened and enhanced ventilation to the atmosphere, leading to a 10-fold decrease of SF\(_6\) concentration. On yearday 89.4, when winds exceeded 20 m s\(^{-1}\), both the SF\(_6\) and \(^3\)He profiles and their ratio were uniform down to 65 m.

7. Seastate

The WaveWatch III hindcast data were selected for the closest gridcell to the SAGE site (47.000° S, 172.5° E), which was very near to the ship position on the second day of the experiment. The 4 panels in Fig. 11 show the ship and NCEP wind field, the significant wave height, \(H_s\), from both WaveWatch III and the radar, the peak period of the wave spectra, and the inverse wave-age which is a measure of wave development. The wave height can be seen to follow the wind trend, with peaks of wave height occurring closely following peaks of wind speed (e.g. a maximum at yearday 88.5 when wave heights reached 6 m). The wave height does decay more slowly than wind speed, as expected of the large travel distances of waves, resulting in significant swell during lulls in the wind. The background swell is never below 2 m significant wave height. The radar-derived wave heights broadly follow the WaveWatch wave heights except they are biased 1 m too low. Additionally, during the height of the storm (yearday 88), the ship motion was too large to obtain reliable radar data.

The peak wave period of the wave spectra, \(T_p\), generally exceeded 10 s, which was typical of the open ocean conditions. The radar estimate of wave period generally agreed within 1.5 s of the WaveWatch hindcast. The sudden dip in period at yearday 93.7 occurred when the locally generated short period sea grew to exceed the amplitude of the long period swell. The peak wave periods were longer for the second release compared with the first, with \(T_p\) values up to 14.6 s (Table 1).

The wave age, defined as \(C_p/U_{10}\), is a measure of the stage of wave development, where \(C_p\) is the phase propagation speed of the peak of the wave spectrum, while the inverse wave age \((U_{10}/C_p)\) is a measure of the degree of wind forcing. The inverse wave age was less than 1 for...
most of the experiments, consistent with a view that the seastate was dominated by swell generated at long distances in the Southern Ocean and propagated to the local site. The exceptions to this occurred at periods of rapid rise in wind speed such as at the peak of the storm on yearday 88, when the local wave field was still building in response to the increase in wind. Thus at the height of the storm, the highest waves were also the youngest waves, which are likely to be the steepest waves (Donelan, 1998). The distribution of wave age (Fig. 12) shows this bias to older waves more clearly. The majority of waves have a wave age greater than 1 (i.e., a phase speed greater than the local wind speed).

Fig. 10. Individual depth profiles of SF₆ concentration (red), ³He (black), and tracer ratio (blue) for sampling stations within the patch. Horizontal lines indicate 3 different estimates of mixing depth: tracer mixed layer depth (TLD, black), density-gradient-proportional depth (zN, green), and depth of maximum buoyancy frequency (zN, blue): (A) first tracer release and (B) second release.

8. Discussion

8.1. Wind speed parameterizations

In refining the accuracy of gas parameterization it is clear that uncertainty in wind speed is important. While the ship wind speed is a direct measurement, it is subject to flow distortion effects. For the *Tangaroa*, these effects are smaller at the foremast than the main anemometer above the bridge, but the foremast winds limit coverage to approximately 70° of the bow when allowance is made to avoid eddies shed by the superstructure from the wind aft of the beam. Awareness and correction for this problem arose from calculating wind drag over the sea (Yelland et al., 1998); it should also be carried out when ship winds are used in the dual tracer experiment, such as Watson et al. (1991) and Wanninkhof et al. (1997), and in other studies of atmospheric fluxes. Sometimes it can be avoided using buoy winds (Wanninkhof et al., 1993; Nightingale et al., 2000a), but this is not often an option in the Southern Ocean. The effect of the air-flow correction in SAGE produced a change in the coefficient of the gas exchange parameterization from 0.241 to 0.341, an increase of 30%. This is broadly in line with the overall reduction in wind speed by the correction of 13%. Effectively, the gas exchange parameterization moved from the Nightingale et al. (2000a) value, to the Wanninkhof (1992) value (Fig. 8). The difference between the QuikSCAT parameterization coefficient, $a_2$, and the overall airflow corrected parameterization was 18%.

Satellite and reanalysis winds are an alternative to the local ship winds, but these are subject to uncertainties and biases. The QuikSCAT winds used here were higher overall than the corrected ship winds, with a resulting less steep parameterization. As noted earlier, on a long-term basis Boutin et al. (2009) have suggested that QuikSCAT overestimates winds by 5%. Applying this correction raises the parameterization curve to between the original and the airflow corrected data. However for experiments on short time scales, such as SAGE, the differences in transfer coefficient were dominated by the short term differences in wind speed arising from short term spatial variability of wind patterns. The NCEP reanalysis was closer to the ship winds, but studies have suggested they significantly underestimate the wind (Smith et al., 2001), possibly due to not capturing sharp pressure gradients. However that comparison between NCEP and ship winds did not account for airflow acceleration over ships. Olsen et al. (2005) also found lower NCEP wind speed than QuikSCAT. If gas exchange parameterizations from diverse experiments are to be compared, it is clear that they should be made on the basis of the same wind product. At the present, it seems that QuikSCAT winds are the most suitable for such a comparison.

The error bars on the $k$ values in the parameterization in Fig. 8 were derived solely from the measured tracer ratios. While most of the
the SAGE data points lie within error bounds of the least squares fitted parameterization curve, the two points at the highest wind speed do not. While the error bars accurately represent the variation of measured data, this does not fully depict the range of physical variation. The points in question correspond to the third and fourth intervals in Fig. 5. Both encompass the strongest wind peak, but that was of limited duration. The average wave height was also of similar value (Table 1). One difference between the intervals is that the third interval experienced shallowing due to the ‘fresh’ water intrusion as discussed in Section 6. In theory this has been accounted for by the choice of $h$ in Eq. (2).

8.2. Tracer depth

The gas transfer velocity is directly dependent on the mixed layer depth (Eq. 2). Underlying this equation are certain assumptions about the mixing of the tracers. First is the assumption that the SF6 layer depth (Eq. 2). Underlying this equation are certain assumptions.

8.3. Seastate

In seeking effects of physics on gas exchange beyond simply wind speed, a relationship with wave height has been seen in experiments (Nightingale et al., 2000a) and proposed theoretically (Woolf, 2005). It is difficult to make a separation between a dependence on wave height and a dependence on wind speed in SAGE over the integration times used for the tracer decay (order 1 day), since the wave height was strongly correlated with wind speed, as expected. From a dynamical point of view, gas exchange is expected to increase strongly with the turbulence and bubble effects arising from wave breaking. Wave breaking need not be directly related to wave height since old swell propagating from distant storms is usually aerodynamically smoother than an actively forced wave field. Sugihara et al. (2007) found that whitecapping generated in a wind-sea tends to decrease in the presence of swell. Other studies have shown that, for the same wind speed, ‘young’ waves are usually steeper and therefore subject to a greater frequency of breaking, while Sugihara et al. (2007) suggest that since the scale of breaking increases with wave age, the whitecap coverage actually increases with wave age.

It should be emphasised that a ‘young’ sea does not imply a sea with low wave height. The storm and associated waves at the start of the experiment had the highest waves (> 6 m) but also the youngest seas; that is to say, they still had further potential to grow and travel faster if the storm had persisted. For the southerly wind direction of the storm, there was ample potential for extremely long fetch (Fig. 4). During SAGE, the sea was not ‘fetch limited’ but ‘duration limited’. This is a major difference between most tank studies and the open ocean, since tank studies are most likely to be fetch limited. Duration limitation can occur in the Southern Ocean as storm features have limited spatial extent and travel rapidly and evolve across the ocean. The distribution of wave age in Fig. 12 shows that during SAGE old waves dominated with a general background swell rarely below 2 m wave height. The results of Sugihara et al. (2007) suggest that under these conditions wave breaking (and bubbles) will not be as intense.

In terms of comparing the two tracer releases with the combined release, the transfer velocity derived using the QuikSCAT wind product gave a consistent result, albeit with a poor $r^2$ value for the second release when the winds varied little. The available fetch for the 2 releases was quite different: essentially unlimited exposure to the Southern Ocean during the first release, but ~200 km for the second release when the wind crossed New Zealand. The wind speed peak was slightly higher (20 m s$^{-1}$) during the first release than the second release (18 m s$^{-1}$), while the mean wind speeds were very similar. Despite this difference in wind history, the gas transfer parameterization analysis gave the same value of gas transfer velocity when the QuikSCAT winds were used. However, the significant wave height was also similar between release 1 and release 2 (4.1 m and 4.0 m, respectively). This is consistent with the view that the waves were duration limited rather than fetch limited, as also reflected in the wave age.

There have been several proposals to expand the range of variables in the gas exchange parameterization. Zhao et al. (2003) proposed a parameterization based on a parameter $R_b$ combining wind stress ($u^*$) with the wavefield peak frequency ($\omega_p$):

$$k_l = 0.13R_b^{0.63}$$

In relation to other sources of uncertainty, the error from this source is ~10% whereas variability from multiple CTD casts ranges from 5% to 75%. It is most likely to be a serious issue when restratification prevents the entire mixed layer ventilating to the atmosphere, or when the mixed layer is rapidly changing, such as the deepening which occurs during a storm.
where $R_H = u^2/\nu_{kg}$, with $\nu_{kg}$ being the kinematic viscosity of air. This fitted wave tank measurements well, where the state of wave development was represented by the spectral peak frequency.

Woolf (2005) proposed two parameterizations combining transfer related to wind stress with transfer related to wave breaking:

$$k = 1.57 \times 10^{-4} u^* (600/\text{Sc})^{1/2} + 3.4 \times 10^{-4} R_{Ha}$$

and

$$k = 1.57 \times 10^{-4} u^* (600/\text{Sc})^{1/2} + 2 \times 10^{-5} R_{Hw}$$

where $R_{Ha} = u^* H/\nu_{kg}$ and $R_{Hw} = u^* H/\nu_{w}$, $H$ is the wave height and $\nu_{w}$ is the kinematic viscosity of water.

These 3 transfer velocities were calculated using the Wave-Watch III seastate data and are shown in Fig. 13 plotted against the measured transfer velocity. The drag coefficient used to calculate $u^*$ was that used by Woolf (2005), i.e. from Large and Pond (1981). It can be seen that the 3 versions significantly overestimate the measured $k$, particularly $R_{Ha}$. For $R_{Hw}$ this may be because of the significant amount of swell present during the experiment. Zhao et al. (2003) make it clear that the parameter should only be applied to the wind-wave part of the wave spectra. Unfortunately the separation of seastate into swell and wind-wave was not available here. The difference between the peak frequency of swell and wind-wave could be up to a factor of 2. The highest $k$ value occurred in a ‘young’ sea with direct wind-wave forcing as noted earlier, and significantly, this point lies close to the measured $k$.

The $R_H$ parameters also produce transfer velocities which exceed the measured values but by a lesser extent. $R_{Hw}$ is dependent on wave height and the combined height of swell and wind-waves has been used here. On the one hand it could be argued that the actively forced wind-waves contribute predominantly to breaking (turbulence and bubbles) and this part of the wave field should be used, but on the other hand, the interaction of swell with wind waves has been shown to affect whitecapping; Sugihara et al. (2007) suggest that whitecapping is suppressed. Until these effects are clearly understood it seems that the parameterization of gas transfer velocity against wind speed alone is a more unbiased approach.

9. Conclusions

Experimental uncertainties associated with the dual tracer experiment contribute to the scatter in the parameterization of gas transfer against wind speed.

- Air flow distortion over the observing platform is often significant. On the Tangaroa during SAGE, the wind speeds from the primary anemometer site above the bridge were accelerated by approximately 13% when integrated over direction and the over the same interval as the dual tracer experiment, contributing a 30% increase in the exchange coefficient if not corrected for. Wind flow accelerations at the foremost will be less, but more restricted in acceptable azimuthal angle.
- The QuikSCAT scatterometer swath wind speeds and ship wind speeds typically agreed to within 10%, but differences arising from the spatial variation of wind patterns were apparent.
- The dual tracer averaging intervals ranged from 24 to 70 h. During this time there were significant changes in mixing layer depth which directly affect the calculation of $k$. The tracer layer depth (TLD) was the optimum parameter to define this depth.
- The Ho et al. (2006) relationship obtained using QuikSCAT winds was a good representation of the gas transfer velocity during both releases:

$$k = 0.266 U^2 (600/\text{Sc})^{0.5}$$

- No significant dependence on wave fetch was found in SAGE, despite the fact that the wind originated from Southern Ocean in the first release, but was intercepted by a land mass in the second. However this is likely to be due to the fact that in both cases, the duration of high winds limited the wave growth. Additional field data are required to distinguish a dependence on wave age versus wave height.
- The parameterization of gas exchange against wind speed was found to be a more unbiased approach than a parameterization against seastate parameters, in the absence of a separation of seastate into wind-sea and swell.

Acknowledgments

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References


