Bubble mediated gas transfer and gas transfersuppression of DMS and CO2
Zavarsky         , Alex; Goddijn-Murphy, Lonneke; Steinhoff, Tobias; Marandino, Christa

Published in:
Journal of Geophysical Research: Atmospheres
Publication date:
2018

The Document Version you have downloaded here is:
Peer reviewed version

The final published version is available direct from the publisher website at:
10.1029/2017JD028071

Link to author version on UHI Research Database

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the UHI Research Database are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights:

1) Users may download and print one copy of any publication from the UHI Research Database for the purpose of private study or research.
2) You may not further distribute the material or use it for any profit-making activity or commercial gain
3) You may freely distribute the URL identifying the publication in the UHI Research Database

Take down policy
If you believe that this document breaches copyright please contact us at RO@uhi.ac.uk providing details; we will remove access to the work immediately and investigate your claim.
Bubble mediated gas transfer and gas transfer suppression of DMS and CO₂

A. Zavarsky¹, L. Goddijn-Murphy², T. Steinhoff¹, and C. A. Marandino¹

Alexander Zavarsky, alexz@mailbox.org

¹GEOMAR Helmholtz-Centre for Ocean Research Kiel, Kiel, Germany
²Environmental Research Institute, University of the Highlands and Islands

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1029/2017JD028071

©2018 American Geophysical Union. All Rights Reserved.
**Abstract.** Direct DMS flux measurements using eddy covariance have shown a suppression of gas transfer at medium to high wind speed. However, not all eddy covariance measurements show evidence of this suppression. Processes, such as wave-wind interaction and surfactants, have been postulated to cause this suppression. We measured dimethyl sulfide and carbon dioxide eddy covariance fluxes during the Asian summer monsoon in the western tropical Indian Ocean (July and August 2014). Both fluxes and their respective gas transfer velocities show signs of a gas transfer suppression above \(10 \text{ m s}^{-1}\). Using a wind-wave interaction we describe a flow separation process that could be responsible for a suppression of gas transfer. As a result we provide a Reynolds number based parameterization, which states the likelihood of a gas transfer suppression for this cruise and previously published gas transfer data. Additionally, we compute the difference in the gas transfer velocities of DMS and CO\(_2\) to estimate the bubble mediated gas transfer using a hybrid model with three whitecap parameterizations.

**Keypoints:**

- Gas transfer velocities of DMS and CO\(_2\) are subject to suppression
- Transformed Reynolds number used to characterize suppression
- No clear bubble signal found during the cruise, despite \(k\) values measured for \(u_{10m} > 15 \text{ m s}^{-1}\)
1. Introduction

Gas flux $F$ across the air-sea interface is commonly described as the product of the concentration difference $\Delta C$ across the interface and the gas transfer velocity $k$ (Equation 1).

$$F = k \cdot \Delta C = k \cdot \left( \frac{C_{air}}{H} - C_{water} \right) \quad (1)$$

The concentration difference represents the gas displacement from equilibrium and acts as the driving force of gas exchange. The Henry’s law constant $H$ represents gas solubility, which depends on salinity and temperature, and allows the conversion between the gas and the liquid phase. Typically, $\Delta C$ is computed from the concentration measurements from 10 m in the atmosphere and 5 m depth in the ocean. It is an approximation to the concentration difference directly at the interface. The gas transfer velocity $k$ can be seen as conductance of gas exchange. A main challenge for the gas exchange community is to find a model or parameterization for $k$ that would be suitable for all gases across a wide range of solubilities and environmental conditions. There are three ways to describe $k$: [1] Mechanistically, which models the gas transfer based on fundamental boundary layer physics; [2] Empirically, which fits a parameter (wind-speed, friction velocity,...) dependent function through directly derived $k$ values; [3] As a hybrid, which is a mechanistic model applied to and fed by directly derived $k$ values.

A mechanistic model is, in theory, universal, but may not describe all important processes influencing gas transfer, as there may be unknown mechanisms at work. Empirical models capture all gas transfer processes, as they are based on measured field data, but mostly lack mechanistic understanding, as complimentary data on the underlying processes are

©2018 American Geophysical Union. All Rights Reserved.
often not obtained. In this study, we concentrate on the hybrid model description of $k$ as this provides the best opportunity to combine in situ measured data and the physical laws governing them.

Direct flux measurements, such as eddy covariance, provide an in situ value for the air-sea gas flux $F_{\text{direct}}$. $F_{\text{direct}}$ can be used to estimate the total gas transfer velocity $k_{\text{total}}$, when the concentration difference is known, by rearranging Equation 1 to result in Equation 2.

$$ k_{\text{total}} = \frac{F_{\text{direct}}}{\Delta C} \quad (2) $$

$$ \frac{1}{k_{\text{total}}} = \frac{1}{k_{\text{water}}} + \frac{1}{k_{\text{air}}} \quad (3) $$

The resulting $k_{\text{total}}$ (Equation 3, [Liss and Merlivat, 1986]) is a combination of the water-side transfer velocity $k_{\text{water}}$ and the air-side transfer velocity $k_{\text{air}}$ (Equation 3). Either fraction can be the limiting component for gas transfer. Using multiple gases with different solubilities one can quantify the different contributions of $k_{\text{water}}$, $k_{\text{air}}$ to the total gas transfer $k_{\text{total}}$. We use direct eddy covariance measurements of carbon dioxide ($\text{CO}_2$) and dimethyl sulfide (DMS) to estimate both contributions to the gas transfer. For sparingly soluble gases like CO$_2$, the transfer is controlled by $k_{\text{water}}$. For more soluble gases like DMS, both terms must be included in the calculation. On a molecular level $k_{\text{water}}$ is also dependent on the viscosity $\nu_{\text{water}}$ of the sea water and the diffusivity $D$ of the gas through seawater, which is represented by the Schmidt number (Equation 4). Schmidt number (Sc) scaling was introduced to make gas transfer velocities of various gases comparable.

$$ Sc = \frac{\nu_{\text{water}}}{D} \quad (4) $$

$$ \frac{k_{\text{water},Sc}}{k_{\text{water},Sc_{\text{ref}}}} = \left( \frac{Sc}{Sc_{\text{ref}}} \right)^n \quad (5) $$

©2018 American Geophysical Union. All Rights Reserved.
The exponent $n$ depends on the surface properties of the water and ranges from $-\frac{2}{3}$ for smooth surfaces to $-\frac{1}{2}$ for rough wavy surfaces [Komori et al., 2011]. For this study, we set $n = -\frac{1}{2}$ and $Sc_{ref} = 660$, which is the Schmidt number of $CO_2$ in seawater at $20^\circ C$ and commonly used as reference point in gas transfer studies. Hereinafter, presented results of gas transfer velocities $k$ correspond to the Schmidt number $Sc = 660$ unless indicated otherwise ($Sc = xx$).

The most widely used parameterizations for $k_{water}$ are dependent on wind speed e.g. Nightingale et al. [2000]; Sweeney et al. [2007]; Ho et al. [2006]; Wanninkhof et al. [2009]. Generally, according to Wanninkhof et al. [2009], parameterizations are described by a 3rd degree polynomial, Equation 6, in $u_{10n}$ (10 m neutral wind speed) based on the dominant role of wind forcing on surface stress, momentum flux, energy dissipation and bubble mediated gas transfer. In Equation 6, one or more coefficients ($p_0$, $p_1$, $p_2$, $p_3$) may be set to zero.

\[
k_{water} = p_0 + p_1 \cdot u_{10} + p_2 \cdot u_{10}^2 + p_3 \cdot u_{10}^3 \tag{6}\]

Eddy covariance measurements have pointed to discrepancies between empirically derived $k$ values and those predicted using wind speed parameterizations. There are various hypotheses used to explain these discrepancies. One major discrepancy is the solubility dependence of gas transfer. Bubble mediated gas transfer, which is strongly solubility dependent and important at high wind speed, prevents a universal $k$ vs wind speed relationship for all gases across a wide wind speed range. Many parameterizations do not perform well at high wind speed, when bubble-mediated exchange becomes more important through white cap formation, wave breaking and bubble formation. Hybrid models
have been developed to tackle this discrepancy at high wind speed. Woolf [1997] presents a hybrid model in which the total gas transfer velocity $k_{water}$ has two components: [1] $k_o$, the interfacial gas transfer which describes the molecular diffusion through the unbroken surface, and [2] $k_b$, the bubble mediated gas transfer, as described in Equation 7.

$$k_{water} = k_o + k_b$$

These hybrid models are based on actual measurements (empirical) of $k_o$ and a model of bubble mediated gas transfer, for example Woolf [1997]; Goddijn-Murphy et al. [2016]. Direct gas transfer $k_o$ scaled to a common Sc, using Equation 5, should be similar for different gases and for the same gas under different physical conditions, but $k_b$ is expected to depend on the solubility of the gas in seawater ($k_b$ increases with decreasing solubility of the gas). Equation 5 is therefore not strictly applicable to insoluble gases, but is commonly applied in existing empirical parameterizations of $k_{water}$. $k_o$ can be determined by measuring a more soluble gas, such as DMS, since DMS is not influenced greatly by bubble mediated transfer. CO$_2$, on the other hand, is influenced by the bubble mediated gas transfer $k_b$ and, therefore, the difference between the CO$_2$ and DMS $k_{water}$ values can be used to estimate the bubble mediated gas transfer velocity [Bell et al., 2017].

In contrast to the gas transfer enhancing bubble effect, four eddy covariance studies [Bell et al., 2013, 2015; Yang et al., 2016] and the update by Blomquist et al. [2017] on Yang et al. [2011] have indicated a suppression of gas transfer velocity at medium to high wind speed. This is an exceptional phenomena, as most models and theories do not include a process that could lead to such a decrease or flattening of $k$ at medium to high wind speed. Generally, there are not many direct flux measurements at wind speed exceeding 12 m s$^{-1}$ (this study, [Huebert et al., 2004; Yang et al., 2011; Bell et al., 2013, 2015; Yang et al., 2016].

©2018 American Geophysical Union. All Rights Reserved.
Interestingly, this phenomena has only been published in relation to these four eddy covariance data sets [Bell et al., 2013, 2015; Yang et al., 2011, 2016] and a wind-wave tunnel experiment [Rhee et al., 2007], all measuring DMS exchange. It is clear that suppression is not a general feature of high wind gas exchange [Blomquist et al., 2017].

Wind-wave interaction has been hypothesized to be the main driver of this suppression. For example, short waves lessen, under the influence of mechanically generated long waves and as a result gas transfer is reduced [Rhee et al., 2007]. Soloviev [2007] investigated the influence of surface wave development on the surface renewal model [Soloviev and Schlüssel, 1994]. They show a flattening of the $k_o$ vs wind speed relationship between 6-10 m s$^{-1}$. The challenges associated with understanding how wind-wave interaction influences gas exchange is that the wave field is multi-spectral and is a superposition of wind sea which is generated by local wind, and swell which originates in the distance. Bell et al. [2013] suggested that the suppressed gas transfer is caused by an influence of wind-wave dynamics on the gas-transfer. The wave crest shields the trough from the ambient wind and therefore decreases tangential stress [Reul et al., 1999; Veron et al., 2007; Reul et al., 2008]. Frew et al. [1990, 2004] investigated the influence of surfactants, generated by phytoplankton, on the air sea gas exchange. Surfactants, which are also thought to dampen small waves, are used as a possible explanation by Bell et al. [2013, 2015]; Blomquist et al. [2017] for the scatter of $k$ vs wind speed, but the surface microlayer and surfactants were not measured in any of these studies. Another hypothesis by Yang et al. [2016] suspects an influence of water drops as a result of wave breaking and high winds. However, this influence is limited to the air-side $k_{air}$ of gas exchange.

©2018 American Geophysical Union. All Rights Reserved.
proposed that the Reynolds number is related to air-sea gas exchange. They parameterized
the wave interaction using wind speed $u_{10\text{m}}$, friction velocity $u_*$, significant wave height
$H_s$ and the kinematic viscosity of water $\nu_{\text{water}}$ (Equations 8 and 9). $Re_{Toba}$ is only valid
for a pure wind-sea case and includes a mechanism of gas transfer suppression. They
propose that between $2 \cdot 10^2 < Re_{Toba} < 10^3$ the drag coefficient decreases and as a
result gas transfer limitation occurs. $Re_{Zhao}$ does not include a suppression mechanism.
Furthermore they are missing the influence of the sea state on the wind-wave interaction,
which is usually expressed as a ratio of wind speed to wave speed and a directional
dependance between wind and wave.

\[ Re_{Toba} = \frac{u_* \cdot H_s}{\nu_{\text{water}}} \]  
\[ Re_{Zhao} = \frac{u_{10\text{m}} \cdot H_s}{\nu_{\text{water}}} \]  
\[ Re_{Brumer} = \frac{u_*^2}{\nu_{\text{water}} \cdot \omega_p} \]

Brumer et al. [2017] use Equations 9 and 10, introduced by [Toba and Koga, 1986], to
find a generalized parameterization of the gas transfer velocity. Instead of the air kinematic viscosity $\nu_{\text{air}}$ they use the kinematic viscosity for seawater $\nu_{\text{water}}$. They analyze
four data sets including those from Knorr11 and SOGasEx cruises, which are discussed in
this manuscript, but do not provide explicitly a parameterization for the suppression of
gas transfer. Still, they include a direct wind-wave interaction using the ratio of friction
velocity $u_*$ over wave period $\omega_p$, but this interaction does not have a directional dependance between wind and wave. Hence their approach is suitable to describe the general turbulence characteristics of gas transfer, but is not sufficient to describe gas transfer suppression.
In this study we want to estimate the interfacial gas transfer $k_o$ using the DMS flux data. The difference between DMS and CO$_2$ flux data gives us an estimate of the bubble mediated gas transfer, which we test against our hybrid model [Goddijn-Murphy et al., 2016]. Both the CO$_2$ and DMS data sets show signs of gas transfer suppression. We present a mechanism which could lead to a suppression of gas transfer and a parameterization which describes the state where this mechanism is substantial. Therefore, we propose the transformed Reynolds number $Re_{tr}$ (Appendix C and Section 3.5) to describe the wind-wave interaction and establish a threshold where gas transfer is suppressed. It is the original Reynolds number $Re = \frac{u_{10} H_s}{\nu_{air}}$ transformed into the wave’s reference system. Through this transformation full vector characteristics of the wind speed as well as the wave’s phase speed are taken into account. The state of the wave field is included through the transformation, as the transformation depends on the velocity difference of wind and wave.

2. Methods and Materials

We performed direct CO$_2$/DMS flux measurements aboard the RV Sonne sailing from Durban, SA to Port Louis, MU (SO 234-2, 8 July - 20 July 2014) and from Port Louis, MU to Malé, MV (SO 235, 23 July - 8 August 2014). The cruise track is shown in Figure 1. Additionally, we recorded bulk air and seawater concentrations of CO$_2$ and DMS. Basic meteorological observations were done by the ship’s automated weather station. We used the NOAA COARE 3.5 algorithm to describe the state of the boundary layer. The wind speed used throughout the text is measured by the ship’s meteorological station and then recalculated by stability parameters of COARE to $u_{10n}$ (Figure 2).
2.1. Eddy covariance

The eddy covariance method measures turbulent scalar fluxes. The flux $F$ is the product of the dry air density $\rho_{\text{air}}$, the fluctuation of vertical wind speed $w'$ and the fluctuation of the air concentration $c'$ (Equation 11). High sampling rate and high precision measurements of vertical wind speed and air concentration are needed in order to capture turbulent deviations from the mean.

$$F = \rho_{\text{air}} \cdot c'w'$$  \hspace{1cm} (11)

Our eddy covariance measurement system aboard the RV Sonne consisted of two parts: [1] The measurement mast at the bow of the ship, which incorporated the sample inlets, the wind measurements and acceleration measurements, which were collocated; [2] The concentration measurements in a lab container, 20 m behind the bow at the forecastle of the ship. We used two ultrasonic anemometers (Campbell CSAT3) which measured the 3-D turbulent wind field in duplicate. They were placed on the port and starboard forward stretching arms of the measurement mast 11 m above sea level. The DMS and CO$_2$ sampling tubes were connected to the respective DMS and CO$_2$ air-sample inlet at the port side sonic anemometer. The port side sonic anemometer was used for all data processing. The starboard sonic anemometer served as a backup. The sampling rate of the sonic anemometers was 30 Hz. For eddy covariance calculations, this sampling rate was then reduced by a running mean and nearest interpolation to the respective lower sampling rate of the DMS or CO$_2$ measurements.

We corrected the wind measurements for ship motion based on Edson et al. [1998]; Miller et al. [2010]. We also included the planar fit and flow distortion update by Landwehr et al. [2015]. Further information on the motion correction is available in the supplement. The

©2018 American Geophysical Union. All Rights Reserved.
required linear-accelerations, angular velocities, ship’s course/heading and ship’s speed were recorded by an inertial navigation unit (30 Hz, Landmark 10, Gladiator Technologies) and a GPS, 1 Hz sampling rate. Both devices were also mounted on the measurement mast. Additionally, we recorded atmospheric properties and navigational data using the ship’s inbuilt sensors at 1 Hz sampling rate. Unless otherwise stated, all data presented were recorded by our eddy covariance measurement system.

2.1.1. DMS eddy covariance measurements

We recorded DMS air concentrations at 5 Hz in the lab container using an atmospheric pressure chemical ionization mass spectrometer (AP-CIMS) similar to those described by Marandino et al. [2007]; Saltzman et al. [2009]. The air was sampled from the mast at the bow of the ship (11 m above sea level) and pumped at 50-70 L min\(^{-1}\) \(\text{Flow}_{\text{total}}\) through a \(\frac{1}{2}\)" diameter, 25 m long polytetrafluoroethylene (PTFE) tube to the AP-CIMS. This flow from the mast was sub-sampled (2 L min\(^{-1}\)) and dried using a Nafion membrane (Perma Pure) prior to analysis by the AP-CIMS. For calibration, we continuously added a deuterated DMS standard (DMS-d3, 2.28 ppm \(C_{\text{tank}}\)) to the inlet at a rate of 2 mL min\(^{-1}\) \(\text{Flow}_{\text{std}}\). Using the count ratio of the deuterated DMS \(\text{Counts}_{66}\) to the natural DMS \(\text{Counts}_{63}\), the mixing ratio of atmospheric DMS \(\text{DMS}_{\text{air}}\) was calculated as follows:

\[
\text{DMS}_{\text{air}} = \frac{\text{Flow}_{\text{std}}}{\text{Flow}_{\text{total}}} \cdot \frac{\text{Counts}_{63}}{\text{Counts}_{66}} \cdot C_{\text{tank}} \tag{12}
\]

The DMS mixing ratios was recorded for 1 hour every 2 hours. A full mass scan from 10-100 and a delay test was done before and after each measurement period. This delay test determined the time an air parcel takes from the air-sampling inlet to the mass spectrometer using multiple valve on/off switches of the deuterated standard.

2.1.2. CO\(_2\) eddy covariance measurements

©2018 American Geophysical Union. All Rights Reserved.
The CO$_2$ eddy covariance measurements were made on the same mast and in the same laboratory container as the DMS eddy covariance system. The air sample was collected next to the DMS air intake and pumped at 15 L min$^{-1}$ through a 25 m, 1/2” DECABON tube to the lab container with the CO$_2$ measurement system. We used a nondispersive infrared measurement system (LI-7200 by Licor) in the setup of Miller et al. [2010] to measure the dry partial pressure of CO$_2$ in the atmosphere. The data was collected at 10 Hz with two in line LI-7200. We placed a Nafion membrane (Perma Pure) between the two LI-7200 to dry the air stream and to ensure no cross-talk from the water vapor fluctuations. The sample air pressure was measured between the two LI-7200 using a pressure transducer (Mensor CPT6100) and corrected to each Licor’s cell pressure using the internal differential pressure transducer. In this analysis only data from the 2nd (dried air stream) LI-7200 is presented.

### 2.1.3. Post processing

In total we recorded 130.15 h of DMS measurements and 281.7 h of CO$_2$ measurements, which fulfilled the relative wind direction criterion of ±90$^\circ$ from the bow and the requirement of steady wind direction (±10$^\circ$) [Landwehr et al., 2015].

We split the DMS and CO$_2$ records into running intervals (step size 10 min), each 29.6 minutes and merged them with the simultaneously recorded wind and navigation data. As a result we obtained 477 DMS and 942 CO$_2$ data records and screened them for spikes, malfunctions, high and low frequency anomalies. The determination of the delay was done in two steps. First we set the delay to the value obtained from the delay tests. Then, to increase the delay precision, we cross correlated the recorded wind $w'$ and the respective air concentration $c'$ and set the delay to the maximum positive correlation (flux out of.
the ocean) or a maximum negative correlation (flux into the ocean). At the right delay time the cospectrum and the cross-correlation graph were screened for anomalies and a decision of pass or rejection was made. Subsequently 435 DMS and 266 CO₂ intervals were corrected for the high frequency loss in the tube. A description of the delay cross-correlation and the high frequency correction is provided in the supplement. Examples of gas spectra and and c’w’ cospectra are in the supplement.

2.2. Bulk air and seawater measurements

The DMS seawater concentration was measured using a purge and trap system attached to a GC-MS system (GC/MS; Agilent 7890A/Agilent 5975C) operating in single ion mode. We sampled every 3 h from a constant stream out of the ship’s moonpool (5 m depth). The samples were measured within 15 min of collection by purging the gases from the water sample for 15 min, drying the gas stream using potassium carbonate and preconcentrating the gases in a trap cooled with liquid nitrogen. After preconcentration the trap was heated and the gases were injected into the GC. We analyzed in total 162 DMS seawater samples. A detailed description of the measurement procedure is provided in Zavarsky et al. [2017].

We used the average DMS mixing ratios from the eddy covariance system as bulk air DMS mixing ratios. These values were compared with measurements using stainless steel air canister samples (25 m sampling height), taken every 3 h at the same time as the DMS seawater samples and analyzed for more than fifty gases, including DMS and isoprene, at the University of Miami. They showed good agreement.

Oceanic measurements of pCO₂ were carried out using the setup described in Arevalo-Martinez et al. [2013]. Water was drawn on board using a submersible pump installed in the ship’s moonpool at approximately 5 m depth and was subsequently drawn at a rate of 2018 American Geophysical Union. All Rights Reserved.
about 5 L min\(^{-1}\) through the Weiss type equilibrator. Sample air from the headspace of the equilibrator was continuously pumped through the instruments and then back to the equilibration chamber forming a closed loop. The air stream was dried using a refrigerated air dryer and a Nafion dryer before being injected into the analyzer (LI-COR, USA; LI-6252) in order to diminish interferences due to the water vapor content of the sample. Every minute a data point was recorded. The LI-COR analyzer was calibrated regularly using three non-zero standards traceable to WMO scale. Atmospheric air measurements were accomplished by drawing air into the system from an air inlet located at the ships mast at about 30 m height. The intake temperature was measured by a calibrated Seabird thermostalinograph (SBE37), which was installed next to the seawater intake. Due to a broken temperature sensor we had to estimate the temperature in the equilibrator by using the temperature readings of an Aanderaa oxygen optode (model 4330) which was installed in a flow-through box next to the Weiss equilibrator. The optode’s temperature was compared to the SBE37. The temperature readings agreed within 0.05°C. Following the SOP described in Dickson et al. [2007] and the procedures described in Pierrot et al. [2009] the pCO\(_2\) at seawater temperature was calculated from measured xCO\(_2\). Based on the accuracy of temperature, pressure and xCO\(_2\) measurements the resulting accuracy of the seawater pCO\(_2\) measurements is estimated to be better than 5 \(\mu\)atm.

### 2.3. Hybrid Model

The hybrid model defines water side gas transfer \(k_{\text{water}}\) (Equation 7) as a sum of direct gas transfer through the unbroken water surface \(k_o\) and bubble-mediated gas transfer through the broken water surface \(k_b\). In the hybrid model, the enhancement of air-sea exchange of poorly soluble gases is solely attributed to wave breaking and associated...
bubble-mediated gas transfer via the Woolf [1997] parameterization. Assuming that bubble-mediated gas transfer is negligible for DMS, linear regressions between $u_{10}$ and $k$ have been used to estimate $k_o$ [Goddijn-Murphy et al., 2012, 2013]. We calculated $k_b$ using Woolf’s model for bubbles with a free and mobile surface, i.e., ‘clean’ bubbles, and for Woolf’s ‘independent bubble model’, where the bubbles exchange gases with surrounding water independently of each other. In a very dense plume, we may expect the gas content of the interstitial water to change during the lifetime of that plume, making gas transfer sensitive to the void fraction (ratio of air volume to total volume) of the bubble plume. However, Goddijn-Murphy et al. [2016] show with Woolf’s dense plume model that for DMS and CO$_2$ realistic void fractions have no or very small effect on $k_b$. Woolf’s bubble model calculates $k_{b,1\%}$ for a whitecap coverage $W$ of 1%. To calculate the bubble term $k_b$ for any whitecap coverage Equation 13 is used.

$$k_b = W \cdot k_{b,1\%}$$

(13)

An alternative approach to the hybrid model, using Equation 13, is an empirical model that relates $W$ to turbulence effects on $k_{water}$ and to bubble-mediated gas transfer [Asher et al., 1996; Asher and Wanninkhof, 1998; Asher et al., 2013]. We estimated $W$ using three common wind speed to $W$ parameterizations proposed by Monahan and Muircheartaigh [1980] (MM), Stramska and Petelski [2003] (SP) for developed seas and Callaghan et al. [2008] (MAP). We selected these three to represent the wide range of $W$-levels at a certain wind speed, especially for high winds, depending strongly on the conditions during the measurements such as wave development (young wind waves or old swell waves) and the directional difference between wind and swell waves [Goddijn-Murphy et al., 2011]. Finally, combining $W$ and $k_{b,1\%}$ (Equation 13) we modeled $k_b$ for DMS and CO$_2$ using

©2018 American Geophysical Union. All Rights Reserved.
concurrent $u_{10n}$, Sc, sea surface temperature (SST) and salinity data, and scaled $k_b$ to $Sc=660$ (Equation 5). This is not strictly correct because Equation 5 applies to direct gas transfer, but Sc scaling enables us to compare $k_{water}$ for DMS and CO$_2$ and to other known $k_{water}$ parameterizations. Waterside direct gas transfer, normalized to Sc=660, $k_{o,660}$ should be the same for DMS and CO$_2$ so that their $k_{water,660}$ difference equals their $k_b,660$ difference. Measurements of total gas transfer velocity of DMS were first corrected for air side gas transfer to estimate $k_{water}$. Because CO$_2$ is sparingly soluble, gas transfer is controlled by water side resistance and we did not need to apply the correction for air side gas transfer. We only used measurements of $k_{water}$ between -10 and 80 cm hr$^{-1}$. More detail about this cutoff is provided in the supplement.

2.4. COARE

The NOAA COARE 3.5 algorithm [Edson et al., 2013] is an update from its first version COARE 2.5 [Fairall et al., 1996a, b] and provides stability parameters and standard meteorological variables of the boundary layer from bulk measurements. We used the ship’s meteorological data and COARE 3.5 to calculate relevant boundary layer parameters and $u_{10n}$. Data outages, if longer than 30 min, of wind speed and wind direction in the ships meteorological system between DOY 209.25 and 211.75 were filled with wind data from the eddy covariance measurement system. The extent of the data outage is shown in the supplement.

2.5. Wave parameters

We obtained global wave parameters from the Wave Watch III (WWIII) model [Tolman, 1997, 1999, 2009]. It is a multi-spectral third generation wind-wave model run by the

©2018 American Geophysical Union. All Rights Reserved.
Marine Modeling and Analysis Branch (MMAB) of the Environmental Modeling Center (EMC) of the National Center for Environmental Prediction (NCEP). The data set used is the production hindcast with NCEP reanalysis wind and ice fields as input forcing. No wave data is assimilated. The model is run at the end of each month with the available data and provides a global analysis of the ocean’s wave field. The temporal resolution is 3 hours and the spatial resolution is $0.5^\circ\times0.5^\circ$. We retrieved wind speed forcing $u_x$, $u_y$, peak wave period $T_p$, significant wave height $H_s$ and peak wave direction $d_p$ for the times of the cruise and then linearly interpolated them to the cruise track. Using Equation 14 [Hanley et al., 2010], we converted the peak wave period $T_p$ to phase speed $c_p$, assuming deep water waves. The peak wave period and direction is including swell and wind sea waves. Arinaga and Cheung [2012] use buoy data to investigate the accuracy of the WWIII model. They use a data set from 2000-2009 to determine a correlation between buoy and WWIII data for $H_s$ of 0.92 and a root mean square error (RMSE) of 0.48 m. They perform a similar analysis for the mean wave period and find a correlation of 0.5 and RMSE of 2.9 s. The error for $T_p$ seems large, however this is entirely based on coastal buoys. We think that WWIII performs better in the open ocean. Additionally, the wave period is larger in the open ocean, which leads to a decrease in the relative error.

$$c_p = \frac{g \cdot T_p}{2\pi}$$  \hspace{1cm} (14)

The wave parameters of the WWIII were used to calculate $\text{Re}_{tr}$ (Appendix C and Section 3.5).
2.6. Kinematic viscosity

The kinematic viscosity was calculated using the air density from the COARE model and the dynamic viscosity adapted by Sutherland’s law [White, 1991] (Equation 15). $T$ is the air temperature.

$$\mu (T) = \mu_0 \cdot \left( \frac{T}{T_0} \right)^{3/2}$$ (15)

$\mu_0 = 1.716 \cdot 10^{-5} \text{ N s m}^{-2}$ at $T_0=273 \text{ K}$ [White, 1991].

3. Results

The cruise took place during July and August 2014 during the Asian summer monsoon season (or southwest monsoon). Large scale meteorological features include northeasterly winds south of the Equator and southwesterly winds north of the Equator. The cruise track, displayed in Figure 1, spanned a range of oceanic areas, from the Agulhas current, the Antarctic circumpolar current (ACC), the Indian Ocean Gyre, the South Equatorial Current, the Equatorial Countercurrent, and the North Equatorial Current. These areas also provided a range of CO$_2$ and DMS air-sea gradients. The average oceanic mixed layer depth was 60 m, SST ranged from 19°C to 25°C. The salinity over the cruise track ranged between 34 and 36 and we encountered generally low nutrient levels (below 0.1 µmol L$^{-1}$ for nitrate and below 0.2 µmol L$^{-1}$ for phosphate). Some areas of enhanced nutrient concentrations were observed between 10° and 5°S. Measured chlorophyll levels were also generally low, 0.05-0.59 µg L$^{-1}$ with a mean of 0.23 µg L$^{-1}$.

3.1. Boundary Layer

Measured wind speed, averaged over 30 min (an eddy covariance interval), was lower than 10 m s$^{-1}$ at the outset of the cruise. Wind speed increased to a maximum of 16 m s$^{-1}$.
after leaving Mauritius and gradually declined towards the Maldives. Lower wind speed prevailed closer to the Equator, which is in agreement with the monsoon circulation wind patterns. The SST was slightly higher than the air temperature over most of the cruise track with a mean difference of 1.59°C. The Monin-Obhukov stability parameter, calculated with the COARE algorithm, indicated a neutral stratification ($\zeta_T \approx 0$) over most of the cruise track. From day of year (DOY) 196-200 and after DOY 217, the boundary layer was found to be unstable, which can be attributed to lower wind speed and the SST being higher than the air temperature during these times (Figures 2 and 3). The average marine boundary layer heights were approximately 0.8 km, relative humidity varied between 50% and 90%, and air temperatures ranged between 14°C and 30°C [Fiehn et al., 2017]. Precipitation was variable over the cruise tracks, which also influenced the boundary layer stability. The basic parameters are shown in Figure 2.

3.2. DMS

Panel C of Figure 3 shows the measured air mixing ratio and the measured water concentration of DMS. During the first leg from DOY 197 to 201 the DMS water concentration was generally low between 0.4-1.0 nmol L$^{-1}$. The air mixing ratio showed low values as well, from 5.8-69.6 ppt, with a mean of 25.0 ppt. The water concentration and air mixing ratio indicate a high supersaturation of DMS in seawater. Eddy covariance measurements began on DOY 197. Wind speed ranged between 2.9-9.9 m s$^{-1}$ from DOY 197 to 201. The average wind speed was 7.6 m s$^{-1}$. This average wind speed combined with the low DMS water concentration resulted in generally low fluxes (0.29-4.32 µmol m$^{-2}$ d$^{-1}$). After leaving Mauritius (after DOY 204), we encountered higher DMS water concentrations of 0.48-3.66 nmol L$^{-1}$. The air mixing ratio closely followed the water concentra-
tion, 19.2-310 ppt with an average of 128.35. We experienced the highest wind speed of 16.3 m s\(^{-1}\) at the beginning of the second leg, which then gradually declined towards the Maldives. The wind speed range was 3.7-16.3 m s\(^{-1}\), with an average of 9.7 m s\(^{-1}\). Elevated wind speed together with elevated DMS water concentrations resulted in the DMS flux values between 0.83-32.78 µmol m\(^{-2}\) d\(^{-1}\). The maximum flux was observed at DOY 207.1 just north of Mauritius. The time series of wind speed, friction velocity, DMS water concentrations, DMS air mixing ratio are shown in Figures 2 and 3. A time series of the DMS flux and DMS gas transfer velocity is displayed in Figure 4.

### 3.3. CO\(_2\)

Figures 3 and 5 show the pCO\(_2\) difference (ΔpCO\(_2\)) between the ocean and the overlying atmosphere and the resulting fluxes. Negative values denote areas where CO\(_2\) is undersaturated in the surface water with respect to the atmosphere and vice versa. Figure 5 compares the measured ΔpCO\(_2\) with the climatological values from Takahashi et al. [2009]. Our data are generally in good agreement, but show some fine structured divergence of up to 10 µatm. During the first part of the data set (before DOY 204) the observed values are all negative, starting from - 20 µatm close to Madagascar and going down to - 40 µatm at the southernmost part of the cruise track at around 30°S (between DOY 196 and 198). At this position a surface drifter was deployed for 48 hours. The ship stayed within 2 nautical miles of the drifter measuring surface water pCO\(_2\) in order to observe diurnal trends by staying in the same water mass. During the drift experiment no diurnal signal could be observed. This corroborates the findings of former studies [Sabine et al., 2000; Bates et al., 2006] that the observed strong undersaturation in the southern Indian Ocean is mostly due to surface water cooling. The minimum values at
DOY 196 (beginning of drift experiment) and DOY 198 (end of drift experiment) are due to observed eddies in this area that have different surface properties than the surrounding water. The second part of the cruise track is characterized by higher pCO₂ values. The observed values follow the climatological values most of the time. Between DOY 212 and 214 (4°S-12°S), the observations differ significantly from the climatological mean by up to 20 µatm. This area is part of the Central Indian Ridge that comes closest to the Chagos-Laccadive Ridge on the east and the Mascarene Plateau on the west. Both features are close to the ocean surface and can influence the upper ocean [Tomczak and Godfrey, 2006]. The SST drops by 1°C which indicates intrusion of deeper water masses to the surface.

Upwelling of deeper (carbon rich) water masses should lead to an increase in pCO₂. We speculate that the observed decrease of 20 µatm might be due to biological activity in this oligotrophic area. Other evidence for enhanced biological activity was found for DMS (section 3.2), halogens [Fiehn et al., 2017] and isoprene [Booge et al., 2017]. During the rest of the cruise track (DOY 215 and later), slight supersaturation of surface water CO₂ was observed, which is typical for tropical warm water regions.

The CO₂ flux and gas transfer velocity are shown in Figure 4. Before DOY 204, the CO₂ flux was negative most of the time with a minimum of -14 mmol m⁻² d⁻¹ and an average of -6.1 mmol m⁻² d⁻¹. Although we measured the highest ∆pCO₂ values during that time, low wind speed led to reduced CO₂ flux. After leaving Mauritius (after DOY 204), the direction of the flux changed twice. This Section of the cruise experienced lower ∆pCO₂, but higher wind speeds than earlier. This resulted in average fluxes with magnitudes similar to those before DOY 204. The average of all negative values (into the ocean) was -6.4 mmol m⁻² d⁻¹ with a maximum of -15.4 mmol m⁻² d⁻¹. The positive values (out of
the ocean) had an average of 4.6 mmol m\(^{-2}\) d\(^{-1}\) with a maximum of 15.1 mmol m\(^{-2}\) d\(^{-1}\).

The low average of the positive flux can be explained by the low wind speed at the end of the cruise.

### 3.4. Gas Transfer Velocity

Figures 6 and 7 show the gas transfer velocity \(k_{\text{total}}\) plotted against wind speed, color coded according to the water concentration (DMS) and the air-sea concentration differences (CO\(_2\)). We averaged the gas transfer velocities into 1 m s\(^{-1}\) wind speed bins. The binned data is plotted as a solid line including the standard deviation of each bin as the error bar.

For DMS (Figure 6), the binned values are above the plotted Nightingale et al. [2000] (N00) parameterization until 10 m s\(^{-1}\) wind speed. They exhibit a linear dependence on wind speed until that point. After 10 m s\(^{-1}\) a change of slope is evident and most \(k\) values lie below N00. As a consequence, we fitted linear curves to parts of the binned data set (Figure 8). The equations for the linear fits, the RSME and \(r^2\) are shown in Table 1. The difference in slopes between \(k\) and wind speed up to 10 m s\(^{-1}\) and beyond 10 m s\(^{-1}\) is significant. Until 10 m s\(^{-1}\) the \(k\) vs \(u\) relation is well described by the linear fit, which is also supported by the \(r^2\) (0.98) and RMSE (0.29). The \(k\) vs \(u\) relationship beyond 10 m s\(^{-1}\) is more scattered which results in a lower \(r^2\) value and an elevated RSME. The slope for the lower wind speed range is approximately three times higher than for the higher wind speed range and the standard deviation of the three highest wind speed bins does not cross the fit of lower wind speed range (Figure 8). The observed change in slope is in agreement with the results from Bell et al. [2013, 2015] showing suppression of \(k\) beyond 10 m s\(^{-1}\). The linear fit to all binned data shows good agreement with the whole
data set ($r^2=0.89$), but can not describe the change in slope (RSME=1.5). Interestingly the overall fit is similar to an updated parameterization by Marandino et al. [2009]. They compiled six DMS eddy covariance measurement campaigns and fit a linear $k$ vs. $u$ parameterization. Goddijn-Murphy et al. [2012] also suggests a linear relation between $k$ and $u$ using field data of eight cruises that provided DMS gas transfer velocity measurements. All DMS parameterizations are presented in Table 1. Generally it appears that the DMS $k$ values exhibit a linear wind speed dependence and can be used as an estimate of the interfacial gas transfer $k_0$. However, it is apparent (Figure 8) that the linear relationship should be split into two separate regimes (above and below 10 m s$^{-1}$). The decreasing slope from the lower to higher wind speed regime is the perceived suppression. This will be discussed in more detail below.

The gas transfer velocity of CO$_2$ in Figure 7 closely resembles the parameterization N00 until 12 ms$^{-1}$. Above 12 ms$^{-1}$ the binned gas transfer velocities are below the N00 curve, but tend to return to the parameterization at the highest wind speed bin. We think that this change in $k$ vs. $u_{10m}$ functional form points towards the suppression phenomenon, as it should affect the interfacial gas transfer of all gases equally. However, due to the likely bubble enhancement of CO$_2$ air-sea exchange compared to DMS at high wind speed (see Section 3.6), the suppression is not as prominent for CO$_2$ as for DMS. Negative gas transfer velocities could be caused by a combination of measurement uncertainty, spatial distance of the flux footprint to the water intake, and an averaging period of 30 mins.

Figure 9 shows binned DMS, fitted with a linear function, and binned CO$_2$, fitted with a quadratic function, over $u_{10m}$. The two curves begin to separate above 11 m s$^{-1}$. A similar overlap and coherence of DMS and CO$_2$ has been previously reported by Miller

©2018 American Geophysical Union. All Rights Reserved.
The data of Bell et al. [2017] show a separation much earlier at around 6 m s\(^{-1}\). They attribute the difference to the bubble mediated gas transfer, which is solubility dependent.

### 3.5. Gas transfer suppression and Reynolds number

The gas transfer velocities of DMS and CO\(_2\) in Figures 6 and 7 show signs of suppressed gas transfer at a wind speed above 10 ms\(^{-1}\) and 12 ms\(^{-1}\), respectively. For DMS, this is underlined by the slopes of the linear fits in Table 1. Similar findings have been reported previously by Bell et al. [2013, 2015]; Yang et al. [2016].

In order to improve the characterization of wind-wave interaction and its influence on gas exchange, we introduce vector characteristics and directional dependencies in the calculation of the Reynolds number. The new parameter is the transformed Reynolds number \(Re_{tr}\) (Equation 16).

\[
Re_{tr} = \frac{u_{tr} \cdot H_s}{\nu_{air} \cdot \cos(\theta)}
\]  

\(u_{tr}\) is the wind speed in the wave’s reference system. The wave’s reference system is the inertial frame of reference defined by the wave speed and the wave direction (swell and wind wave combined). The length scale is the significant wave height \(H_s\). The angle \(\theta\) describes the directional dependency and is the angle between the wind direction and the wave direction in the wave’s system. Until now parameterizations (e.g. Reynolds number or wave age, Equations 8-10) have used absolute quantities, but our parameterization has the advantage that both wind and wave velocities are treated as vectors at the transformation. We use a Galilean transformation to move the Reynolds number and the wind-wave interaction into the wave’s reference system. The Navier-Stokes equation is invariant under this transformation. A detailed description of the transformation and
the derivation of Equation 16 is available in the Appendix.

It is possible to deduce properties of the suppression, given the circumstances of this phenomenon and the fact that, so far, the suppression has only been seen in data retrieved from eddy covariance measurements: The suppression is [1] a feature of medium to high wind speed, but not universally present [2] a result of a mesoscale process [3] a process possibly linked to a wind-wave interaction. We also point out that eddy covariance is so far the only technique that measures transfer velocities of relatively soluble gases. For these gases the interfacial gas exchange $k_o$ is dominant. Measurements of $k$ using the dual tracer technique, however, use insoluble gases, for which $k_b$ become more important.

If the mechanism causing the suppression influences $k_o$, it would be likely that eddy covariance measurements exhibit these characteristics. As stated in the introduction, Bell et al. [2013] suspect a possible screening of wind speed by high waves or swell, which would agree with all of the deduced properties. Indeed laboratory studies [Kawai, 1982; Veron et al., 2007] have discussed and shown a flow separation between the wind above the crest and the flow entering the trough. Veron et al. [2007] measured flow separation at low wind speed and found a drop in wind speed and tangential stress in the flow separation regime. Furthermore, Yang and Shen [2017] provide a direct numerical simulation of wind-wave interaction at three different wave age cases. Through quadrant analysis they simulate the influence of waves and wave age on turbulence and, hence, on the scalar transport. Yet they provide neither a positive nor a negative overall correlation of wave age and scalar transport. They state two main weaknesses of their simulation: [1] The use of single frequency waves in their simulation. In the real world, open ocean waves and swell have a broad frequency spectrum; [2] Wind direction and wave direction are always
perfectly aligned in their simulation, which is not true for the real world case.

We conceptualize air flow above waves to air flow around a cylinder [Shapiro, 1961; Mathieu, 2000; Toba et al., 2006]. This standard model can be used as an analogy for our wind-wave interaction scheme [Toba et al., 2006]. At low Reynolds numbers $Re_{tr} < 10^2$, a Stokes flow establishes with respect to the wave’s phase speed. With increasing relative velocity and Reynolds number $10^2 [Re_{tr}] 10^4$, a laminar boundary layer flow is established with a separation point at the leeward face. At this separation point the flow is detached from the sea surface and forms a vortex and, subsequently, a van Karman vortex street behind the wave. At $Re_{tr} > 10^5$, the separation point moves further leewards and decreases the area of flow separation, until the boundary flow turns fully turbulent $Re_{tr} \approx 10^5$ and the flow separation is extinguished. We hypothesize that a detached flow regime above the wave limits gas transfer. At higher Reynolds numbers, when the turbulent boundary layer is again completely attached to the surface, the gas transfer follows the generally accepted wind speed gas transfer relationships. We include the horizontal angle of attack by introducing the angle $\theta$, relative to the wave’s direction into the equation. It is the angular difference between the wave direction and the wind direction in the wave’s reference system. Wind flowing at $\theta = 90^\circ$, for example, does not experience a wave crest or trough, but a corrugated surface. The significant wave height, in this case, is reduced to zero, because $\cos (90^\circ) = 0$. For all angular values in between $0 < \theta < \pm180^\circ$, the significant wave height turns into an effective wave height by the factor of $\cos (\theta)$. Angles lower than $90^\circ$ specify a wind direction unidirectional to the wave direction, while angles greater than $90^\circ$ specify a counter-direction between wind and wave direction. We do not expect a dependence of gas transfer on the sign of $Re_{tr}$ and, in fact, do not see this dependence.
in the data. Therefore the absolute value of $Re_{tr}$ is used. We also expect a lower $Re_{tr}$ limit for the gas transfer suppression. According to the flow around a cylinder theory the airflow at $Re_{tr} < 100$ is attached to the surface, which means no gas transfer suppression. However, these conditions rarely occur. Rearranging Equation 16 and setting $\nu_{air} = 10^{-5}$, $H_s = 1$ results in

$$100 > \frac{u_{tr} \cdot n_{u,air}}{10^{-5}} \cdot cos(\theta)$$  \hspace{1cm} (17)$$

$$0.01 > u_{tr} \cdot cos(\theta)$$  \hspace{1cm} (18)$$

A non-suppressing gas transfer at $Re_{tr} < 100$ occurs at $u_{tr}$=0.01 m s$^{-1}$ (if $\theta=0^o$) or $\theta > 89^o$ (if $u_{tr}$=1 m s$^{-1}$). A combination of both cases is also possible, but it is hardly imaginable that gas flux can be measured under these circumstances. As a consequence, we ignore this lower limit.

The gas exchange limiting threshold value for $|Re_{tr}|$ is set to $6.96 \cdot 10^5$ based on the residuals of the measured DMS gas transfer velocities in relation to the fit displayed in Figure 10. The threshold lies in the predicted range where the flow separation is destroyed by the increasing turbulent boundary layer flow. The residuals in relation to the choice of the threshold is shown in the supplement. The separation of the gas transfer velocity for the SO234-2/235 cruises in a gas limiting $|Re_{tr}| < 6.96 \cdot 10^5$ and a non-limiting $|Re_{tr}| > 6.96 \cdot 10^5$ regime is shown in Figure 10 for DMS and Figure 11 for CO$_2$. It is apparent that the gas transfer velocities of the suppressed regime are significantly below the linear fit for DMS and the N00 parameterization for CO$_2$. We associate the return of the CO$_2$ gas transfer velocity above 15 m s$^{-1}$ with the incipient bubble effect, which might compensate for the gas suppression effect. The exceptionally high data points around 10 m s$^{-1}$ and 13 m s$^{-1}$ in the limiting case for DMS (Figure 10, left panel) are associated...
with low DMS water concentrations, where scatter in the measurement is enhanced. The very low gas transfer velocities between 12 and 15 m s\(^{-1}\) are close to the gas transfer limiting threshold. It is also notable that for DMS and CO\(_2\) an overlap, with respect to wind speed, of suppressed and non-suppressed gas transfer velocities is present (Figures 10 and 11). This means our parameterization Re\(_{tr}\) is not a function of wind speed only, but describes the wind-wave interaction.

Figure 12 (right panel) shows wind speed vs a global probability density for the year 2014 of Re\(_{tr}\). The data has been retrieved from the WWIII model. The left panel shows the ratio of instances of gas suppression (below the threshold) and the total number of data points over wind speed. The ratio is described in Equation 19.

\[
r = \frac{\sum \prec 6.96 \cdot 10^5}{\sum \prec 6.96 \cdot 10^5 + \sum \succ 6.96 \cdot 10^5}
\]

(19)

A white line is drawn along the threshold of +6.96\(\cdot\)10\(^5\) and a dashed line along −6.96\(\cdot\)10\(^5\). The area of suppressed gas transfer is between the dashed and solid white line, as there should be no directional dependency. Globally, in 2014, 19\% of all data points are within the gas transfer limiting regime. Between the wind speed of 12 - 17 m s\(^{-1}\) close to 30\% of all data points would be in a gas transfer limiting regime.

We tested the new Re\(_{tr}\) parameterization against previously published data of DMS eddy covariance direct flux measurements (SOGasEx [Yang et al., 2011], Knorr11 [Bell et al., 2013], SOAP [Bell et al., 2015], this data set and Hiwings [Blomquist et al., 2017]). We should be able to calculate the transformed Reynolds number Re\(_{tr}\) for the wind-wave interactions during previous cruises and explain if they were in a gas transfer limiting or a non-limiting gas transfer regime. The Re\(_{tr}\) was calculated using wind speed, wind direction and the wave data from WWIII along the previous cruise tracks. As we do not
have information about exact measurement timing for the published cruise data sets, we cannot match their measured gas transfer velocities with $\text{Re}_{tr}$ in exact temporal space as in Figures 10 and 11. We can statistically determine the number of gas transfer limiting incidents at a certain wind speed at the general time and place of the cruises. The data of the five cruises (SOGasEx, Knorr11, SOAP, this data set and Hiwings) is shown in Figure 13. The left panels show the number of instances above or below the $\text{Re}_{tr}$ threshold. The right panels show the ratio as described by Equation 19. Additionally the $k$ wind speed relationship of the respective cruise is plotted. At the SOGasEx cruise (top right panel Figure 13), originally no suppression was present, but with the update by Blomquist et al. [2017] newly published data above 15 m s$^{-1}$ show gas transfer suppression. This can be supported by our $\text{Re}_{tr}$ reanalysis. The ratio of limiting to non-limiting instances stays below 0.2 (less than 20% of total instances) for most of the time and increases at a wind speed of 15 m s$^{-1}$ (grey shaded area). The ratio of the Knorr11 cruise peaks twice (gray shaded area), around 8 ms$^{-1}$ and between 12-18 m s$^{-1}$. At the same time the gas transfer velocity flattens and at the second incident even decreases. For SOAP, the gas suppression occurs between 10.5-15 m s$^{-1}$. The ratio-peak at 14 m s$^{-1}$ corresponds with a drop in the gas transfer velocity. The SOAP cruise is a special case, because the whole wind speed range was experienced several times during the cruise. Many instances of high winds without gas transfer suppression occurred, which drives down the ratio. For SO234-2/235, the suppression starts at 9.5 m s$^{-1}$, which is also coincident with an increase in the ratio. It seems that above the ratio of 0.2 suppressed gas transfer is highly likely. The Hiwings cruise includes DMS gas transfer velocities up to 19 m s$^{-1}$. They do not show signs of gas transfer suppression. This can be supported by the $\text{Re}_{tr}$ calculation.
The ratio stays below 0.2 at all times. This is an example that gas transfer suppression is not a general feature of high wind speed.

3.6. Bubble mediated gas transfer

In Figure 14, $k_b$ calculations using field data of $u_{10n}$, Sc, SST, and salinity are shown together with directly derived $k_{total}$ values. $k_{water}$ DMS [Goddijn-Murphy et al., 2012], modeled using measured $k_{total}$, is shown in Figure 14 (right panel). $k_{water}$ is on average 1.4 cm h$^{-1}$ higher than total measured $k_{total}$, because of air side resistance. The bubble component is commonly neglected in DMS gas transfer, but our calculations show a non-negligible contribution for stronger wind speed, which is confirmed by Blomquist et al. [2017]; at the high end of the range ($u_{10n} \approx 16$ m s$^{-1}$), we estimate $k_b$ to be 6, 11, and 17 cm h$^{-1}$ using W-parameterizations MAP, MM and SP respectively.

For $k_{water}$, the linear regression slope with $u_{10n}$ over the whole range was 2.0±0.2. The slope of $k_{water}$ is similar to the one derived by Marandino et al. [2009] and slightly lower than the one derived by Goddijn-Murphy et al. [2012] (Table 1). We subtracted the slopes of the three $k_b$ estimates (MAP 1.6 cm h$^{-1}$, MM 1.3 cm h$^{-1}$, SP 1.0 cm h$^{-1}$) from the slope of $k_{water}$ to derive $k_o$ (Equation 7). However, these regressions do not account for the two distinct wind speed regimes over (gas transfer suppression) and under 10 m s$^{-1}$ (Figure 8). Following Wanninkhof et al. [2009], we applied a 3rd degree polynomial fit to $k_{water}$ against $u_{10n}$ (Equation 6).

The same calculations were repeated for CO$_2$ (Figure 14, left panel), but we did not correct for air-side resistance as air-sea gas transfer of CO$_2$ is dominated by waterside resistance. Because CO$_2$ is less soluble than DMS, the bubble component of gas transfer
is expected to be more important (Figure 14, left panel). As explained in Section 2.3, $k_o$, scaled to a common Schmidt number, should be the same for DMS and CO$_2$.

$$\Delta k_{\text{water}} = \Delta k_{\text{total}} = (k_{o,CO_2} + k_{b,CO_2}) - (k_{o,DMS} + k_{b,DMS}) = k_{b,CO_2} - k_{b,DMS} \quad (20)$$

We also estimate $\Delta k_{\text{water}}$ using the hybrid model with the three whitecap parameterizations (Figure 14).

We applied separate fits of Equation 6 to DMS and CO$_2$ data, and subtracted the fit coefficients $p_i$ (Equations 21). The error $\Delta d_i$ was estimated by the hypotenuse of the individual uncertainties of the fit coefficients with 95% confidence bounds (Equation 22).

$$p_i = p_{i,CO_2} - p_{i,DMS} \quad (21)$$

$$\Delta d_i = \sqrt{\Delta p_{i,CO_2}^2 - \Delta p_{i,DMS}^2} \quad (22)$$

The results, coefficients and error estimates are shown in the supplement, show that there was no difference in the measured data.

The difference $\Delta k_{\text{water}}$ between concurrent (measured within 1 hour) DMS and CO$_2$ gas transfer velocity measurements vs $u_{10n}$ at $\text{Sc}=660$ is shown in Figure 15. The exponential fit by Bell et al. [2017] is added for comparison. The difference in calculation between the $\Delta k_{\text{water}}$ from Figure 15 (right) and the results from Equation 21 is that in the first case concurrent measurements were subtracted and then plotted vs wind speed. In latter case $k_{\text{water}}$ of CO$_2$ and DMS were separately fitted with a polynomial vs wind speed and then subtracted. Both methods show no significant difference between the data sets. Details are in the supplement.

An overlap of CO$_2$ and DMS transfer velocities up to 8 m s$^{-1}$ is also reported by Miller et al. [2009]. The data sets of Bell et al. [2017] and Blomquist et al. [2017] show a clear

©2018 American Geophysical Union. All Rights Reserved.
separation of CO$_2$ and DMS gas transfer velocities around 6 m s$^{-1}$. To show similarities and differences between the three data sets, we compiled the environmental conditions of these cruises in Table 2. Bell et al. [2017] and Blomquist et al. [2017] experienced the lowest temperatures and, therefore, the highest solubility of CO$_2$ in seawater. They also share a similar CO$_2$ flux magnitude which is different to Miller et al. [2009] and this study. The flux magnitudes reported by Bell et al. [2017]; Blomquist et al. [2017] are two times higher larger and only going into the sea surface. During Miller et al. [2009] and this study the ocean acts as both source and sink for CO$_2$. Memery and Merlivat [1985] proposed an asymmetry in the bubble mediated gas transfer. Flux into the ocean is more affected by bubbles than flux out of the ocean. A change in flux direction could therefore support and overlap of DMS and CO$_2$ flux values.

From this comparison we hypothesize an unknown influence of solubility or an unaccounted influence of the flux magnitude and direction on the bubble mediated gas transfer. Further measurements of both gases simultaneously, under a range of environmental conditions, are needed to elucidate the underlying processes.

4. Conclusion

We directly measured DMS and CO$_2$ fluxes in the Indian Ocean and derived gas transfer velocities for both gases. There have only been three previous directly measured CO$_2$ and DMS flux and k comparisons before this one ([Miller et al., 2009; Bell et al., 2017; Blomquist et al., 2017]). The DMS gas transfer relationship k vs u appears to be a linear relationship, whereas the CO$_2$ relationship appears to be related to the N00 parameterization, which is a quadratic function. However, both data sets hint to a suppression of gas transfer at high wind speed.

©2018 American Geophysical Union. All Rights Reserved.
We report a gas transfer suppression above 11 m s\(^{-1}\) and propose a mechanism parameterized by the transformed Reynolds number \(Re_{tr}\). The mechanism is based on wind-wave interaction and is most importantly dependent on the relative velocities of the wave and the wind. The parameterization is verified using this data set and previously published gas transfer velocities. We suggest a threshold of \(|Re_{tr}| = 6.96 \cdot 10^5\) when gas transfer suppression occurs. \(Re_{tr}\) can be easily calculated during research cruises as well analyzed for previous cruises to assess the influence of wind-wave interactions. This parameter can also be used to predict gas transfer suppression using weather and wave forecast models.

The \(k_b\) wind speed dependence of this study can the findings of Bell et al. [2017]. At low to medium wind speed the gas transfer velocity of DMS is higher than CO\(_2\). \(\Delta k_{\text{water}}\) data of Figure 15 supports this conclusion. For \(\Delta k_{\text{water}}\) in this figure the fit by Bell et al. [2017] is an upper boundary. We report generally lower \(\Delta k_{\text{water}}\) values vs wind speed and a large number of negative values.

Our results in combination with previous studies show that direct gas transfer measurements of two or more gases are necessary to understand and pinpoint processes influencing air-sea gas exchange. These processes have to be taken into account in established gas transfer parameterizations. This is especially important for the quantification of bubble-mediated gas transfer. Interfacial gas transfer velocities \(k_o\) from gases with a negligible bubble-mediated transfer can be used to understand the effect of gas transfer suppression, as suppression seems to affect \(k_o\) only. Calculating gas fluxes using the bulk formula (Equation 1) and usual gas transfer velocity parameterizations might lead to an overestimation due to unaccounted gas transfer suppression events.
Appendix A: Galilean transformation and the Navier-Stokes Equation

A coordinate transformation is a way of simplifying forces, velocities and boundary conditions. It is important that conservation laws and physical principles are conserved and obeyed, which we achieve using a Galilean transformation. The Galilean transformation is a transformation into a different inertial system. This means that no external forces or pseudo forces have to be considered. Forces, that apply in the original frame of reference, apply the same way in the new frame of reference. Any transformation to a rotating (Coriolis force) or accelerated (inertia) reference system will result in the introduction of pseudo forces.

The Navier-Stoke Equation (NSE), Equation A1, is the fundamental equation that describes the flow and turbulence of, in this case, incompressible fluids. $u$ is the velocity vector in three dimensions, $x$ is the coordinate, $\nu$ the kinematic viscosity and $p$ the pressure field.

$$\frac{\partial u_i}{\partial t} + u_i \cdot \nabla u_i = -\frac{1}{\rho} \frac{\partial p}{\partial x_i} + \nu \cdot \nabla^2 u_i$$ (A1)

The NSE is invariant under the Galilean transformation [McComb, 2005] given in Equation A2, where $c$ is the constant transformation velocity and $\tilde{x}_i$, $\tilde{u}_i$ are the respective coordinate and velocity vectors in the transformed system.

$$x_i = c \cdot t + \tilde{x}_i$$

$$u_i = c + \tilde{u}_i$$ (A2)

©2018 American Geophysical Union. All Rights Reserved.
Appendix B: Reynolds number

The Reynolds number is derived from the NSE (Equation A1) equation by choosing scaling factors which introduce non-dimensional quantities. Velocity \( u \), position \( x \) and their deduced properties are scaled by the respective velocity and length scale \( V \) and \( L \) (Equations B1 -B5).

\[
\hat{u} = \frac{u}{V} \tag{B1}
\]
\[
\hat{x} = \frac{x}{L} \tag{B2}
\]
\[
\hat{p} = \frac{p}{\rho V^2} \tag{B3}
\]
\[
\frac{\partial}{\partial t} = \frac{L}{V} \frac{\partial}{\partial t} \tag{B4}
\]
\[
\hat{\nabla} = L \nabla \tag{B5}
\]

Inserting this into Equation A1 leads to

\[
\frac{V^2}{L} \frac{\partial \hat{u}}{\partial t} + \frac{V^2}{L} \hat{u} \nabla \hat{u} = -\frac{1}{\rho} \frac{\rho V^2}{L} \frac{\hat{p}}{\partial \hat{x}} + \nu \frac{V}{L^2} \hat{\nabla}^2 \hat{u} \tag{B6}
\]

Multiplying Equation B6 by \( \frac{L}{V^2} \) provides the non-dimensional Reynolds number \( \frac{V \cdot L}{\nu} \) which scales the diffusion term (Equation B7).

\[
\frac{\partial \hat{u}}{\partial t} + \hat{u} \nabla \hat{u} = -\frac{\hat{p}}{\partial \hat{x}} + \nu \frac{V}{L} \hat{\nabla}^2 \hat{u} \tag{B7}
\]

The Reynolds number is deduced directly from the NSE independent of the reference system and, therefore, also invariant under a Galilean transformation. The factor \( \cos(\theta) \), where \( \theta \) is the angle between the wind and the wave, is added for describing directional dependencies of the wave height. It is applied in the new reference frame [Högström et al., 2011] and, therefore, does not interfere with the transformation. We use the kinematic viscosity of air. Zhao and Toba [2001] use the kinematic viscosity of water. We think.
this is mathematically incorrect. It violates the spatial integrity of the NSE. Zhao and Toba [2001] use the NSE air but the viscosity of the water. However, \( \nu_{\text{water}} \) and \( \nu_{\text{air}} \) are at the surface interface only different by a constant factor, which would just shift the Reynolds number scale by a constant factor. Nonetheless, we want to compare the Reynolds number to already established air-flow models (for example, air flow around a sphere) and therefore think it is important to use \( \nu_{\text{air}} \).

**Appendix C: Calculation of Re_{tr}**

Figure 16 shows the transformation of the wind in the earth’s reference system \( u_{10n} \) (solid arrow) into the wave’s reference system \( u_{tr} \) (dotted arrow). The wave is traveling from right to left as seen in the wave’s phase speed vector \( c_{p} \) (dashed arrow). \( \theta \) is the angle between \( u_{tr} \) and \( c_{p} \).

The vectorial components of \( u_{tr} \) can be calculated using Equation C1

\[
\begin{pmatrix}
  u_{tr,x} \\
  u_{tr,y}
\end{pmatrix} =
\begin{pmatrix}
  u_{10,x} \\
  u_{10,y}
\end{pmatrix} -
\begin{pmatrix}
  c_{p,x} \\
  c_{p,y}
\end{pmatrix}
\]  

Using the vector \( u_{tr}^* \), the absolute wind speed in the wave’s reference system is

\[
u_{tr} = \sqrt{u_{tr,x}^2 + u_{tr,y}^2} \tag{C2}\]

\( \theta \) can be calculated using the dot product (Equation C3).

\[
\begin{pmatrix}
  u_{tr,x} \\
  u_{tr,y}
\end{pmatrix} \cdot \begin{pmatrix}
  c_{p,x} \\
  c_{p,y}
\end{pmatrix} = \cos(\theta) \cdot |u_{tr}^*| \cdot |c_{p}^*| \tag{C3}\]

The transformed Reynolds number \( Re_{tr} \) is then

\[
Re_{tr} = \frac{u_{tr} \cdot H_s}{\nu_{air} \cdot \cos(\theta)} \tag{C4}\]
Appendix D: Wave age

Previously used wind-wave interaction parameters such as wave age $w_a$ (Equations D1-D2) include absolute values of wind speed $u_{10n}$ and $c_p$ wave’s phase velocity. They do not represent a Galilean transformation and do not provide a vector representation of the interacting velocities and are, therefore, not suitable for describing the wind-wave interactions. Using the directional factor $\cos(\theta)$ in the Equations (Equations D1-D2) introduces some directional dependencies, but is not a substitute for a complete vector representation.

\[
\begin{align*}
    w_a &= \frac{c_p}{u_{10}} \\
    w_a &= \frac{c_p}{u_{10} \cdot \cos(\theta)} \quad \text{(D1)} \\
    w_a &= \frac{c_p}{u^*} \\
    w_a &= \frac{c_p}{u^* \cdot \cos(\theta)} \quad \text{(D2)}
\end{align*}
\]

Parameterizations based on the friction velocity $u^*$, such as Toba’s Reynolds number $Re_{Toba}$, are invariant under the Galilean transformation. McComb [2005] states that turbulence and velocity fluctuations are automatically Galilean invariant, as they are differences. However, they lack the wind-wave interaction as they describe only the turbulence of the wind field.

Appendix E: Threshold

Figure 17 shows the cumulative residuals of the measured DMS and CO$_2$ transfer velocities vs the linear fit for DMS and N00 for CO$_2$. The residuals are plotted versus $Re_{tr}$. The cumulative residual value (y-axis) is the sum of all residuals with a $Re_{tr}$ smaller than the x-axis value. For DMS, the residual is the difference between the measured gas...
transfer velocities and the linear fit shown in Figure 10 of the main manuscript. For CO$_2$, the reference is the N00 parameterization shown in Figure 11. The first distinct local minimum ($Re_{re} = 6.9 \cdot 10^5$) is used as a threshold between suppressed and non-suppressed gas transfer velocities. Transformed Reynolds numbers to the left of the threshold (red line) are significantly lower than the fit. The line tends to stay horizontal to the right of the threshold, which indicates an even distribution around the fit. The threshold is determined from the DMS data set because it is less influenced by bubble mediated gas transfer.

Figure 18 shows the individual residuals between the measured DMS and CO$_2$ gas transfer velocities and the fits in Figures 10 and 11 of the main manuscript. The vertical line denotes the threshold between suppressed and non-suppressed gas transfer velocities.

Acknowledgments. The authors thank Kirstin Krüger, the chief scientist of the RV Sonne cruise (SO234-2/235), as well as the captain and crew. E. Atlas helped in measuring the canister samples. Dennis Booge measured the DMS seawater concentration. We thank the Environmental Modeling Center at the NOAA/National Weather Service for providing the WaveWatch III data. This work was carried out under the Helmholtz Young Investigator Group of C. Marandino, TRASE-EC (VH-NG-819), from the Helmholtz Association. L. M. Goddijn-Murphy acknowledges support from the European Space Agency (ESA) Support to Science Element (STSE) projects OceanFlux Greenhouse Gases (contract 4000104762/11/I-AM) and OceanFlux GHG Evolution (4000112091/14/I-LG). The cruise 234-2/235 was financed by the BMBF, 03G0235A. The authors declare no competing financial interests. The data is stored at the data portal of GEOMAR Kiel and can be accessed through http://portal.geomar.de .
References


©2018 American Geophysical Union. All Rights Reserved.


©2018 American Geophysical Union. All Rights Reserved.


Shapiro, A. (1961), *Shape and Flow*, Heinemann, Garden City, N.Y.


©2018 American Geophysical Union. All Rights Reserved.


©2018 American Geophysical Union. All Rights Reserved.


Zavarsky, A., D. Booge, A. Fiehn, K. Krger, E. Atlas, and C. Marandino (2017), The influence of air-sea fluxes on atmospheric aerosols during the summer monsoon over the


Table 1. Equations of the linear fits to the DMS k vs wind speed transfer velocity. $r^2$ and the root mean square error (RMSE) are shown in the last two columns. Marandino et al. [2009] and the top three parameterizations are shown in Figure 8. Goddijn-Murphy et al. [2012] is added to this table as a comparison.

<table>
<thead>
<tr>
<th>fit</th>
<th>$k_{660}$ [cm h$^{-1}$]</th>
<th>$r^2$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>linear fit to all</td>
<td>$k_{\text{total}} = 2 \cdot u_{10n} + 0.94$</td>
<td>0.89</td>
<td>1.5</td>
</tr>
<tr>
<td>linear fit $\dot{\gamma}10$ m s$^{-1}$</td>
<td>$k_{\text{total}} = 3.1 \cdot u_{10n} - 5.37$</td>
<td>0.98</td>
<td>0.29</td>
</tr>
<tr>
<td>linear fit $\ddot{\gamma}10$ m s$^{-1}$</td>
<td>$k_{\text{total}} = 1.13 \cdot u_{10n} + 12$</td>
<td>0.37</td>
<td>1.81</td>
</tr>
<tr>
<td>Marandino et al. [2009]</td>
<td>$k_{\text{total}} = 2 \cdot u_{10n} + 1$</td>
<td>0.126</td>
<td>1.563</td>
</tr>
<tr>
<td>Goddijn-Murphy et al. [2012]</td>
<td>$k_{\text{total}} = 2.4 \cdot u_{10n} - 5$</td>
<td>N/A</td>
<td>4.044</td>
</tr>
<tr>
<td>Goddijn-Murphy et al. [2012]</td>
<td>$k_{\text{water}} = 2.6 \cdot u_{10n} - 5.7$</td>
<td>N/A</td>
<td>4.021</td>
</tr>
</tbody>
</table>
Table 2. Comparison of CO₂, during which DMS was simultaneously measured, gas transfer velocity measurement campaigns. 'In' and 'out' denote values at conditions of oceanic uptake of CO₂ (in) and oceanic outgassing of CO₂ (out).

<table>
<thead>
<tr>
<th>property</th>
<th>Miller et al. [2009]</th>
<th>Bell et al. [2017]</th>
<th>Blomquist et al. [2017]</th>
<th>this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>SST[°C] min/avg/max</td>
<td>9 / 13 / 20</td>
<td>7 / 10 / 19</td>
<td>2 / 11 / 21</td>
<td>19 / 22</td>
</tr>
<tr>
<td>Wind speed[m s⁻¹] avg/max</td>
<td>6.7 / 11.5</td>
<td>8.9 / 19.4</td>
<td>11.4 / 24.3</td>
<td>8.9 / 15.8</td>
</tr>
<tr>
<td>ΔpCO₂[μatm] avg</td>
<td>-55.2</td>
<td>-60</td>
<td>-38.1</td>
<td>-30.6 (in)</td>
</tr>
<tr>
<td>CO₂ flux [mol m⁻² y⁻¹] avg</td>
<td>-3.3 (in) / 1.7 (out)</td>
<td>-7</td>
<td>-7.1</td>
<td>-2.3 (in) / 1.7 (out)</td>
</tr>
</tbody>
</table>
Figure 1. Cruise track with day of year (DOY) 2014 indicated. The mean SST, from ERA-interim, for the times of the cruise is color coded in the background.
Figure 2. Boundary layer properties during the cruise. [A] Wind speed measured by the sonic anemometer and wind speed measured by the ship’s meteorological station. Both values were corrected using COARE to 10 m neutral wind speed. [B] Friction velocity retrieved directly by the eddy covariance (EC) system (blue) and the COARE algorithm (red) using the ship’s met station data. [C] Monin-Obhukov stability parameter. [D] Relative humidity (red) and rain rate (blue).
Figure 3. Sea surface properties. [A] Air temperature (red) and SST (blue) [B] Salinity. [C] DMS water concentration (blue) and air mixing ratio (red). [D] CO₂ partial pressure difference between atmosphere and surface water.
Figure 4. Fluxes and gas transfer velocities. [A] DMS flux [B] CO$_2$ flux [C] CO$_2$ gas transfer velocity [D] DMS gas transfer velocity.
Figure 5. Measured air-sea CO$_2$ partial pressure difference between air and water (red). Negative values denote undersaturation of the ocean with respect to the atmosphere. Climatological partial pressure difference between air and water (black) by Takahashi et al. [2009]
Figure 6. DMS gas transfer velocities versus wind speed. The DMS water concentration is color coded and the binned gas transfer velocity is plotted as a solid line. The dashed line is the Nightingale et al. [2000] parameterization as reference. Error bars denote the standard deviation of the gas transfer velocities within the bin.
Figure 7. CO₂ gas transfer velocities versus wind speed. The CO₂ partial pressure difference is color coded and the binned gas transfer velocity is plotted as a solid line. The dashed line is the Nightingale et al. [2000] parameterization for reference. Error bars denote the standard deviation of the gas transfer velocities within the bin.
Figure 8. Binned (size 1 ms$^{-1}$) DMS gas transfer velocities and linear fits of the binned data below 10 m s$^{-1}$ and above 10 ms$^{-1}$. An overall fit and the linear parameterization, updated from Marandino et al. [2009], is added.
Figure 9. Binned gas transfer velocities of DMS and CO₂ (solid line with markers) vs wind speed. The DMS gas transfer velocity is fitted with a linear relationship (black solid line), the CO₂ transfer velocity is fitted with a quadratic relationship (red solid line). The dashed lines represent the area of 50% fit probability.
Figure 10. Influence of wind-wave interaction on DMS gas transfer. [Left] Suppressed transfer velocities ($|\text{Re}_{tr}| < 6.96 \cdot 10^5$) measured during SO234-2/235. [Right] Non-suppressed transfer velocities ($|\text{Re}_{tr}| > 6.96 \cdot 10^5$). For comparison a linear fit through the non-suppressed transfer velocities is added to both panels. The color shows the transformed Reynolds number $\text{Re}_{tr}$. ©2018 American Geophysical Union. All Rights Reserved.
Figure 11. Influence of wind-wave interaction on CO$_2$ gas transfer. [Left] Suppressed transfer velocities ($|Re_{tr}| < 6.96 \times 10^5$) measured during SO234-2/235. [Right] Non-suppressed transfer velocities ($|Re_{tr}| > 6.96 \times 10^5$). For comparison the N00 parameterization is added to both panels. The color shows the transformed Reynolds number $Re_{tr}$. ©2018 American Geophysical Union. All Rights Reserved.
Figure 12. We used the global 2014 WWIII data to calculate the transformed Reynolds number. [Right] The global 2014 probability density for the $Re_{tr}$ parameter with respect to wind speed. The suppressed gas transfer regime is between the dashed and solid white lines. [Left] The ratio of non-suppressing (outside the white lines) to suppressing (between the white lines) incidents over wind speed.
Figure 13. A statistical analysis of DMS gas transfer velocity suppression for three previously published cruises and this data set. All data sets are based on eddy covariance fluxes and show DMS gas transfer velocities. The left panel shows the absolute numbers of limiting (dashed) and non-limiting (solid) occurrences, the right panel shows the ratio (solid) of limiting occurrences to the total occurrences. The gas transfer velocity measured at these cruises is shown in the right panel as a dashed line. The grey areas denote the occurrence of gas transfer suppression. The data sets are SOGasEx [Yang et al., 2011] with an update by Blomquist et al. [2017], Knorr11 [Bell et al., 2013], SOAP [Bell et al., 2015], this data set (SO 234-2/235) and Hiwings Blomquist et al. [2017].
Figure 14. Gas transfer velocity scaled to $Sc=660$ as a function of $u_{10n}$ for CO$_2$ [left], and DMS [right]. Water side gas transfer (black), total gas transfer for DMS (green), and bubble mediated gas transfer, $k_b$, derived using the independent bubble model and W parameterizations of MAP, MM and SP, in red, blue and cyan, respectively. Measured water side data are binned in 1 m s$^{-1}$ $u_{10n}$ bins. Solid lines are 3rd degree polynomial fits to the measured water side data. The dashed line in the left CO$_2$ plot is the polynomial fit from the right panel.
Figure 15. Time series of $\Delta k_{water}$ of concurrent (measured within 1 hour) CO$_2$ and DMS measurements [left panel]. $\Delta k_{water}$ of the same data set vs wind speed [right panel]. The solid line in the right panel is the fit by Bell et al. [2017].
Figure 16. Schematic of the transformation of the wind $u_{10n}$ (solid arrows) in the Earth’s reference system into the wave’s reference system $u_{tr}$ (dotted arrows). The wave travels from left to right. The dashed vertical lines denote the wave’s crests. $\theta$ is the angle between the phase speed $c_p$ (dashed arrows) and $u_{tr}$. 

©2018 American Geophysical Union. All Rights Reserved.
Figure 17. The cumulative sum of the residuals between measured DMS and CO$_2$ gas transfer velocity and the fits shown in Figures 10 and 11 of the main manuscript. The x-axis is the transformed Reynolds number. The threshold between suppressed and non-suppressed gas transfer velocities is set to the first local minimum of the DMS residual. The red line denotes the Re$_{tr}$ value of the threshold.
Figure 18. The residuals between the individual measured DMS and CO₂ gas transfer velocities and the fits shown in Figures 10 and 11. The x-axis is the transformed Reynolds number. The vertical line denotes the used threshold $Re_{tr} = 6.96 \cdot 10^5$ between suppressed and non-suppressed gas transfer velocities.