Chapter 7
The Role of Physical Chemical Properties of Gases in Whitecap Facilitated Gas Transfer

Penny Vlahos and Edward C. Monahan

Abstract Air-sea gas exchange is one of the most important processes that controls both biogeochemical cycles and the earth's climate. The need to accurately quantifying gas exchange under the range of temperatures, wind speeds and gases has been recognized as a priority over the last three decades and parameterizations have improved over this period. To date however, there remains a concern of applying parameterizations tuned to a subset of gases broadly to many gases. Here we present some of the physical chemical differences across gases that when considered could lead to better gas flux estimates and improve the margins of error in air-sea gas exchange.

7.1 Introduction

The ocean-atmosphere boundary layer has a crucial role in regulating earth's climate, however currently, global climate models are unable to capture many key physical and chemical processes in the ocean-atmospheric system (Rosenfeld et al. 2014). Significant improvements have been made over the last 30 years though much work is still needed to shift from empirically to theoretically based models.

Gas transfer across the air-sea interface is proportional to the concentration gradient of a gas i in air (C_{ia}) and water (C_{iw}) and a transfer velocity k

$$F = k\Delta C_{iaw} \tag{7.1}$$

The transfer velocity depends on the gas in question, the media it is moving through and the thickness of the boundary layer. The exact expression for k has case specific forms that include

---

P. Vlahos (✉) · E. C. Monahan
Department of Marine Sciences, University of Connecticut, Mansfield, USA
e-mail: Penny.vlahos@uconn.edu

P. Vlahos (ed.), *Recent Advances in the Study of Oceanic Whitecaps*,
https://doi.org/10.1007/978-3-030-36371-0_7

$$k = D_i/z \tag{7.2}$$

the diffusion coefficient of i in water D_i and boundary layer thickness z which applies well to continuous quiescent (flat) interfaces where wind speeds (u) are <3 m/s. The most commonly used expression in air-ocean transfer is based on a k that is proportional to the water-side friction velocity u_* and the dimensionless Schmidt number $Sc = \nu / D_i$ where ν is the kinematic viscosity of water wherein

$$k = u * Sc^{-n} \tag{7.3}$$

In this expression the exponent n depends on the sea state where n = 2/3 for a continuous but wavy water surface and n = 1/2 for a discontinuous rough surface.

By rearranging these expressions for k we find that

$$z = Di^{(1-n)} v^n / u* \tag{7.4}$$

and therefore u_* and z are inversely proportional. The values for D_i and ν are based on certain assumptions, that is, for a given temperature and pressure, assuming ideal solutions where i is the gas and w is a homogeneous solution of water (or seawater) and i and w do not interact with one another.

Over the past century investigators have modeled gas exchange in both experimental and field settings and have produced several versions of Eq. 7.3 such that

$$k = \alpha U^b \tag{7.5}$$

The values for a and b are usually derived from direct observation of a specific gas and the Sc number is absorbed in the proportionality constant α (Table 7.1).

Table 7.1 Frequently cited parameterizations that have been applied to gas exchange studies over the last 40 years (U_{10} is the wind speed or wind speed equivalent, measured 10 m above the sea surface)

	Parameterization $k(cmh^{-1})$	Gases	Source
Freshwater	$k = 0.36(4.1 + 0.417\ U^2{}_{10})^{0.5} U_{10}$	CO_2	Kanwisher (1963)
Freshwater	$k = 0.63(6.1 + 0.63\ U_{10})^{0.5} U_{10}$	O_2	Mackay and Yeun (1983)
Seawater	$k = 0.17\ U_{10}$ if $U_{10} < 3.6\ ms^{-1}$ $k = 2.85\ U_{10} – 9.65$ if $3.6 < U_{10} < 13\ ms^{-1}$ $k = 5.9\ U_{10} – 49.3$ if $U_{10} > 13\ ms^{-1}$	CO_2	Liss and Merlivat (1986)
Freshwater	$k = 1.024^{(Tw\text{-}10C)}(4.2 \times 10^{-6}\ U_{10}^{0.5})$ if $U_{10} < 5.5\ ms^{-1}$ $k = 1.024^{(Tw\text{-}10C)}(0.32 \times 10^{-6}\ U_{10}^{2})$ if $U_{10} > 5.5\ ms^{-1}$	O_2	Banks (1975)
Seawater	$k = 0.31\ U_{10}^{2}(Sc/660)^{-1/2}$	CO_2	Wanninkhof (1992)
Seawater	$k = (0.029\ U_{10}^{3} + 5.4)(660/Sc)^{0.5}$	CO_2	Edson (2011)
Seawater	$k = 0.251\ U_{10}^{2}(Sc/660)^{-1/2}$	CO_2	Wanninkhof (2014)

Generally, these dependencies have evolved from lab to field-based concentration gradients to eddy diffusivity methods (Fairall et al. 2000) and will continue to evolve with improved higher resolution measurements as they emerge. What is evident in these parameterizations is that they are primarily governed by the physical field (wind speed) and chemical differences among diffusing gases are absorbed in parameterization constants.

7.2 Chemical Properties

Investigators have long recognized that utilizing parameterizations derived for specific gases does not account for chemical enhancement effects including the direct reaction of ammonia and carbon dioxide gases with water to produce ammonium and carbonic acid (Johnson 2010). These chemical reactions should be considered on an individual gas basis. There are also physical-chemical differences among gases that may impact their air-water gas exchange relative to other gases. Some of these include:

7.2.1 Size and Geometry

The larger the molecule, the larger the diffusional cross section and therefore the more water or air that needs to be displaced. This is largely accounted for in D_i. The geometry of a molecule greatly impacts it effective radius as it diffuses and the more irregular the geometry, the more orientation can impact exchange and is less constrained in D_i. Table 7.2 summarizes a representative list of diffusion coefficients for common gases in seawater.

Table 7.2 Diffusion coefficients for common gases in water at 25 °C in seawater

Gas	Molecular weight (g/mol)	Approximate diameter (10^{-10}m)	$D_i(cm^2s^{-1})$	Source
He	4.002	0.62	8.03×10^{-5}	Jahne et al. (1987)
H_2	2.016	1.24	4.91×10^{-5}	Jahne et al. (1987)
N_2	14.01	2.38	2.00×10^{-5}	Jahne et al. (1987)
O_2	32.00	2.28	2.42×10^{-5}	Jahne et al. (1987)
Ar	39.95	2.00	2.50×10^{-5}	Jahne et al. (1987)
CO_2	44.01	2.36	1.91×10^{-5}	Zeebe et al. (2011)
DMS	62.13	3.08	1.34×10^{-5}	Saltzman et al. (1993)

7.2.2 Polarity

Whether a molecule is polar, non-polar or as is often the case amphiphilic (has both polar and non-polar parts) will have significant impact on its mobility in water. Polar-molecules may interact with surrounding water molecules and ions and therefore do not acting as an "ideal" non-interacting mixture would assume. Non-polar molecules are less interactive with their surrounding media but require more energy to be dissolved in water and displace existing hydrogen bonds between water molecules. Often these molecules tend to seek "lower" energy environments such as the air sea boundary layer where fewer water molecules require displacement.

7.2.3 Solubility & Vapor Pressure

Similarly, solubility is extremely important in air water exchange. Gases that are highly soluble will tend to remain in solution and less likely to move into air whereas gases that are less soluble will tend to seek a phase where less energy is required to accommodate it. Each gas has a unique solubility dependence in water with respect to changes in temperature and salinity and this is well described in Wanninkhof (1992) for several common gases.

7.2.4 Henry's Law Constant

Ultimately it is the ratio of preference in air to preference in water (vapor pressure/solubility) that determines a gas's likelihood to remain in or evade bulk seawater. For example, a substance may have both low solubility and low vapor pressure but the ratio of the two determines the relative preferred state. Table 7.3 summarizes these parameters for common gases at 25 °C. Note, all of these gases have very low solubilities relative to vapor pressure and therefore encounter the majority of their resistence to air-sea gas transfer in the water phase. These gases are "water-side controlled".

Table 7.3 Henry's Law Constants for common gases at 25 °C (Sander 2015)

Gas	K_H(mol/(m^{3}Pa))
H_2	7.7×10^{-6}
O_2	1.3×10^{-5}
N_2	6.4×10^{-6}
CO_2	3.4×10^{-5}
He	3.8×10^{-6}
Ar	1.4×10^{-5}

7.3 The Altered Sea State

At high wind speeds (ie >15 m/s) the sea state is altered sufficiently that there is a regular discontinuity in the surface resulting in whitecaps and bubbles and a surface ocean that has a corresponding steady state concentration of bubbles, particularly in the top 10 m. These discontinuities markedly increase the air-water surface area through both bubbles on the water side and sea spray on the air side. The extent of surface area of the air-water interface has been constrained as both a bubble surface area (Vlahos and Monahan, 2009) and sea spray surface area (Monahan et al. 2017). The increase in the air water boundary layer can be estimated by Eq. 7.6 for entrained bubbles (Φ_B).

$$\Phi_B = 0.090 \times (U_{10}/10)^3 \qquad \text{in m}^2\text{per m}^2\text{sea surface} \tag{7.6}$$

At a given wind speed (U_{10}, ms^{-1}), the total air-water surface area added by bubbles is Φ_B. Therefore the at wind speeds of 10 ms^{-1}, average aggregate bubble area beneath a square meter of sea surface is estimated to be 0.090 m^2 and the total air-water surface area is 1.09 m^2. At wind speeds of 18 ms^{-1} Φ_B is 0.52 and the air-water boundary surface area beneath 1 m^2 of ocean surface reaches 52%. The total air-water surface area A becomes 1 + 0.52 or 1.52 m^2 per m^2 sea surface. Therefore it is at high wind speeds where data is curently severley lacking, that these phenomena are expected to become significant.

Vlahos and Monahan (2009) argue that this altered sea state (>18 ms^{-1}) significantly changes the effective solubility of a dissolved compound, particularly if it is bipolar or amphiphilic and is likely to adhere to, and be more impacted by, the air-water interface (Fig. 7.1). To account for this influence on gas exchange they

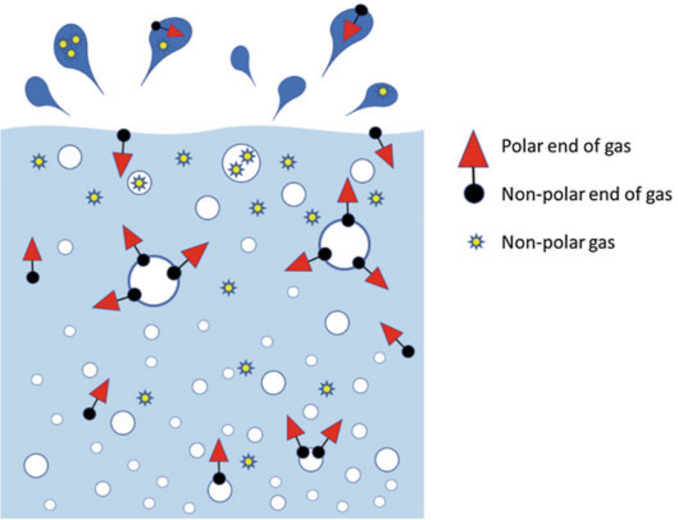

Fig. 7.1 Schematic of how bubbles and sea spray extent the air-water boundary layer and offer an extended interface for molecules to diffuse through and adsorb to

suggest using an effective solubility that considers sorption to the interface. Therefore, for surface active gases this alters the apparent solubility and would attenuate gas exchange (see eqs. 11 and 12 in Vlahos and Monahan (2009)). This shift in gas exchange would be as long lived as the sustained wind events.

Sea spray surface area is a secondary process that extents the air-sea boundary layer which becomes significant above 15 ms^{-1} as is inferred from Fig. 2 in Monahan et al. (2017). See in particular the curve on this figure derived from Anguelova et al. (2019). The volume fluxes of sea spray are reasonably constrained in terms of winds speed however the actual surface area of the droplets is dependent on the time aloft and net evaporation that may occur (primarily driven by relative humidity) and more work is needed to establish a relationship for sea spray that is equivalent to Eq. 7.6. The role of sea spray in gas transfer is expended upon in Chap. 9 by Staniec et al.

In addition to the formation of entrained air and spray, it is also important to know the actual residence time of these phenomena in order to properly constrain their impact.

7.4 NOAA COARE Model

The Coupled Ocean-Atmosphere Response Experiment (COARE) (Fairall et al. 2011) is one of the most comprehensive gas exchange models to date and has been tuned to 79 gases. The algorithm has high accuracy between wind speeds of 2-18 ms^{-1} and is less certain at higher windspeeds primarily due to a lack of field data. The algorithm includes bubble driven transfer from Woolf (1997) though sea spray is not currently included. The model is based on CO_2 parameterizations but has been extended to include reactive species in eq. 18 of Fairall et al. (2011) and chemical parameterizations of Johnson (2010) and Rowe et al. (2011) that consider gas solubility and diffusivities. Though these inclusions present an important first step in improving gas specific gas transfer rates, there remains a need to consider polarity and surface activity (i.e. an affinity for interfaces), particularly for volatile organic compounds, which changes the effective solubility of a molecule in turbulent bubble containing waters (Vlahos and Monahan 2009).

7.5 Field Data

Field studies have compared CO_2 (non-polar) and DMS (polar) gas exchange in several regions. Bell et al. (2013) performed measurements in the North Atlantic and found that although DMS transfer velocities varied linearly with wind speed up to 11 ms^{-1}, at high wind speeds fluxes were lower than predicted and the linear relationship failed. Interestingly, the heat transfer coefficient did not have this trend but rather continued to increase linearly. The authors attribute this to the interfacial control of DMS gas transfer. Figure 7.2 below appears as Figures 3 and 7 in Bell et al. (2013) and shows that DMS fluxes diverge most under conditions of high significant wave height and % whitecap coverage (a proxy for bubbles). The figures also show significant departures between CO_2 and DMS at high wind speeds (Fig. 7.2c) and clear consensus across DMS studies (Fig. 7.2d).

In the Southern Ocean Yang et al. (2011) also found lower transfer velocities for DMS than those predicted and reported in warmer regions. The authors found that normalizing to temperature could account for some of these regional differences though this was not pronounced for other gases such as CO_2. Here too the increased solubility of DMS was considered the primary factor controlling this attenuation of

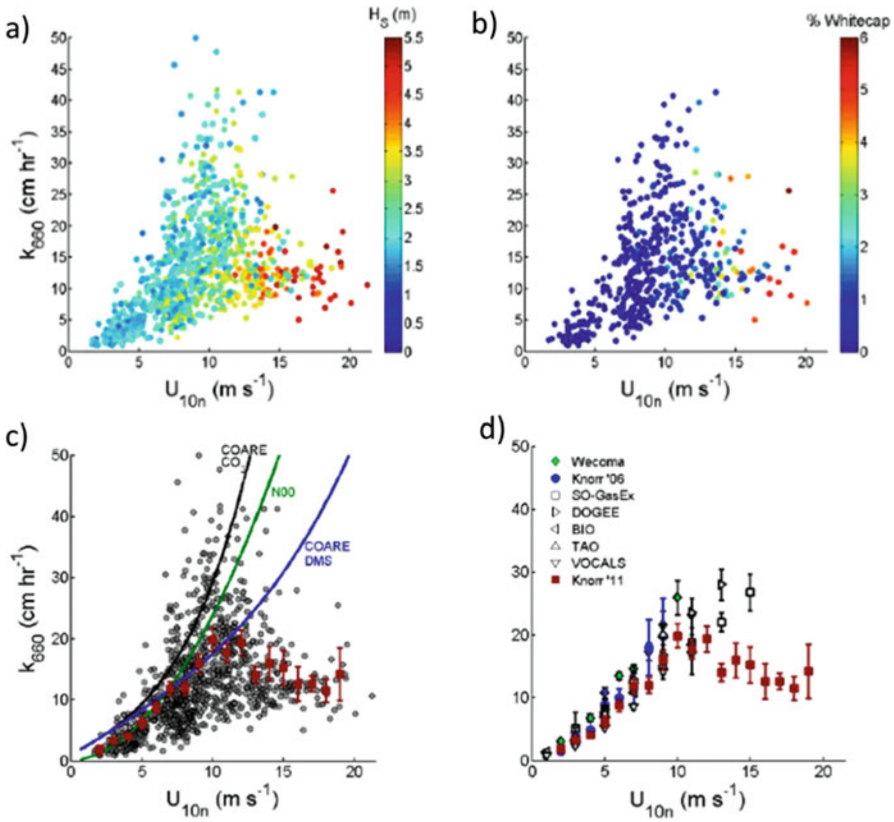

Fig. 7.2 From Bell et al. (2013): Gas transfer coefficient of DMS plotted as a function of wind speed (**a**) symbol color indicates significant wave height (**b**) color indicates % whitecap coverage (**c**) mean DMS transfer coefficients (red squares) and ± std. error compared to predicted values using NOAA COARE model for CO_2, DMS and the Nightingale et al. (2000) parameterization (NOO) (**d**) average transfer coefficients across other DMS eddy covariance methods (Wecoma – Marandino et al. 2007; Knorr_06 – Marandino et al. 2008; SO-Gas-Ex – Yang et al. 2011; DOGEE – Huebert et al. 2010; BIO – Blomquist et al. 2006; TAO – Huebert et al. 2004; VOCALS – Yang et al. 2011)

DMS gas exchange. This regional difference is consistent with white capping and therefore bubble plume differences in colder versus warmer latitudes at a given wind speed, addressed in Chap. 4 of this book.

Finally, satellite-based retrievals of air-sea gas transfer velocities are emerging and offer promise for capturing remote and high wind gas exchange. Frew et al. (2007) developed a scatterometer-based algorithm from QuikSCAT normalized radar backscatter to estimate gas transfer velocity via remotely sensed sea surface roughness. Goddijn-Murphy et al. (2012) compared satellite altimeter backscattering with eddy covariance measurements taken in the field to predict DMS gas transfer. Their results were comparable to those obtained from wind speed over the wind ranges studied. It is reasonable to expect that these remote sensing applications will lead to advances in air sea gas exchange.

7.6 Conclusions

As our sampling ability improves, so does our understanding of air sea gas exchange and the differences among gases. To date the most comprehensive model is the NOAA COARE model in its most recent form as described above. It is likely that over the next two decades, highly resolved measurements will lead to gas exchange parameterizations that are based on physical-chemical properties of gases. In addition, the role of sea spray and other turbulent phenomena at high wind speeds should be prioritized as these are currently not well constrained and observations are severely lacking.

Acknowledgements The authors would like to acknowledge funding from the National Science Foundation grant numbers 1356541 and 1630846.

References

Anguelova, M., Barber, R. P., Jr., & Wu, J. (2019). Spume drops produced by the wind tearing of wave crests. *Journal of Physical Oceanography, 29*, 1156–1165.

Banks, R. B. (1975). Some features on wind action on shallow lakes. *Proceedings of the American Society of Civil Engineers, 101*, 813.

Bell, T., Bruyn, W., Miller, S., Ward, B., Christensen, K., & Saltzman, E. (2013). Air/sea DMS gas transfer in the North Atlantic: Evidence for limited interfacial gas exchange at high wind speed. *Atmospheric Chemistry and Physics, 13*, 11073–11087. https://doi.org/10.5194/acp-13-11073-2013.

Blomquist, B. W., Fairall, C. W., Huebert, B. J., Kieber, D. J., & Westby, G. R. (2006). DMS Sea-air transfer velocity: Direct measurements by eddy covariance and parameterization based on the NOAA/COARE gas transfer model. *Geophysical Research Letters, 33*, L07601. https://doi.org/10.1029/2006gl025735.

Edson, J., Fairall, C., Bariteau, L., Zappa, C., Cifuentes-Lorenzen, A., McGillis, W. M., Pezoa, S., Hare, J., & Helmig, D. (2011). Eddy-covariance measurement of CO2 gas transfer velocity during the 2008 Southern Ocean gas exchange experiment: Wind speed dependency. *Journal of Geophysical Research, 161*. https://doi.org/10.1029/2011JC007022.

Fairall, C. W., Hare, J. E., Edson, J. B., & McGillis, W. (2000). Parameterization and micrometeorological measurements of air-sea gas transfer. *Boundary-Layer Meteorology, 96*, 63–106. https://doi.org/10.1023/A:1002662826020.

Fairall, C. W., Yang, M., Bariteau, L., Edson, J. B., Helmig, D., McGillis, W., Pezoa, S., Hare, J. E., Huebert, B., & Blomquist, B. (2011). Implementation of the coupled ocean-atmosphere response experiment flux algorithm with CO2, dimethyl sulfide, and O3. *Journal of Geophysical Research, 116*, C00F09. https://doi.org/10.1029/2010JC006884.

Frew, N. M., Glover, D. M., Bock, E. J., & McCue, S. J. (2007). A new approach to estimation of global air-sea gas transfer velocity fields using dual-frequency altimeter backscatter. *Journal of Geophysical Research, 112*, C11003. https://doi.org/10.1029/2006JC003819.

Goddijn-Murphy, L., Woolf, D. K., & Marandino, C. (2012). Space-based retrievals of air-sea gas transfer velocities using altimeters: Calibration for dimethyl sulfide. *Journal of Geophysical Research, 117*, C08028. https://doi.org/10.1029/2011JC007535.

Huebert, B. J., Blomquist, B. W., Hare, J. E., Fairall, C. W., Johnson, J. E., & Bates, T. S. (2004). Measurement of the sea-air DMS flux and transfer velocity using eddy correlation. *Geophysical Research Letters, 31*, L23113. https://doi.org/10.1029/2004GL021567.

Huebert, B. J., Blomquist, B. W., Yang, M. X., Archer, S. D., Nightingale, P. D., Yelland, M. J., Stephens, J., Pascal, R. W., & Moat, B. I. (2010). Linearity of DMS transfer coefficient with both friction velocity and wind speed in the moderate wind speed range. *Geophysical Research Letters, 37*, L01605. https://doi.org/10.1029/2009gl041203.

Jahne, B., Heinz, G., & Dietrich, W. (1987). Measurement of the diffusion coefficients of sparingly soluble gases in water. *Journal of Geophysical Research: Oceans, 92*, 10767–10776. https://doi.org/10.1029/JC092iC10p10767.

Johnson, M. T. (2010). A numerical scheme to calculate temperature and salinity dependent air-water transfer velocities for any gas. *Ocean Science, 6*, 913–932. https://doi.org/10.5194/os-6-913-2010.

Kanwisher, J. (1963). On the exchange of gases between the atmosphere and the sea. *Deep Sea Research, 10*, 195–207.

Liss, P. S., & Merlivat, L. (1986). Air-sea gas exchange rates: Introduction and synthesis. In P. Buat-Menard (Ed.), *The role of air-sea exchange geochemical cycling* (pp. 113–127). Dordrecht: D. Reidel.

Mackay, D., & Yeun, A. T. K. (1983). Mass transfer coefficients for volatilization of organic solutes from water. *Environmental Science & Technology, 17*, 211–233.

Marandino, C. A., De Bruyn, W. J., Miller, S. D., & Saltzman, E. S. (2007). Eddy correlation measurements of the air/sea flux of dimethylsulfide over the North Pacific Ocean. *Journal of Geophysical Research-Atmospheres, 112*, D03301. https://doi.org/10.1029/2006JD007293.

Monahan, E. C., Staniec, A., & Vlahos, P. (2017). Spume drops: Their potential role in Air-Sea gas exchange. *Journal of Geophysical Research-Oceans, 122*. https://doi.org/10.1002/2017JC013203.

Marandino, C. A., De Bruyn, W. J., Miller, S. D., & Saltzman, E. S. (2008). DMS air/sea flux and gas transfer coefficients from the North Atlantic summertime coccolithophore bloom. *Geophysical Research Letters, 35*, L23812. https://doi.org/10.1029/2006JD007293.

Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liddicoat, M. I., Boutin, J., Upstill-Goddard, R. C. (2000). In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers. *Global Biogeochemical Cycles, 14*(1), 373–387. https://doi.org/10.1029/1999GB900091.

Rosenfeld, D., Sherwood, S., Wood, R., & Donner, L. (2014). Climate effects of aerosol-cloud interactions. *Science, 343*, 379–380. https://doi.org/10.1126/science.1247490.

Rowe, M. D., Fairall, C. W., & Perlinger, J. A. (2011). Chemical sensor resolution requirements for near-surface measurements of turbulent fluxes. *Atmospheric Chemistry and Physics, 11*, 5263–5275. https://doi.org/10.5194/acp-11-52632011.

Saltzman, E. S., King, D. B., Holmen, K., & Leck, C. (1993). Experimental-determination of the diffusion-coefficient of Dimethylsulfide in water. *Journal of Geophysical Research Oceans, 98*, 16481–16486.

Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics, 15*(8), 4399–4981. https://doi.org/10.5194/acp-15-4399-2015.

Vlahos, P., & Monahan, E. C. (2009). A generalized model for the air-sea transfer of dimethylsulfide at high wind speeds. *Geophysical Research Letters, 36*, L21605. https://doi.org/10.1029/2009GL0400695.

Wanninkhof, R. (1992). Relationship between gas exchange and wind speed over the ocean. *Journal of Geophysical Research, 97*, 7373–7381. https://doi.org/10.1029/92JC00188.

Wanninkhof, R. (2014). Relationship between wind speed and gas exchange over the ocean revisited. *Limnology and Oceanography-Methods, 12*, 351–362. https://doi.org/10.4319/lom.2014.12.351.

Woolf, D. K. (1997). Bubbles and their role in gas exchange. In P. S. Liss & R. A. Duce (Eds.), *The sea surface and global change* (pp. 173–206). Cambridge, U. K.: Cambridge University Press. https://doi.org/10.1017/CBO9780511525025.007.

Yang, M., Blomquist, B. W., Fairall, C. W., Archer, S. D., & Huebert, B. J. (2011). Air-sea exchange of dimethylsulfide in the Southern Ocean: Measurements from SO GasEx compared to temperate and tropical regions. *Journal of Geophysical Research-Oceans, 116*, C00F05. https://doi.org/10.1029/2010jc006526.

Zeebe, R. E. (2011). On the molecular diffusion coefficients of dissolved CO_2, HCO_3^- and CO_3^{2-}, and their dependence on isotopic mass. *Geochimica et Cosmochimica Acta, 75*(2011), 2483–2498. https://doi.org/10.1016/j.gca.2011.02.010.