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Examining Dissolved Gases in a Changing Climate

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Examining Dissolved Gases in a Changing Climate
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University of Connecticut, [2020]

Abstract
Changing climate scenarios predict a variety of effects across land, ocean, and atmosphere. In this dissertation the effect of several climate change related phenomena on dissolved gases in the coastal ocean and across the ocean-atmosphere interface is examined. Warming temperature, as predicted by the IPCC (2014), has direct impacts on the capacity of water to act as a reservoir for dissolved gases through its effect on their solubility (Chang, 2010). The first portion of this dissertation addresses dissolved gases in a coastal estuary, where warming is expected to be accelerated relative to the open ocean. A representative gas, oxygen, is examined in the context of temperature and salinity. A 25 year data set in Long Island Sound (UConn_2016_DEEP_LIS_Data) was used in order to assess these trends. Temperature was found to be increasing at an average rate of $0.08 \pm 0.03 \, ^\circ C \, yr^{-1}$ while dissolved oxygen decreased at a rate of $0.03 \pm 0.01 \, mg \, L^{-1} \, yr^{-1}$. Correlating the solubility of dissolved oxygen and temperature trends found that the temperature increase was potentially responsible for 33-100% of the observed decrease in oxygen over the time period sampled. This has implications for both the management and the understanding of reservoirs of dissolved gases. Climate change scenarios also predict an increase in both the number and severity of extreme weather events (IPCC, 2014). This is likely to increase the occurrence of sea spray and any gas exchange associated with those droplets. Due to sampling difficulties, current parameterizations of sea spray generation and any associated exchange are not well constrained. Building on the microphysical framework provided by the Andreas (2013) model, a model of the gas transfer associated with an individual droplet, with the intention of scaling to global relevance, is the secondary focus of this dissertation. It was found that, at wind speeds $>20 \, m \cdot s^{-1}$, sea spray has the capacity to contribute
to gas flux and at 30 m·s⁻¹ may be on the same order of magnitude as the general interfacial flux for certain gases. This contribution appears to have particular significance for regions of the Southern Ocean and storm events.
Examining Dissolved Gases in a Changing Climate

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B.A., Drew University, [2015]

A Dissertation
Submitted in Partial Fulfillment of the
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at the
University of Connecticut

[2020]
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This dissertation represents 5 years of work on dissolved gases and sea spray. It also represents a host of experiences and friendships that I might never have gained otherwise. So thank you, reader; I hope you find this dissertation as interesting and enlightening as I have. I can’t wait to see what comes next.
# Table of Contents

## Introduction
- Motivation and Methods ......................................................... 1
- A Brief Overview of Sea Spray .................................................. 3
- Novel Considerations .................................................................. 5
- Overarching Hypotheses ............................................................ 6
- Objectives of this Thesis ............................................................ 6
- Citations .................................................................................... 7

## Chapter 1. Timescales for determining temperature and dissolved oxygen trends in the Long Island Sound (LIS) estuary (Staniec & Vlahos, DOI:10.1016/j.csr.2017.09.013) ......................................................... 10
- Highlights/Abstract .................................................................... 10
- Methods .................................................................................... 14
  - Trend Detection .................................................................... 14
  - Application to the Long Island Sound ...................................... 15
- Results and Discussion ............................................................... 19
  - Quality Control and Sampling Bias .......................................... 19
  - Autocorrelation ..................................................................... 22
  - Time Required for a Significant Trend, n* ............................... 22
  - Salinity .................................................................................. 23
  - Temperature .......................................................................... 24
  - Dissolved Oxygen ................................................................. 27
  - Overall Rates of Change .......................................................... 28
  - Correlation of DO and T ............................................................ 29
- Conclusions ............................................................................... 30
- Acknowledgements ..................................................................... 31
- Citations .................................................................................... 31
- Supplementary ........................................................................... 35

## Chapter 2. Spume Drops: Their Potential Role in Air-Sea Gas Exchange (Monahan, Staniec, and Vlahos. 2017 DOI: https://doi.org/10.1002/2017JC013293) ................................................................. 40
- Abstract .................................................................................... 40
- Plain Language Summary ........................................................... 40
- Introduction ............................................................................... 41
  - 1.1 Relevant Gas Transfer Time Scales ....................................... 41
  - 1.2 Spume Drop “Piston Velocity” .............................................. 44
  - 1.3 Rationale for Ignoring Bubble-Produced Droplets When Spume Drops Are Present ............................................................... 45
- Spume Drop Production Functions ............................................. 48
  - 2.1 V(U) Derived From the $\partial F_1(U)/\partial R$ Expression of Monahan et al. (1986) ................................................................. 49
  - 2.2 V(U) Expression Found in Bortkovskii (1987) ..................... 49
  - 2.3 V(U) Derived From a Combination of $\partial F_0(U)/\partial R$ and $\partial F_1(U)/\partial R$ by Andreas (1992) ......................................................... 50
2.4 \( V(U) \) Derived From a Fixed Drop Spectrum and a \\( \partial F_1(U)/\partial R \) by Wu (1993) .......................................................... 51
2.5 \( V(U) \) Expression Based on Material in Fairall et al. (1994) ............ 54
2.6 \( V(U) \) Expression Developed by Andreas (1998) ................................ 56
2.7 \( V(U) \) Expression Based on Laboratory Findings of Anguelova et al. (1999) ................................................................. 57
2.8 \( V(U) \) Derived From \( V(u^*) \) Contained in Kudryavtsev (2006) ........... 59
2.9 \( V_{\beta=1.2} \) and \( V_{\beta=0.2} \) Based on Field-Based and Laboratory-Based Results in Zhao et al. (2006) ................................................. 60
2.10 \( V(U) \) of Fairall and Banner Model as Described in Fairall et al. (2009) ................................................................. 61
2.11 \( V_b(U) \) Production Flux \( V_b(U) \) and \( V_b(U) \) Suspended Fraction Flux From Mueller and Veron (2009) ........................................... 62
2.12 \( V(U) \) Expression Described in Andreas et al. (2010) ............. 63
2.13 \( V(U) \) Derived From “Equilibrium Assumption” \( \partial F/\partial R \) of Jones and Andreas (2012) ......................................................... 64
2.14 \( V(U) \) Expression Based on Laboratory Results of Ortiz-Suslow et al. (2016) ................................................................. 65

Air-Sea Gas Transfer Via Spume Drops Compared to Bubble and Interfacial Air-Sea Gas Transfer ............................................................... 67

3.1 \( V(U):k(U) \) Ratios When Only the “Geometrical” Mechanism Is Operative ................................................................. 68
3.2 The Case Where the Wet Bulb Mechanism Is Paramount .......... 74
3.3 The Case Where the Delta-T Mechanism Holds Sway ............... 75
Conclusions ................................................................. 77
Acknowledgments ................................................................. 79
A Note For The Defense of the Dissertation ........................................ 79


Abstract ................................................................. 85
Drop Size and Evolution ................................................................. 87
Influence of \( \Delta T_{air-water} \) (Air-Water Temperature Difference) ............... 88
Influence of Gas Type ................................................................. 89
Gas Exchange upon Initial Injection ................................................................. 89
Gas Exchange Associated with Radial Equilibration ......................... 90
Global Perspectives ................................................................. 91
Contribution to Gas Exchange ................................................................. 93
Acknowledgements ................................................................. 98
Citations ................................................................. 98
Supplemental ................................................................. 102

Methods ................................................................. 103
Microphysical Model ................................................................. 103
Chemical Modifications ................................................................. 104
Regional Data Analysis ................................................................. 106
Introduction

Motivation and Methods

The ocean is inherently important to biogeochemical cycling of gases. Gases form integral parts of the biological and chemical processes in the ocean. Understanding the way that gases cycle into and out of the ocean and the processes that drive these fluxes is important for our present understanding of the global ocean and atmosphere, and for predicting how those reservoirs and fluxes will change as we move into the future. Current predictions of climate change include the well-established general increase in temperature associated with greenhouse gases, as well as an increase in “extreme weather events” such as hurricanes and tropical cyclones (IPCC, 2014). Both of these trends have the capacity to affect gases dissolved in the ocean. This dissertation proposes to examine dissolved gases, particularly in the context of potential effects on their reservoirs and flux mechanisms. Herein we address the fundamental understanding of dissolved gases by examining reservoirs of dissolved oxygen over a long term time series in an estuarine system and later by investigating the potential role of sea spray in moving gases into and out of the ocean.

Temperature is a well-known driver of solubility. Increases in temperature, as predicted by the IPCC, have the capacity to reduce the solubility of gases, driving them out of the ocean (Chang, 2010). The first chapter of this dissertation addresses the potential impact of changing temperatures on dissolved gas reservoirs in a representative estuarine system. Coastal estuarine systems are likely to respond more quickly to warming temperatures than the open ocean and can act as a suitable bellwether for trends. The Connecticut Department of Energy and Environmental Protection (CT DEEP) has maintained a long term time series in Long Island Sound, an estuary between the state of Connecticut and the titular Long Island, which empties into the Mid Atlantic Bight (Lee and Lwiza, 2008, UConn_2016_DEEP_LIS_
Data). This time series takes samples at a variety of stations across the length and breadth of the Sound on a monthly or bimonthly basis based on the season. They have maintained this data archive since 1991. The data is publically available though, to date, it has not been used extensively outside the scope of the Long Island Sound Study (LISS). We hypothesized that the temperature, salinity, and dissolved oxygen time series collected by CT DEEP could provide valuable insight into the changing dynamics of coastal environments and, in particular, their dissolved gas reservoirs. Chapter one calculates trends in Long Island Sound for temperature, salinity, and dissolved oxygen and ascertains whether they are statistically significant using a novel approach from atmospheric and open ocean data sets. These trends are calculated for surface and bottom waters across the length of the Sound and inter-comparison to other coastal systems and the open ocean is investigated. Finally, the potential for correlation between the statistically significant trends of oxygen and temperature to examine the possibility that temperature acts as a driver of dissolved gas concentration is evaluated.

Dissolved gases are also affected by the various methods of gas invasion and evasion from the water. Temperature and salinity may act as drivers but there are also a variety of mechanisms by which gases are moved across the ocean atmosphere barrier and many of these mechanisms are directly tied to the influence of wind on the ocean surface. Higher global wind speeds and increasing “extreme events” are likely to influence waves and subsequently the gas transfer facilitated by wave action. Literature on the transfer of gases in the ocean has currently focused on the impact of bubble plumes which are entrained into the surface ocean by breaking waves (Stanley et al., 2009, Deike et al., 2017, Emerson and Bushinsky, 2016). However, there is an analogous opposing mechanism to this transfer, the gas exchange facilitated by sea spray droplet. To fully understand and model the transfer of gases between the ocean and atmosphere
this transfer mechanism must be examined and quantified. It seems reasonable to assume that sea spray droplets have the potential to play a role in gas exchange, especially in high wind speeds, where they have already been implicated to have effects on the formation of tropical storms and the momentum, sensible heat, and latent heat fluxes therein (Veron, 2015, Cochran et al., 2017, Andreas, 1995). The second, third, and fourth chapters of this dissertation address the potential for gas exchange through sea spray droplets by examining the theoretical underpinnings of gas transfer and applying them to the evolution of a sea spray droplet. A model is constructed based on Andreas (2013) microphysical model which calculates the two step evolution of a sea spray droplet upon ejection from the sea surface, with regards to size and temperature. The size and temperature evolution is used to inform the equilibrium concentration of various gases in the droplet via modified Henry’s Law constant calculations (Sander, 2015, Masterton, 1975). The evolution of these gas concentrations is then used to calculate a potential flux of gases due to sea spray using a variety of sea spray generation fluxes (Bortkovskii, 1987, Anguelova et al., 1999, Fairall et al., 1994, Andreas, 1998).

A Brief Overview of Sea Spray

The majority of this thesis is concerned with the potential impact of sea spray on gas exchange. Few studies to date have examined the potential for sea spray droplets to act as a carrier of gases into or out of the ocean. One notable exception is the Andreas et al (2017) which makes a theoretical foray into the governing timescales to ascertain whether gas transfer would even be possible in the brief time that most droplets spend aloft.
This is not the only uncertainty which complicates the study of sea spray. Understanding the pivotal role that sea spray plays began in the 1960’s, including E.C. Monahan’s pioneering work in sea spray observations, which recognized that the production of sea spray was non-linearly related to wind speed (Monahan, 1968). Since then, sporadic efforts have attempted to characterize the nature, size, and distribution of sea spray across different sea states and wind speeds followed by efforts to elucidate their role in transporting heat, moisture, and momentum (Andreas et al., 2015; Bao et al., 2011; Andreas et al., 1995). One of the major barriers to understanding spray is the uncertainty associated with sea spray generation functions. Sea spray is generated broadly by two methods; bubble mediated droplets formed when plumes of bubbles entrained by breaking waves rise to the surface and burst, generating film and jet droplets (Andreas et al., 1995), and wave mediated droplets which are torn from wave crests by the wind and shear, generating spume droplets (Andreas et al., 1995). The details of wave mediated droplet formation remain a subject of study even now, with the tearing of spray from ligaments and in a “bag breakup” mechanism being documented as recently as Veron (2012) and Troitskaya et al. (2017). Due to the uncertain nature of the formation mechanisms, the most common parameterizations of sea spray generation correlate winds speed with water volume transported using theoretical and experimental data. Size spectrums at different wind speeds are variable and dependent on the methods used to obtain them. Laboratory experiments usually use falling water jets or glass frits to create rising bubble plumes (Rouault et al. 1991; Edson and Fairall 1994; Edson et al. 1996; Meskhidze et al., 2013). Observations of this process in situ are complicated by the nature of sea spray itself, which is generated at the surfaces of breaking waves and becomes more plentiful as the wind increases. Wave mediated droplets remain the purview of empirical observations and wind-wave tunnels which have their own limitations in
both practicality and instrumentation (Anguelova et al., 1999). Data for correlating these generation functions remains relatively sparse (Veron, 2015).

**Novel Considerations**

This dissertation represents a series of novel contributions to the study of dissolved gases both in substance and in methodology. Chapter 1, which has been published (Staniec & Vlahos, 2017), represents the first application of the particular Tiao et al (1990) and Weatherhead et al (1998) statistical method to the coastal ocean. It also represents the first statistical quantification of LIS time series trends while drawing a connection between the temperature and dissolved oxygen. Chapter 2 has also been published (Monahan et al., 2017) and represents our attempt to evaluate the strengths and weaknesses of the current sea spray generation functions. As these currently span orders of magnitude we attempt to evaluate the assumptions and appropriateness of each across wind speeds. This chapter highlights the wide variety of sea spray generation functions which are currently available and indicates that a major source of uncertainty is likely the choice of sea spray generation for scaling. This evaluation constrains the upper and lower bound of generation functions while highlighting the inherent uncertainties and biases present in the sampling and experimental methods used to formulate generation functions. Please note that this chapter represents work by Edward C. Monahan and Penny Vlahos which has been supplemented by Allison Staniec and is included for the sake of completeness.

Chapter 3 of this dissertation contains the first attempt to model gas exchange for spray droplets in the creation of MATLAB model by which these calculations could be automated. This chapter presents the methodology and assumptions used to calculate the gas exchange of a single sea spray droplet as well as making a first attempt at scaling the droplet to environmental and global relevance. The model created in this chapter is referred to as the Andreas Gas Exchange Spray
model or AGES. The AGES model is assessed based on representative regional global values of surface ocean and air parameters to evaluate differences across regions and the potential contribution of sea spray is evaluated through a representative droplet. This model evolves as we continue to refine the estimates of gas exchange.

Chapter 4 is a preliminary attempt at scaling up of that sea spray gas transfer using the physical chemical AGES model and the variety of volume fluxes evaluated in Chapter 2. This is done to better constrain the preliminary estimate presented in Chapter 3. We also make an attempt at quantifying a number flux to indicate how much each droplet size contributes to overall gas exchange as the radius of the droplet determines how long it takes for the droplet to reach equilibrium. This dissertation represents a first attempt at modeling and quantifying the gas transfer potential of sea spray droplets.

**Overarching Hypotheses:**

- Climate induced warming will have significant impacts on coastal zone oxygen budgets.
- Predicted increases in high wind events and storms will impact air sea gas exchange through the influence of sea spray.
- Sea spray is a significant component of air-sea gas exchange at high wind speeds.

**Objectives of this Thesis:**

- Examine the long term trends of a dissolved gas in a coastal environment in the context of major drivers of gas exchange like temperature and salinity.
- Translate and modify an extant sea spray model for use in gas exchange calculations.
• Use the gas exchange sea spray model to determine the likely direction and amount of gas exchange for a series of representative non-reactive gases.

• Scale a single droplet spray model with both bulk volume and sea spray spectra to estimate the global relevance of gas exchange via sea spray.

Citations


LIS Data Source: UConn_2016_DEEP_LIS_Data Connecticut Department of Energy and Environmental Protection. 〈ftp://nopp.dms.uconn.edu/pub/〉


Chapter 1. Timescales for determining temperature and dissolved oxygen trends in the Long Island Sound (LIS) estuary (Staniec & Vlahos, DOI:10.1016/j.csr.2017.09.013)

Highlights

• Examines rates of change of temp and dissolved oxygen in LIS from 1991 to 2013.
• Temperature (T) has increased at a rate of at least 0.08 ± 0.03 °C yr\(^{-1}\).
• Dissolved oxygen (DO) has decreased at a rate of 0.03 ± 0.01 mg L\(^{-1}\) yr\(^{-1}\).
• T increase is sufficient to account for 33 to 100% of the decrease in DO.

Abstract

Long-term time series represent a critical part of the oceanographic community's efforts to discern natural and anthropogenically forced variations in the environment. They provide regular measurements of climate relevant indicators including temperature, oxygen concentrations, and salinity. When evaluating time series, it is essential to isolate long-term trends from autocorrelation in data and noise due to natural variability. Herein we apply a statistical approach, well-established in atmospheric time series, to key parameters in the U.S. east coast's Long Island Sound (LIS) estuary. Analysis shows that the LIS time series (established in the early 1990s) is sufficiently long to detect significant trends in physical-chemical parameters including temperature (T) and dissolved oxygen (DO). Over the last two decades, overall (combined surface and deep) LIS T has increased at an average rate of 0.08 ± 0.03 °C yr\(^{-1}\) while overall DO has dropped at an average rate of 0.03 ± 0.01 mg L\(^{-1}\) yr\(^{-1}\) since 1994 at the 95% confidence level. This trend is notably faster than the global open ocean T trend (0.01 °C yr\(^{-1}\)), as might be expected for a shallower estuarine system. T and DO trends were always significant for the existing time series using four month data increments. Rates of change of DO and T in LIS are strongly correlated and the rate of decrease of DO concentrations is
consistent with the expected reduced solubility of DO at these higher temperatures. Thus, changes in T alone, across decadal timescales can account for between 33 and 100% of the observed decrease in DO. This has significant implications for other dissolved gases and the long-term management of LIS hypoxia.

Long-term time series (LTTS) are just emerging in the oceanographic community relative to atmospheric and terrestrial systems. Among the oldest lasting time series for multi-parameter hydrographic and oceanographic data are Hydrostation “S,” which was started in the early 1950s in Bermuda and the pier data from Woods Hole which started in 1886, (Windsor 2003, Michaels and Knap 1996, Nixon et al., 2004). Oceanographic monitoring stations have historically collected data which includes air and water temperatures, salinity, wind speeds, and wave heights; parameters which arise from their origins as meteorological data sets (Karl and Lukas 1996). In the last decade, as instrumentation has evolved, time series have expanded to include pCO$_2$, pH, and other chemical and biological parameters (Windsor, 2003). These data sets capture monthly, seasonal, annual, and decadal changes in ocean chemical, physical, and biological systems. They also represent a recent ability to track decadal trends in key parameters in the midst of a changing climate, where trends are defined as significant shifts in the mean (Chatfield, 2013). However, evaluating trends on such long time scales requires an assessment of the minimal time required to confirm a significant change within the “noise” of natural variability in seasonal, interannual, and decadal fluxes (including both large and small scale physical phenomena).
Tiao et al. (1990) and Weatherhead et al. (1998) provide a comprehensive methodology to calculate the amount of time necessary for a significant detection of a trend at a given confidence level. This method has been successfully applied to atmospheric data (Tiao et al., 1990, Weatherhead et al., 1998) and recently to the open ocean by Henson et al. (2016). The method emphasizes the need to analyze trends and spatial correlations in the context of autocorrelation in the data. The method combines the magnitude of the trend, the noise in the data, and normalizes the data by autocorrelation to yield $n^*$, the number of years required in a time series to confirm a linear trend at a specific significance level. The major advantage of the $n^*$ method is that it does not have intrinsic requirements in terms of total observation time (Tiao et al., 1990, Hirsch et al., 2010). This makes the approach adaptable for application in a broader range of time series to identify the adequacy of the resolution and to identify additional resolution where needed to achieve a given statistical confidence. This study uses the Tiao et al. (1990) method in the U.S. East Coast’s Long Island Sound (LIS) estuary inspired by Henson et al. (2016) though results are expected to differ from these open ocean estimates (as coastal systems likely respond differently due to the significant influence of local weather patterns). LIS provides a suitable example because of its long history as an urban estuary, its recurring issues with hypoxia, and because it has been monitored for over 20 years, through the Long Island Sound Study and the Connecticut Department of Energy and Environmental Protection (CT DEEP) (Wolfe et al., 1991, Kaputa and Olsen, 2000, UConn_2016_DEEP_LIS_Data, LISS Biennial Report, 2004).

Long Island Sound is a partially mixed estuary (Turekian et al., 1994). It is 185 km long and 30 km wide near the center though it narrows at both the eastern and western ends and opens to the Atlantic Ocean primarily at the eastern end. The eastern end contains a deep swift channel
and is guarded by several small islands, including Fisher’s Island and Plum Island. The western end opens to the Atlantic via the East River. LIS is separated into three distinct sections by a series of irregular sills; the deeper, well scoured eastern basin (90 m average depth) and the shallower central and western basins (40 m average depth). The western basin experiences recurring hypoxia annually. This low oxygen deep water zone has expanded spatially over the last 60 years despite nitrogen mitigation strategies (LISS CCMP, 1994). The extent of LIS hypoxia is expected to be impacted by a combination of anthropogenic nutrient inputs and physical mixing conditions. Dissolved oxygen (DO) in marine systems is also expected to decrease as the result of increasing global average temperatures (Matear and Hirst, 2003) and reductions in DO have been detected in rivers (Jassby and Van Nieuwenhuyse, 2005) and estuaries of other temperate coastal regions over the last three decades. Physical shifts in large scale atmospheric and current patterns (e.g., the North Atlantic Oscillation (NAO)) as well as local shifts in water masses can also drive these local trends as has been suggested in other regions (Gilbert et al. 2005). These trends are of particular interest in estuaries since they are linked to possible broadening and intensification of existing seasonal hypoxia and anoxia events. In LIS these trends are particularly important as the ability to predict the extent of hypoxia is poorly constrained and remains a priority.

Since 1991, LIS has been monitored on a monthly basis at 48 stations along its axis for a series of parameters, including nutrients, DO, temperature (T), and salinity (S) both in the surface and at depth (Lee and Lwiza, 2008). In this analysis the Tiao et al. (1990) method was applied to DO, T, and S from these data sets. Three stations were chosen along the west-east axis of LIS allowing an assessment across the inland western shore, the central estuary, and the eastern mouth of the estuary bordering the adjacent Mid-Atlantic Bight continental shelf.
Methods

Trend Detection

This study uses the approach of (Tiao et al., 1990 and Weatherhead et al., 1998) adapted by Henson et al. (2016). Briefly, the method evaluates the magnitude of a linear trend and the noise in a time series to calculate how many years of observations are necessary before a trend can be distinguished from observations and a target confidence interval. The data is fit to a linear trend,

\[ Y_t = \mu + \omega X_t + N_t \]  \hspace{1cm} (1)

where \( Y_t \) is the time series data (e.g., temperature at time \( t \)), \( \mu \) is the y-intercept, \( \omega \) is the magnitude (slope) of the trend, \( X_t \) is time and \( N_t \) is the noise of the data which depends on the variability (both natural and analytical), autocorrelation (seasonal and interannual cycles), and the length of the data period (Tiao et al., 1990, Weatherhead et al., 1998, Henson et al., 2016). In effect it is a linear trend plus noise.

The number of years required in a time series to confirm a linear trend at a specific significance level is calculated using

\[ n^* = \left( \frac{3.3 \sigma_n}{|\omega|} \sqrt{\frac{1+\Phi}{1-\Phi}} \right)^{2/3} \]  \hspace{1cm} (2)

where the standard deviation of the noise, \( \sigma_n \), is scaled by the target confidence level (a coefficient of 3.3 for 95% confidence) and normalized to the slope, \( \omega \). This right term is then corrected by the first order auto-correlation coefficient term \( \Phi \), used to represent autocorrelations in the data series that result from lag terms due to persistent weather conditions and natural temporal patterns, including possible long-term and/or climatic forcing mechanisms (i.e. the NAO). This analysis lags the autocorrelation calculations by one bin (i.e. for the two month bins
the lag is two months). Oscillating phenomena such as the NAO are captured in the autocorrelation coefficient and contribute by extending the value of $n^*$ and thus the required observational period. The precision of trend estimates depends critically on the magnitude of $\Phi$. The parameters are combined to determine $n^*$, the amount of time required to establish the trend (i.e. years). A significant limitation of this method is that it assumes a linear trend, and therefore does not account for non-linear rates of change. Although the trend that is identified is significant over a period of $n^*$, projections to future rates of change should be made conservatively and become less accurate for every additional $n^*$ years projected. The best results for the $n^*$ estimations are reached when additional sources of instrument or measurement error are minimal, or can be calculated with enough accuracy to be removed. When not accountable, any additional sources of error contribute to overall noise and increase the amount of required observation time estimated as $n^*$ (Tiao et al., 1990). In this case, the remarkable consistency in methodology, instrumentation, and calibration of the CT DEEP data for T, DO, and salinity program over its entire time period minimizes this source of error. The method requires that the data points be grouped into evenly-spaced temporal bins and the additional parameters are calculated according to these bins.

*Application to the Long Island Sound*

The monitoring program in the Long Island Sound has a fairly large number of stations that are scattered along both the length and breadth of the Sound and are sampled almost monthly by the Connecticut Department of Energy and Environmental Protection (DEEP). For this analysis, three observing stations were chosen along the central west-east axis of the LIS: A4, H4, and M3. A4 is located in the western end of the LIS at 73° 44' 3" W, 40° 52.35' 21" N with an average depth of 32.6m and has been sampled since December 1994. H4 is near the
center of the LIS with a depth of 23.7m, located at 72° 56' 2.4" W, 41° 6' 6" N, and has been sampled since June 1994. The final station is M3 which is located at the eastern end of LIS and correspondingly has a much deeper average depth of 72.6m, at 72° 3' 12" W, 41° 14' 13.8" N. It has been sampled since January 1991 (Figure 1). LIS is roughly 6, 30, and 19 km wide at stations A4, H4, and M3 respectively. The original DEEP station names have been preserved in this study to facilitate future comparisons.

![Map of Long Island Sound with Stations]

**Fig. 1** Selected stations monitored (approximately monthly) year-round by DEEP in the Long Island Sound

Three parameters were selected for this analysis and both bottom and surface measurements were included; T as a major physical control and climate indicator, DO due to the pervasive seasonal hypoxia events in LIS and as a representative dissolved gas, and finally S was chosen as a relatively conservative variable with reasonably accurate and reliable time series,
which is expected to vary on much longer timescales due to the large fraction of saline continental shelf water in LIS and low residence time of freshwater (between 3 to 6 months) (Vlahos and Whitney, 2017).

Data were retrieved from the DEEP Water Quality Monitoring Database for the four stations and time series were plotted for surface and bottom T, DO, and S (ftp://nopp.dms.uconn.edu/pub/). Noise was defined as the standard deviation of the bin (Weatherhead et al. 1998) and two month, four month (Feb-May, June-Sept, Oct-Jan) and yearly bins were compared. The binned averages of the parameters were plotted over time and fit to a linear model to give the slope of the trend (Figure 2).
Fig. 2 Surface Temperature and Dissolved Oxygen (4 month) plotted against time for all three stations. A4 is located at the western end of the Sound, H4 near the center, and M3 at the eastern end of the Sound. X-axis is noted in calendar dates in order to more accurately depict the timing and overlap of collected data and slopes shown on graphs are day$^{-1}$. 
**Results and Discussion**

*Quality Control and Sampling Bias*

Due to the sampling scheme of the DEEP data set (water samples taken at discrete times with 2-4 weeks between cruises) steps were taken to assess and mitigate bias due to frequency of sampling and time of day of sampling. In order to ensure that the lower frequency at which the DEEP data set was collected was reasonably representative of the Sound, the data set was compared to a shorter, higher frequency data set. The University of Connecticut maintains a series of buoy stations throughout the Sound, known collectively as the Long Island Sound Integrated Coastal Observing System (LISICOS). These buoys were instituted in 2006 and collect surface temperature data every fifteen minutes. The LISICOS time series were binned in increments equal to those in this study (2 month, 4 month, and annual). Figure 3 is a plot of the T values derived from both time series from 2007 to 2013, where the two time series overlap. There is good agreement in both data sets (1:1) with a slight tendency in the DEEP data set to yield lower temperatures which would bias towards lower rates of temperature change though this effect is expected to be minor. Based on this assessment, the DEEP data was deemed temporally representative of the Sound. This was consistent for both 2 and 4 month bins, although the annual bins were too small a sample size to resolve.
Fig. 3. LISICOS data versus CT DEEP surface data shows a one to one ratio.

Shifts in time of day of sampling were also investigated as a second source of sampling bias (i.e. warming or cooling biases or diurnal DO differences). The time of day at station over the entire time series was plotted to detect shifts in sample collection for the three stations (Figure 4). Generally, the DEEP time series is consistent in its time on station. The westernmost station, A4, had an average sampling time of 12:04 pm and the standard deviation was 68 minutes over 20 years. The station time shows an average shift from noon to 11:40 am (about 20 minutes) over the span of 1994 to 2013. The easternmost station is similarly consistent with an average sampling time at 9:40 am and a standard deviation of about 90 minutes. The shift between 1991 and 2013 is 40 minutes earlier in the day. The central station (H4) shows the most significant shift in sampling time over the sampling period of about 115 minutes; moving from before noon (11:15 am) to early afternoon (1:10 pm) equivalent to a warming bias of about +0.18°C derived from the higher resolution LISICOS time series. This correction was applied to the trend analysis of the central LIS surface waters as a linear correction over time. The shift in DO cannot be determined using the LISICOS data set, though it would be expected that any bias
due to the shift in sampling time from 11am to 1pm would be in the positive direction for DO in the central Sound (H4) due to primary production.

![Graphs of Time of Day of Sampling at Each Station](image)

**Fig. 4** Time of day of sampling at each station.

As the analysis is focused on trends and not absolute values, consistency in the station sampling time over the entire decadal time series minimizes sampling bias by minimizing noise due to diurnal variations (Tyler *et al.*, 2009). If the amplitude of the diurnal cycle does not change, then these trends are representative of an overall T change in LIS; however, if the diurnal cycle is shifting (i.e. a larger amplitude in the daily cycle), this could bias results. Comparison of averages obtained during different fixed times of day from the higher frequency LISICOS time series did not indicate a change in diurnal amplitude for T and DO in the 2006 to 2013 period and thus this was not considered to be a source of bias in trend analysis.
Furthermore, as we are examining trends not absolute values we do not consider differences in sampling time between stations to be a source of bias.

**Autocorrelation**

An important component in environmental time series is the intrinsic autocorrelation in data that must be accounted for. Large autocorrelation leads to greater uncertainty in the predicted trends and therefore a longer period required for the confirmation of a trend at a given significance level. Autocorrelation for the bins was calculated with a lag of one bin (i.e., the two month bins were lagged by two months). The autocorrelation coefficients (Φ) in the analysis are summarized in Tables S.2 and S.3. Generally, the greatest autocorrelation coefficient (0.53 to 0.37) occurs in the shortest, two month bins as would be expected in a marine time series where environmental conditions persist longer in the water than in the atmosphere above. Four month bins yield negative autocorrelation coefficients which are consistent with noise in the data from seasonal cycling. Finally, the annual bins yield slightly lower autocorrelation coefficients (between 0.41 and 0.17). The results are an increase in n*, the time required to confirm trends, in the two month and annual bins and a slight reduction in n* for the 4 month bins (due to negative autocorrelation coefficients).

**Time Required for a Significant Trend, n***

The Tiao *et al.* (1990) method identifies the amount of time necessary for the confident detection of a trend in a time series, with the caveat that the trend is assumed to be linear. Linear trends are helpful for detecting overall increases or decreases in target parameters. Application of the Tiao *et al.* (1990) method results in a series of n* values which are specific to each variable, bin size, and station within the Sound (Table S.1). These represent the number of years that each trend already shown in the available data must persist in order to be considered significant.
LIS n* values for the three parameters appear to be driven primarily by the magnitude of the trend rather than the standard deviation (noise) or autocorrelation components (Table S.2, S.3). For example, a greater standard deviation for the surface (0.60) than bottom T (0.53) of the annual A4 bins would indicate that the surface T should take longer to be resolved based on equation 2, but the relatively large magnitude of the trend (0.04 °Cy⁻¹) overwhelms this such that the bottom T trend (0.01 °Cy⁻¹) yields a smaller signal to noise ratio and thus a greater n* than the surface T. Consistently in all bin versions of this analysis and for all parameters, the slope of the trend (ω) is the dominant driving factor in determining n*.

**Salinity**

As expected, S had the highest n* values for almost every bin size and station. All but two n* values are beyond the current observational period. On average it takes several decades for a significant change in S to be confirmed across LIS. This is primarily driven by the small ω value, corresponding to a small rate of change, in equation 2. Trends for S are smaller than the corresponding T and DO trends, as salinity operates on relatively longer timescales. There are two trends that are significant within the existing time series, for the 4 month (seasonal bins) of central and eastern LIS surface waters. Both predict a modest freshening of 0.011 and 0.037 g/kg/year in surface waters. This is consistent with long-term trends of increased precipitation and base river discharge from eastern Connecticut and a large portion of New England into LIS mainly via the Connecticut River which represents 70% of the freshwater input to LIS (Hodgekins and Dudley, 2011, Lee and Lwiza, 2008). The Tiao et al. method predicts that additional freshening trends across LIS may be confirmable by the year 2070 in surface waters.
Temperature

All station trends predict an increase in T in both surface and deep waters independent of bin size or location (Figure 5). Warming surface T trends in the western sound (at station A4) require an average of 19 ± 5 years to be significant at the 95% confidence level and the increase in T over this period is 0.04°C yr\(^{-1}\) for 4 month bins. The western bottom water T trends are the only non-confirmable trends and require 5-20 more years beyond the current available time series to confirm an average warming trend of 0.04 ± 0.03°C yr\(^{-1}\).

Surface T at the central LIS is the quickest to show a significant trend with an n* of only 11 years in 4 month bins. Regardless of binning, this station (H4) shows detectable T trends in less than twenty years (11 ± 3 years on average), making the current data set adequate for confidently identifying an upward trend in both surface and bottom waters. The trend for surface waters and bottom waters is 0.10°C yr\(^{-1}\) and 0.07 °C yr\(^{-1}\), respectively.

Finally, the Eastern LIS time series at station M3 yields a warming trend of 0.04 ± 0.02°C yr\(^{-1}\) over 23 ± 12 years of observations in surface waters. The 4 month bins lead to the lowest n* values consistently at this site of 12 ± 2 years (0.09 ± 0.03°C yr\(^{-1}\)). 4 month bins in the bottom waters at M3 have a warming trend of 0.11°C yr\(^{-1}\). This is consistent with Central LIS bottom water warming rates.

Averaging the 4 month bin rates of change gives an overall warming trend of 0.08 ±0.03°C yr\(^{-1}\). This average covers the entire length of the Sound and both surface and bottom water trends are included. The 4 month bins are used for this overall rate as they consistently give significant trends.

Current average global circulation models and observations over the past century predict ocean temperature increases at approximately 0.1- 0.2° C per decade (0.01- 0.02 °C yr\(^{-1}\)) (IPCC,
These predictions range slightly according to latitude from 0.004 to 0.016 °C yr\(^{-1}\) (Deser et al., 2010). However, under warming climate conditions, in shallow estuaries, influenced by their proximity to land and freshwater inputs including groundwaters, warming would be more pronounced. Thus we are not surprised to see a larger rate of change in LIS. This is due to the accelerated warming of land and shallow surface waters relative to open ocean waters surrounded by a vast ocean heat sink. Warming trends in other temperate estuaries have been summarized in Table 1 for comparison to this study. Trends are consistent though warming rates have been markedly increasing over the last two decades which corresponds to the period of this analysis. Seekell (2007) found that since 1946 the Hudson River Estuary has warmed steadily at a rate of 0.01 °C yr\(^{-1}\) though between 1977 and 2006 the rates have doubled to 0.02 °C yr\(^{-1}\). Warming rates in the Delaware Estuary and Narragansett Bay also show accelerated warming over shorter, more recent time series, compared to longer timescales. In other regions like the San Francisco Estuary shorter, more recent time series show even greater rate increases over longer time series.
<table>
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Table 1. Comparison of rates of change of temperature in various estuaries across the United States

The warming rates obtained in this study are consistent with rates obtained in other coastal regions over the same time periods and greater than rates based on longer time scales. Whether this recent accelerated warming persists remains to be seen. Extrapolating to the next few decades requires caution in that, though the rates are significant, the time series itself is short and there is no way to confirm that slopes will not shift. However, based on these data, the estimate for LIS temperature change by 2050 is an increase of 2 ± 1 °C.
Dissolved Oxygen

DO trends are consistently negative over all stations and depths (Figure 5). A detectable net decrease in oxygen is consistent with the increase in temperature over the same time period. At the western end of the Sound, changes in surface DO are detectable in the shortest amount of time; an average of $12 \pm 2$ years for all bin sizes. The 4 month bins are significant in the least amount of time with bottom waters yielding a decreasing trend of $-0.03 \text{ mg L}^{-1} \text{ yr}^{-1}$ significant in only 11 years of the time series. Surface waters show a significant trend even sooner with an $n^*$ of 9 years and a trend of $-0.04 \text{ mg L}^{-1} \text{ yr}^{-1}$. All the western LIS bins have significant surface DO trends that average to $-0.05 \pm 0.02 \text{ mg L}^{-1} \text{ yr}^{-1}$.

The central LIS, (H4), has a fairly similar range of $n^*$, $15 \pm 3$ years on average for surface DO and a wider spread of $20 \pm 17$ years for bottom DO. All three bins have significant trends for surface DO averaging at $-0.02 \pm 0.01 \text{ mg L}^{-1} \text{ yr}^{-1}$. The bottom water 4 month bins are within the LTTS window and yield significant rates of bottom DO decreases at $-0.03 \text{ mg L}^{-1} \text{ yr}^{-1}$.

The eastern Sound at Station M3 takes a noticeably longer time to confirm a significant trend with average $n^*$ of $45 \pm 26$ years. In fact, the only significant trends for Station M3 are from the 4 month bin which is $-0.02 \text{ mg L}^{-1} \text{ yr}^{-1}$ for both surface and bottom DO. One possible explanation for the longer time period to confirm a significant trend is the increased mixing that station M3 experiences due to its position behind Fisher’s Island resulting in periods where flow reversals occur and dynamics vary considerably leading to higher variations (noise) and smaller trends (Schmalz and Devine, 2003).

Open Ocean DO trends from 1960 to 2010 reported by Stramma et al., (2012) show an overall global upper ocean (defined as roughly 300m) decrease of $-0.002 \text{ mg L}^{-1} \text{ yr}^{-1}$ with regional rates between $-0.03 \text{ mg L}^{-1} \text{ yr}^{-1}$ and $+0.02 \text{ mg L}^{-1} \text{ yr}^{-1}$. The overall decrease in LIS DO reported in
this study remarkably falls within the range at -0.03 ±0.01 mg L\(^{-1}\)y\(^{-1}\). As the LIS is significantly shallower (average depth 30m) the rates of DO decrease are reasonable.

Over the last 5 decades there has also been a 2% decline in open ocean DO and global models predict an additional 1 to 7% decrease in total ocean dissolved oxygen inventories by 2100 (Schmidtko et al., 2017). Coastal zone DO inventories are likely to be on the upper end of these estimates or higher due to shorter response times to various factors including T, increased nutrient flux and/or increased carbon remineralization. Our DO inventories in LIS over the past 2 decades have decreased on the order of 6% or 3% per decade. A cumulative decrease in DO of 1.0 ± 0.3 mg L\(^{-1}\) is predicted by 2050 based on this analysis.

**Overall Rates of Change**

![Overall Rates of Change](image)

*Fig 5.* Average trends in temperature and dissolved oxygen from east to west.

Application of the \(n^*\) method to LIS indicates that both T and DO measurements have reached or are close to reaching the time scales necessary to confirm significant trends. There is a consistent upward trend in both surface and deep T in the Long Island Sound which is present regardless of location, binning, and averaging. There is no clear west to east trend in surface
water T (Figure 5). DO trends are consistently decreasing, indicating a loss of standing oxygen stocks which is independent of the recurring hypoxia events. Of particular interest is the fact that oxygen loss is enhanced in the Western and Central bottom waters of the Sound; the portions of the Sound which are subject to hypoxia.

*Correlation of DO and T*

Based on the ratio of the DO to T rates in this study of $0.03 \pm 0.01 \text{ mgL}^{-1}\text{yr}^{-1}$ and $0.03 \degree \text{C yr}^{-1}$ the rate of change of DO to T is $-0.4 \pm 0.2 \text{ mgL}^{-1}\degree \text{C}^{-1}$. The solubility change of DO in seawater based on standard solubility curves between 0 and 20 °C and a salinity of 30 g/kg is approximately $-0.21 \text{ mg L}^{-1}\degree \text{C}^{-1}$. The ratio in this study was between 0.2 and 0.6 and therefore overlaps with the expected change due to standard solubility. It is possible therefore that temperature can account for between 33 and 100 % of the decrease in DO. It is also plausible that DO reductions are compounded by other factors such as nutrient loads and changes in physical forcings that could contribute to the upper estimates of this ratio.

DO and T are both independent parameters in the DEEP time series and the agreement between their rates of change is remarkable and indicates that T trends could be used to predict maximum DO concentrations in LIS. This is in agreement with previous studies of hypoxia in LIS which indicate a correlation between T and bottom DO (Lee and Lwiza, 2008). The negative correlation of DO and T implies sensitivity of DO stocks to large scale climate oscillations such as El Nino and the NAO which can have significant effects on inter-annual temperature differences.

Note, however, that the general downward trend of the NAO index over the period of interest (namely 1991 to 2013) would normally be associated with a cooling trend as strongly
positive NAO indices are associated with warmer temperatures across the eastern coast of the United States (NOAA, 2017, Taylor and Stevens, 1998).

This is an important result for the long-term management of LIS which has been increasingly concerned with attempts to understand and ameliorate the spreading hypoxia, particularly in the western to central LIS where it occurs annually. Warming water will generally deplete the standing stock of dissolved oxygen as solubility, and thus the capacity of the water to contain dissolved oxygen, is reduced. Such solubility reductions with temperature are true for many gases including CO$_2$, CH$_4$, and N$_2$. These results indicate that regardless of nitrogen mitigation strategies there will be lower average DO standing stocks stored in LIS waters which may tend to exacerbate the occurrence of seasonal hypoxia once additional limitations of stratification and increased respiration rates are compounded.

**Conclusions**

To our knowledge, this paper represents the first application of the Tiao et al. method to LTTS in a coastal estuarine system. It confirms a warming trend of 0.08 ± 0.03 °C yr$^{-1}$ across LIS and a decrease in DO of -0.03 ± 0.01 mg L$^{-1}$ yr$^{-1}$ over the 1991 to 2013 period. The correlation between the rate of change in T and the rate of change in DO implies that long-term processes operating on decadal timescales control these trends and that the decrease in LIS DO can be accounted for solely through increases in T on these timescales though the range of uncertainty allows for other factors to influence DO. This may contribute to LIS hypoxia events over time and may have similar implications for reduced DO in other coastal and estuarine systems. An additional important implication of this work is the influence of this warming on other dissolved gas solubilities in semi-enclosed estuaries for gases such as CO$_2$, CH$_4$, and N$_2$ that are highly sensitive to temperature and may follow similar reductions in standing stock.
Acknowledgements

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Citations


**Supplementary**

**Fig. S.1** Time series data (raw) for Station A4 in the western end of the Sound spanning January 1994 to November 2013. Trend analysis is included here to emphasize the magnitude of the slope/signal with respect to the variations of the raw time series. The x-axis is noted in calendar dates in order to more accurately depict the timing and overlap of collected data. Slopes shown on graphs are day\(^{-1}\).
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**Table S.1** All calculated n* values in years for LIS. Shaded values depict those that are within the time series and therefore significant (>95%).
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Table S.2 Components used to calculate n* for temperature. Linear regression slopes (ω) were confirmed with the Thiel-Sen estimator (insensitive to outliers) to lie within the 95% confidence limit.
Noise (N_t) & Standard Deviation of Noise (σ_n) & Slope (ω) in years & φ & \sqrt{(1+φ)/(1-φ)} & N^* \\
\hline
A4 & 2 month & Surface DO & 1.25 & 0.69 & -0.07 & 0.49 & 1.70 & 14 \\
& Bottom DO & 1.38 & 0.69 & -0.04 & 0.45 & 1.62 & 22 \\
4 month & Surface DO & 1.78 & 0.49 & -0.04 & -0.42 & 0.64 & 9 \\
& Bottom DO & 0.64 & 0.57 & -0.03 & -0.49 & 0.59 & 11 \\
Annual & Surface DO & 2.62 & 0.39 & -0.03 & 0.11 & 1.12 & 12 \\
& Bottom DO & 3.95 & 0.41 & -0.01 & 0.16 & 1.17 & 27 \\
H4 & 2 month & Surface DO & 0.77 & 0.44 & -0.03 & 0.46 & 1.64 & 17 \\
& Bottom DO & 0.93 & 0.51 & -0.07 & 0.45 & 1.63 & 11 \\
4 month & Surface DO & 1.14 & 0.42 & -0.01 & -0.35 & 0.70 & 16 \\
& Bottom DO & 1.39 & 0.46 & -0.03 & -0.47 & 0.60 & 9 \\
Annual & Surface DO & 1.67 & 0.25 & -0.02 & -0.14 & 0.87 & 12 \\
& Bottom DO & 2.61 & 0.25 & 0.00 & -0.15 & 0.86 & 39 \\
M3 & 2 month & Surface DO & 0.56 & 0.41 & -0.01 & 0.43 & 1.59 & 44 \\
& Bottom DO & 0.54 & 0.39 & -0.01 & 0.43 & 1.58 & 33 \\
4 month & Surface DO & 0.88 & 0.40 & -0.02 & -0.40 & 0.65 & 13 \\
& Bottom DO & 0.86 & 0.42 & -0.02 & -0.41 & 0.65 & 13 \\
Annual & Surface DO & 1.50 & 0.24 & 0.00 & 0.05 & 1.05 & 83 \\
& Bottom DO & 1.48 & 0.22 & 0.00 & -0.09 & 0.91 & 51 \\

Table S.3 Components for n* calculation for dissolved oxygen. Linear regression slopes (ω) were confirmed with the Thiel-Sen estimator (insensitive to outliers) to lie within the 95% confidence limit.
<table>
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<tr>
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<th>Standard Deviation of Noise (\sigma_n)</th>
<th>Slope (\omega) in years</th>
<th>\varphi</th>
<th>\sqrt{(1+\varphi)/(1-\varphi)}</th>
<th>N*</th>
</tr>
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<td>Annual</td>
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Table S.4 Components for n* calculation for salinity

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<tr>
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Table S.5 Global average and range of n* (years) for time series compared to LIS data. Global data taken from Henson et al. 2015.
Chapter 2. Spume Drops: Their Potential Role in Air-Sea Gas Exchange (Monahan, Staniec and Vlahos; DOI: https://doi.org/10.1002/2017JC013293)

Abstract
After summarizing the time scales defining the change of the physical properties of spume and other droplets cast up from the sea surface, the time scales governing drop-atmosphere gas exchange are compared. Following a broad review of the spume drop production functions described in the literature, a subset of these functions is selected via objective criteria, to represent typical, upper bound, and lower bound production functions. Three complementary mechanisms driving spume-atmosphere gas exchange are described, and one is then used to estimate the relative importance, over a broad range of wind speeds, of this spume drop mechanism compared to the conventional, diffusional, sea surface mechanism in air-sea gas exchange. While remaining uncertainties in the wind dependence of the spume drop production flux, and in the immediate sea surface gas flux, preclude a definitive conclusion, the findings of this study strongly suggest that, at high wind speeds (>20 m s\(^{-1}\) for dimethyl sulfide and >30 m s\(^{-1}\) for gases such as carbon dioxide), spume drops do make a significant contribution to air-sea gas exchange.

Plain Language Summary
This paper evaluates the existing spume drop generation functions available to date and selects a reasonable upper, lower and mid range function that are reasonable for use in air sea exchange models. Based on these the contribution of spume drops to overall air sea gas exchange at different wind speeds is then evaluated to determine the % contribution of spume. Generally below 20ms\(^{-1}\) spume drops contribute <1% of gas exchange but may account for a significant amount of gas exchange at higher wind speeds.
1 Introduction
Spume drops are very large drops, having radii typically between 30 μm to several millimeters
(Andreas, 1992). These drops are produced by the most prevalent direct mechanism of salt water
drop production, the mechanical disruption of wave crests (Monahan et al., 1983). This
mechanism only becomes significant at high wind speeds (>9 m s\(^{-1}\); Monahan et al., 1986).

There are two outstanding questions that have to be answered before the possible significance of
spume drops, under high wind conditions, to air-sea gas transfer can be confidently assessed. The
first relates to the gas transfer time scales between drops and air, and the second to the bulk gas
transfer, or piston velocity from, or to, the population of drops.

1.1 Relevant Gas Transfer Time Scales
The first of the two questions, simply put, is whether the typical spume drop is airborne long
enough to lose a significant fraction of the gas dissolved in the drop before it falls back into the
ocean, or to gain sufficient gas in this interval, to come to near equilibrium with the marine
atmospheric boundary layer (MABL), when this layer is depleted, or enriched, with this gas vis-
a-vis the surface layer of the ocean. This was addressed in a recent paper (Andreas et al., 2015)
that treated the physical time scales that govern the rate of change of the temperature and of the
radius (and hence salinity) of such airborne drops and that characterize their time aloft, as well as
the three physicochemical time scales that define the rate at which gases (a) cross from the bulk
MABL, to the immediate surface of such a drop, (b) cross through the drop surface, and then (c)
diffuse into the interior of this drop, in the case of invasion (and in reverse order in the case of
evasion). When we review a typical plot of time scales, for carbon dioxide at a wind speed of a
modest 12 m s\(^{-1}\) (Andreas et al., 2015, Figure 3, right-hand plot), we see that only two gas
transfer time scales, the time scale for crossing through the drop interface (identified as being
derived from Seinfeld and Pandis (2006) and the time scale associated with this diffusion of the
gas into the deep interior of the drop, appear to be long enough to preclude the effective
exchange of this gas if the drop's radius is larger than \(~130 \mu m\). We should note that the
interfacial time scale attributed to Seinfeld and Pandis (2006) has been misidentified on this
figure (it is actually an interior diffusion time scale, which explains why it falls directly on the
curve identified as the interior diffusion time scale), and recognize that these diffusional time
scales are based on the assumption that the diffusion of the gas into the interior of the drop is a
consequence of pure molecular diffusion.

When it is acknowledged that each such spume drop is produced by the violent mechanical
disruption of a wave crest, and that during such a drop's relatively short time airborne it is
buffeted by the turbulence of the lower MABL, it should be apparent that this drop is constantly
oscillating and subject to surface shear forces throughout its lifetime, and thus any gas entering
(or leaving) the deep interior of the drop will be moved along by turbulent diffusion. Since
turbulent diffusion is much more effective than molecular diffusion, it is reasonable to conclude
that the appropriate time scale for diffusion within the interior of a spume drop is at least an
order of magnitude shorter than the molecular diffusion time scale plotted on this figure, and thus
the content of a gas (CO\(_2\) in this example) in all spume drops, even those with radii approaching
1 mm, will have time to approach equilibrium with the gas content in the bulk of the MABL.

It should be noted that the \(T_T\) plotted in Andreas et al. (2015, Figure 3) is the time scale
associated with the spume drop's adjustment to its equilibrium temperature, which is not the
temperature of the bulk MABL, but rather the evaporation equilibrium temperature, which for
drops of 100 \(\mu m\) radius and larger, is within a few tenths of a degree Celsius of the wet-bulb-
thermometer temperature associated with any given bulk MABL air temperature and relative
humidity (RH; see Andreas, 1995, right-hand plot of Figure 1). (The slight deviation of the
temperature of an evaporating spume drop from the wet bulb temperature is due to the fact that
such droplets are made of saline, not fresh, water, and that their surfaces are curved, and thus the
air-water interface is not a planar one (Andreas, 1995).) It should also be noted from this same
Figure 1 that spume drops of this radius will have reached this evaporation temperature in less
than a second in the MABL and thus will return to the sea at a temperature close to the wet bulb
temperature. Returning to Andreas et al. (2015, Figure 3), we observe that for spume drops larger
than ~30 μm the time scale associated with drop radius adjustment is longer than the time the
droplet is airborne, and thus such spume drops will return to the ocean having experienced, at
most, minor shrinkage.
Figure 1. Spume drop volume production functions. These 16 spume generation functions, expressed in mm$^3$ m$^{-2}$ s$^{-1}$, are based on expressions or figures found in the publications listed in the key, and plotted against the 10 m-elevation wind speed, expressed in m s$^{-1}$.

1.2 Spume Drop “Piston Velocity”

The second outstanding question that has to be answered is, for a given 10 m-elevation wind speed ($U$; and MABL stability and wave development), what is the production flux of spume drops per unit area of sea surface? Specifically, as will be seen below, we need to know what the
aggregate volume flux of spume drops is for a given wind speed, i.e., \( V(U) \). Recall that the governing equation for air-see, or air-drop, gas exchange is simply

\[
F = k(C_w - H p_o)
\]

where \( F \) is the air-drop gas exchange flux (mol m\(^{-2}\) s\(^{-1}\)), \( k \) is the gas exchange coefficient (m s\(^{-1}\)), \( C_w \) is the dissolved gas concentration in the surface layer of the ocean (mol m\(^{-3}\)), \( H \) is the Henry's law constant (mol m\(^{-3}\) atm\(^{-1}\)), and \( p_o \) is the partial pressure of the gas (atm) in question in the bulk MABL. (Given a spume drop's size and origin, it does not have the initial gas concentration of the oceanic microlayer, but rather a gas concentration approaching that of the bulk surface layer of the ocean.) We note that \( k \), which has the dimensions of \([L T^{-1}]\), is often referred to as the piston velocity, and that while the \( V(U) \) expressions discussed below are expressed in terms of mm\(^3\) m\(^{-2}\) s\(^{-1}\), these quantities also have the fundamental dimensions of \([L T^{-1}]\). Both \( k \) and \( V(U) \) are not only dimensionally the same, they both physically represent the vertical velocity of the gas in question across the air-sea interface. In this case \( V(U) \) is simply the piston velocity in the expression for air-drop gas exchange, which can now be written as follows, where \( V(U) \) is now expressed in m s\(^{-1}\):

\[
F = V(U)(C_w - H p_o)
\]

Note that \( V(U) \) can be obtained from field measurements or inferred from production flux parameterizations.

1.3 Rationale for Ignoring Bubble-Produced Droplets When Spume Drops Are Present

Before we go further with our estimate of the spume-drop-mediated gas flux, we need take a moment and describe why we are ignoring the sea spray droplets produced when bubbles rise to the sea surface and burst, i.e., the film droplets and jet droplets.
Film droplets are produced when the film of water covering the top of such a bubble, i.e., the bubble cap, having drained sufficiently, shatters producing great numbers of quite small, typically submicrometer, droplets (Blanchard, 1954; Mason, 1957), while jet droplets are formed at the tip of the vertically rising Rayleigh jet that forms out of the bottom of the hemispherical cavity that is left in the water surface immediately after the rupture of a bubble cap (Kientzler et al., 1954; Woodcock et al., 1953). The resulting jet droplets have radii typically in the range of 1–20 μm. This decision to ignore the role in sea-air gas exchange of these drops that have their origins in bursting bubbles needs to be justified, as such droplets, per unit droplet volume, would seem to be more effective at transferring gas from the ocean to the atmosphere than spume drops, given that their fractional change in volume much exceeds that of the briefly airborne spume drop. If the RH of the marine atmospheric boundary layer is low enough, i.e., much below 72% (the deliquescence humidity of sodium chloride is 75.5%, but shrinking saline droplets can exist as supersaturated metastable droplets in the atmosphere; see e.g., Rood et al., 1989; Tang & Munkelwitz, 1994), such jet droplets, and certainly film droplets would evaporate to dry salt particles, given that they typically reside in the atmosphere long enough to do so, and would clearly transfer in this case all of their original gas content to the atmosphere. Even in that instance where the RH of the atmosphere was 80%, such jet droplets and film droplets would shrink by evaporation to one-half their original radii, i.e., to one-eighth their original volumes. But since in this circumstance their salinity would increase by a factor of 8, and as the solubility of the gases of interest decrease as the droplet's salinity increases, the resulting saline drop would retain significantly less than one eighth of its original dissolved gas. Note that the typical spume drop's volume, and hence salinity, will undergo negligible change while it is airborne. The factor
that causes significant change in a gas's solubility in a spume drop is associated with the often marked change in temperature of such a large drop.

We can estimate ∂F_0(U)/∂R, the bubble-mediated droplet, i.e., the jet droplet and film droplet, incremental production flux by combining Monahan et al. (1986, equations 3-5), and arrive at V_0(U), the jet droplet aggregate volume production flux by the application of equation 3,

\[ V_0(U) = \int 4\pi R^3 / 3 \partial F_0(U) / \partial R dR \]

which, using the notation of Monahan et al. (1986), can be rewritten as equation 4,

\[ V_0(U) = 2.42 \times 10^{-5} U^{3.41} \int R \Delta(dN/dR) dR \]

where the quantity Δ(dN/dR), can be evaluated from their equation 5 or obtained from the relevant curve in their Figure 3. When one or the other of these steps is carried out one finds that the jet droplet and film droplet aggregate volume flux, V_0(U), at a wind speed, U, of 10 m s\(^{-1}\) is 1.34 \times 10^{-3} \text{ mm}^3 \text{ m}^{-2} \text{ s}^{-1}, at a U of 20 m s\(^{-1}\) it rises to 1.43 \times 10^{-2} \text{ mm}^3 \text{ m}^{-2} \text{ s}^{-1}, and at a U of 30 m s\(^{-1}\) it reaches only 9.36 \times 10^{-2} \text{ mm}^3 \text{ m}^{-2} \text{ s}^{-1}. These numbers, which reflect in large measure the fact that the peak in the jet and film droplet volume production spectrum occurs at a radius well below 4 μm, are several orders of magnitude less than the various spume drop aggregate volume fluxes at these wind speeds, as described in the literature and discussed later in this paper.

The following section describes the results of our recent review of the literature on spume drop production, starting with the early estimate found in Monahan et al. (1986) and including spume production models published as recently as 2016. This has resulted in a greatly altered spume drop generation function landscape from that summarized in Andreas (1998).
2 Spume Drop Production Functions

If we are to assess the relative contribution, at various wind speeds, of spume drops to the sea-to-air flux of a variety of gases, as compared to the bubble-mediated and interfacial air-sea exchange of these gases, we need to identify a robust wind-dependent spume drop aggregate volume flux expression. This section describes our review of the spume drop production literature, starting with the early estimate found in Monahan et al. (1986) and including spume production models published as recently as 2016.

As is apparent from Anguelova et al. (1999, Figure 5) and Veron (2015, Figure 6), it will be a challenge to arrive at any consensus spume drop number flux, never mind a consensus spume drop aggregate volume flux. As Anguelova et al. (1999) make clear, not all of the F(U) expressions attributed to other authors and plotted on their figure are descriptions of strictly spume drop number flux, but even so, the great disparity in amplitude of these F(U) functions at various wind speeds (often varying from one another by 2 or 3 orders of magnitude at a particular value of U), and the great variation in the several exponential-in-U expressions (as is clear from the slopes of these expressions on this semilogarithmic plot), suggest that a universal spume drop volume flux expression may, currently, be hard to find.

We will begin our search for a consensus spume drop volume production flux, V(U), by considering the various F(U) functions cited by Anguelova et al. (1999), and other F(U) and V(U) expressions that have been found in the literature, treating then in the order of their publication. All of the V(U) functions we make reference to are to be found plotted in Figure 1.
2.1 V(U) Derived From the $\partial F_1(U)/\partial R$ Expression of Monahan et al. (1986)

Monahan et al. (1986) derived their $\partial F_1(U)/\partial R$ expression using the wind dependence of spray flux measured in a wind-wave flume by Wu (1973), as based on their fitting of a straight line to the $\ln F_1(U)$ versus $U$ values replotted from Wu's Figure 10. Monahan et al. (1986) then combined this wind dependence with a spume drop number production spectrum, $\partial F_1/\partial R$, based on their combination of the wind-wave flume drop spectra found in Wu (1973) and in Lai and Shemdin (1974), to arrive at a tentative $\partial F_1(U)/\partial R$ expression. The rapid increase with wind speed of the $V_1(U)$ resulting from the application of equation 5,

$$V_1(U)=\int 4\pi R^2/3\partial F_1(U)/\partial R\,dR$$

as is apparent from Figure 1, seemed consistent with the rapid increase in concentration, $\partial F_1(U)/\partial R$, when the wind speed reached approximately 9 m s$^{-1}$, of drops with radii of 45 and 91 µm previously measured at a height of 0.13 m over the open ocean surface, by Monahan (1968). It should be noted that Monahan et al. (1986) stated that their spume drop production flux “is clearly in need of extensive revision to rid it of unrealistic features.” Elsewhere in this same paper the authors stated that the shortcomings of their $\partial F_1/\partial R$ expression were such that “its use is not recommended.” While the bubble-mediated spray droplet production flux, $\partial F_0(U)/\partial R$, in Monahan et al. (1986) has stood the test of time, we reiterate our belief that the preliminary $\partial F_1(U)/\partial R$ expression in that paper, and any $V_1(U)$ expression derived from it, should not be used for spume drops.

2.2 V(U) Expression Found in Bortkovskii (1987)

The three points that define the V(U) curve in Figure 1 are based on the mass flux values for three wind speeds listed in Bortkovskii (1987, Table 3.8). This table is the distillation of a long,
formal, mathematical analysis which ultimately relied in part on the drop data collected at an elevation of 0.13 m reported in Monahan (1968). Given that we are confident in retrospect that all drops measured with radii greater than 91 μm, and the preponderance of drops with radii greater than 45 μm, were spume drops, we conclude that much of each of the mass fluxes reported in Bortkovskii's Table 3.8 were spume drops. The spume drop production values at three wind in Bortkovskii (1987) are based on observational and theoretical considerations that are reasonable and thus we adopt this as the upper bound expression for spume drop production.

2.3 $V(U)$ Derived From a Combination of $\frac{\partial F_0(U)}{\partial R}$ and $\frac{\partial F_1(U)}{\partial R}$ by Andreas (1992)

Andreas, observing “that the spume generation term that Monahan et al. proposed yields far too many large droplets,” developed a general spray generation function that included a bubble-mediated, spray term, $\frac{\partial F_0(U)}{\partial R}$ from Miller (1987) and a spume drop term, $\frac{\partial F_1(U)}{\partial R}$, based on observations reported in Wu et al. (1984). (Andreas did assume that Miller's expression, which extended to droplets with radii of 15 μm, included some spume drops. See also, Miller and Fairall (1988).) The relevant curve in Figure 1 was generated by reading $\frac{\partial V}{\partial R}$ points off Andreas (1992, Figure 3) and then obtaining the various $V(U)$ values by graphical integration. The spume and spray drop production function found in Andreas (1992) relies heavily on the spume drop observations reported in Wu et al. (1984) and in large measure reflect the $V(U)$ wind speed dependence shown in the Wu (1993) spume production function. We will set aside the Andreas (1992) function for essentially the reason given below for rejecting the Wu (1993) spume drop production function.
2.4 $V(U)$ Derived From a Fixed Drop Spectrum and a $\partial F_1(U)/\partial R$ by Wu (1993)

Wu, agreeing with Stramska (1987) and Andreas (1992) among others, set out to improve the Monahan et al. (1986) spume drop volume production function. He also addressed his concern that the Andreas (1992) model did “not rectify the overproduction contained in that [model] of Monahan et al., except at very high winds.” Specifically in developing his model he developed the wind-invariant shape of his drop size spectrum based on his laboratory (Wu, 1973) and field (Wu et al., 1984) measurements of large drops. He obtained the wind dependence of drop production for his model from estimating the rate of drop production for various wind stress values in his wind-wave tank experiments, and then inferring from these wind stresses the equivalent 10 m elevation wind speeds to be associated with these drop production values. The resulting exponential wind dependence of his drop production model, $F_1 \sim e^{0.875U}$, was much weaker than the wind dependence, $F_1 \sim e^{2.08U}$, in the Monahan et al. model, as is apparent in Figure 1. This relevant curve on the figure was developed by first multiplying the piecewise expression for $\partial F_1(P_s)/\partial R$ (Wu's equation 10) by $4\pi R^3/3$ to obtain $\partial V_1(P_s)/\partial R$, and then graphically integrating this expression over $R$ to obtain $V_1(P_s)$ before substituting, by means of Wu's equation 9 the above mentioned wind dependence, $P_s(U)$, to obtain the required $V_1(U)$.

While the resulting Wu (1993) $V(U)$ is an improvement on the $V(U)$ obtained using the $\partial F_1/\partial R$ of Monahan et al. (1986), it still predicts too many drops. At a wind speed of 33.1 m s$^{-1}$, this expression predicts that one and a half liters of spume drops would be generated every second from 1 m$^2$ of sea surface. This will strike many seagoing scientists as too great a production of spume.

Rather than relying on intuition, one may calculate the wind speed where the fraction of the wind work per unit time on the surface of the ocean that goes directly into wave breaking minus that
fraction that goes into the drift current, a net quantity we will designate as \( W_{\text{rate}} \), is equal to the energy expended per unit time to elevate that second's production of spume drops, \( V_{\text{wa}}(U) \), to a height of 0.1 m. In this exercise, we thus ignore the fact that the spume drop injection into the MABL represents only a trivial fraction of the energy dissipated when a wave breaks. The rate of work by the wind on the surface of the ocean can be estimated by the use of equation 6,

\[
W_{\text{rate}}(U) = \tau_{\text{air}}(U) \times v_{\text{drift}}(U)
\]

where \( W_{\text{rate}} \) represents the rate, in W m\(^{-2}\), at which the wind does work on the sea surface, \( \tau_{\text{air}} \) is the tangential wind stress on the sea surface, in N m\(^{-2}\), and \( v_{\text{drift}} \) is the wind-induced drift velocity of this surface, in m s\(^{-1}\). This expression is similar to one found in Wu (1979).

The classic Ekman spiral would suggest that (in the Northern Hemisphere) the immediate surface drift current would flow at 45° to the right of the wind direction. Using surface drifters, field studies have shown that surface currents move directly downwind, or at most a few degrees to the right of the wind direction (Monahan et al., 1984; Pilgrim, 1975). Thus, for our calculations, we will assume that \( \tau_{\text{air}} \) and \( v_{\text{drift}} \) are collinear.

The values used for \( \tau_{\text{air}} \) were obtained for the higher wind speeds of interest by extrapolating a power law fit to the COARE 3.5 \( \tau_{\text{air}} \) expression plotted in Edson et al. (2013, Figure 3, bottom). While acknowledging the theoretical efforts to define the ocean surface drift velocity in terms of the 10 m-elevation wind speed and other geophysical parameters (e.g., Bye et al., 2017; Kraus, 1977), here we again turned to the “best fit” values of \( v_{\text{drift}} \) derived from drifter field experiments (see Monahan et al., 1984, and other studies cited in that publication). The expression thus chosen for \( v_{\text{drift}} \) is given in equation 7,

\[
v_{\text{drift}} = 0.03 \times U
\]
where $U$ is the 10 m-elevation wind speed. The estimate of the energy expended per unit time to elevate that second's production of spume drops to a height $h$, $P_{\text{spume}}$, in $W \, m^{-2}$, was obtained by the application of equation 8,

$$P_{\text{spume}} = \rho gh V_{Wu}(U)$$

where $\rho$ is the density of sea water in $kg \, m^{-3}$, $g$ is the acceleration due to gravity, in $m \, s^{-2}$, $h$ is the “typical” ejection height of spume drops in meters, and $V_{Wu}(U)$ is Wu's spume drop volume production function expressed in $m^3 \, s^{-1} \, m^{-2}$.

Not all of the momentum flux into the sea surface, i.e., $T_{\text{air}}$, goes into the wave field (Melville, 1996). Based on both field and laboratory studies, Snyder et al. (1981) and Hsu et al. (1982) concluded that the fraction of this momentum flux that went directly into the wave field was in the range of 40–60%. Subsequently, Rapp and Melville (1990) from their laboratory studies found that while “a significant fraction of the momentum flux from the atmosphere may pass through the wave field (50% or more); most of it is lost to currents by breaking in the generation region.” Based on these findings, we will assume as an upper bound that 30% of the work per unit time which the wind does on the sea surface will go into wave breaking, excluding that fraction which is lost subsequent to wave breaking into enhancing the drift current. We also will assume that this 30% will go into the injection, per unit time, of spume drops to an elevation of 0.1 m in the MABL. This spume drop injection elevation assumption is consistent with the wind flume observations of Anguelova et al. (1999) and Ortiz-Suslow et al. (2016) as well as with the low-elevation, open ocean, measurements of large drops made during relatively high winds by Monahan (1968) and deLeeuw (1986). These assumptions are summarized in equation 9,

$$0.3 T_{\text{air}}(U) \times v_{\text{drift}}(U) = \rho gh V_{Wu}(U) = 0.1 \rho g V_{Wu}(U)$$
where again, 0.1 m represents \( h \), the typical height to which we have assumed that the spume drops are ejected to above the wave crests. Acknowledging that not all spume drops are ejected upward, none-the-less this equation should yield an extreme upper bound on the wind speed that could possibly support the spume production if Wu's (1993) spume production model is valid. The wind speed that satisfies equation 9 is 32.8 m s\(^{-1}\). The assumptions underlying this equation are unrealistically favorable for the injection into the MABL of spume drops, and the energy required for the exponentially growing spume drop production suggested by Wu (1993) grows with wind speed more quickly than the rate of actual energy input of the wind that goes into wave breaking. Thus, it can with certainty be concluded that the work the wind does on the ocean surface is insufficient to sustain the great rate of production of spume drops described in Wu (1993) even at wind speeds much lower than 32.8 m s\(^{-1}\). We therefore choose to set aside the Wu (1993) \( V(U) \) expression.

2.5 \( V(U) \) Expression Based on Material in Fairall et al. (1994)

Fairall, Kepert, and Holland's expression for the spray aggregate volume production is a combination of the expression of Miller (1987) for bubble-mediated spray production and the function of Wu et al. (1984) for spume drop production, following the approach of Andreas (1992). Assuming that the shape of this spray-spume production expression is invariant to changes in wind speed, and thus to changes in whitecap coverage, this combined volume production function as plotted in their Figure 3 is “normalized” to 100% whitecap coverage. The wind dependence of this production function is then obtained by multiplying the expression plotted on this figure by the whitecap coverage dependence on wind speed as given by Monahan and O'Muircheartaigh (1980, equation 5), which appears here as equation 10.
This formula yields $W(U)$ as the simple fraction of the ocean surface covered by whitecaps at wind speed $U$ which is deemed by Fairall and coauthors to be the appropriate quantity to multiply the “normalized” spray-spume production curve of Fairall et al. (1994) by to obtain the aggregate volume production at this wind speed. (It should be noted that our understanding of the wind dependence of whitecap coverage has been elaborated upon since the Monahan and O'Muircheartaigh (1980) paper, see, e.g., Monahan and O'Muircheartaigh (1986) and more recently Monahan et al. (2015).) Their Figure 3 depicts both the bubble-mediated spray production curve and the combined spray and spume production curve. Since in this paper we are interested in the spume production function, we have graphically integrated the combined production curve from a drop radius of 40 μm, where the spume drops represent some 46% of the total volume production, on up to the largest drop radius shown on this figure. At a drop radius of 60 μm the spume drops represent no less than 96% of the total volume production, and at even larger radii the bubble-mediated spray contribution is negligible. It is the resulting Fairall et al. (1994) spume $V(U)$ curve that appears in Figure 1.

By way of an historical footnote: while the original Beaufort Wind Force Scale was all about the sailing characteristics of nineteenth century men-of-war (Kinsman, 1969), over the years wind speed equivalents to the various Beaufort wind forces have been introduced, some of which include for each such force descriptions of the appearance of the sea surface (e.g., Meteorological Office, 1978). This U.K. Met. Office publication (Table 3.1) in its description of Beaufort Force 6, “Strong Breeze,” includes the statement “Probably some spray,” and gives the average wind velocity associated with this Force as 24 knots (12.3 m s$^{-1}$). The description of Beaufort Force 9, “Strong Gale,” in this same table includes the admonition “Spray may affect
visibility,” and gives the mean wind speed associated with this Force as 44 knots (22.6 m s⁻¹).

Clearly the spray drops that one can see with the unaided eye must be spume drops, not the microscopic droplets produced by the bubble-mediated mechanisms. And equally clearly, the modern Beaufort scale's description of the change with wind speed of the spray loading of the atmosphere is consistent with the wind speed dependence of large drops as reported by Monahan (1968), and not the more modest wind dependence of whitecap coverage. (The Met. Office Beaufort scale indicates that at Force 6 “white foam crests are more extensive everywhere” and at Force 9 reports “dense streaks of foam along the direction of the wind.”)

Table 1. Boundary Conditions for the Three Spume Drop Gas Exchange Mechanisms

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>H₂O sat. of atmosphere a</th>
<th>Gas in equil. across sea surface b</th>
<th>T_{air} = T_{water}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometrical</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Wet bulb</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Delta T</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

- a Corresponds to a relative humidity of 98.2% when air over sea water of 35 psu.
- b When net diffusive transfer of gaseous species is 0 across air-sea interface, i.e., when C_{W} – H_{p_a} = 0.

Since Fairall et al. (1994) have assigned the relatively low wind dependence of whitecapping to spume drop production, compared to the much higher dependence inferred from, e.g., Monahan (1968), we select the Fairall et al. (1994) V(U) expression as representative of a reasonable lower bound expression for spume drop production.

2.6 V(U) Expression Developed by Andreas (1998)

This expression was generated by starting with the Smith et al. (1993) function which these authors intended to represent both the bubble-mediated spray production and the spume drop production as a function of wind speed. Andreas, in the current paper, then modified what was
judged to be the bubble-mediated portion of the Smith et al production function by multiplying it by a factor of 3.5 to bring it into correspondence with the $\partial F_0/\partial R$ expression found in Monahan et al. (1986), and then adjusted the spume drop portion of the Smith et al. production spectrum to correspond to the production function of these drops, $\partial F_1(U)/\partial R$, that would be required to maintain their low-elevation concentration as described in Wu et al. (1984). This last step seemed to be called for, given that the Smith et al. (1993) aerosol measurements were made with instruments “upon a 10 m tall scaffolding tower positioned close to the high-water mark at the top of a gently sloping beach” (Smith et al., 1993), and that their size spectra, measured about “14 m above mean sea level,” end with droplets of 25 µm radii, it can be argued that their instruments would have detected few, if any, of the larger spume drops. (See also the section on Site Considerations, that appears on pp. 55–56 in Park, 1985.) The modelling of Mueller and Veron (2009) suggests that at a wind speed of 20 m s$^{-1}$ less than 1% of the spume drop mass produced at the sea surface is effectively suspended in the marine atmospheric boundary layer. The curve in Figure 1 identified with Andreas (1998) was obtained by the graphical integration under the curves in Andreas (1998, Figure 4) over drop radii from 20 to 400 µm, and as such are meant to represent the V(U) values for the spume drops in these spectra. With these concerns about the wind dependence of the spume drop production ascribed to by Wu, we therefore set aside the V(U) expression developed by Andreas (1998).

2.7 $V(U)$ Expression Based on Laboratory Findings of Anguelova et al. (1999)

This V(U) expression is based on video observations of spume drops with radii of 450 µm and greater made by Anguelova and colleagues in the relatively large wind-wave-current facility of the University of Delaware. Reference wind speeds were measured for each experimental run.
with a Pitot tube and converted to 10 m-elevation wind speeds as per Wu (1968, 1980). The interpretation of these observations was informed by a knowledge of the importance of wave breaking rates. Specifically, Figure 2b in Anguelova et al. provided curves of $\partial F_1(U)/\partial D$ versus $D$ for four wind speeds. The points on each of these curves, having been converted to $\partial F_1(U)/\partial R$, were each multiplied by $4\pi R^3/3$ and then integrated over $R$ to provide $V(U)$ values, which appear in Figure 1. The resulting $V(U)$ expression has been deemed a “typical” spume drop production function and will be used as such in the modelling described later in this paper. This median expression, and one other that is introduced below, are described as “typical” in light of their amplitudes which fall between the lower and upper bounds, particularly in the low wind speed range (10–15 m s$^{-1}$).
Figure 2. Spume drop volume production functions and air-sea gas exchange coefficients both expressed as piston velocities in μm s\(^{-1}\). The five spume drop generation functions plotted are those designated as “typical” from Anguelova et al. (1999) and from Zhao et al. (2006); as “upper bound,” from Bortkovskii (1987); and as “lower bound,” from Fairall et al. (1994) and from Andreas et al. (2010). The three air-sea gas transfer coefficients for CO\(_2\) included on this figure are from Liss and Merlivat (1986), the quadratic k(U) expression from Wanninkhof and McGillis (1999), and the cubic k(U) expression from this same publication. The air-sea DMS transfer coefficient included on this figure is from Vlahos and Monahan (2009).

2.8 \(V(U)\) Derived From \(V(u^*)\) Contained in Kudryavtsev (2006)

The spume aggregate volume flux, \(V\), as a function of friction velocity, \(u^*\), presented in this paper by Kudryavtsev (2006), and illustrated in his Figure 2b, is attributed to Andreas (1998) where it was originally expressed as a function of \(U\), the 10 m-elevation wind speed. Since in arriving at the \(V(U)\) curve attributed to Andreas (1998) in Figure 1, we considered only drops
with radii greater than 20 μm, and Kudryavtsev in preparing the spume drop curve on his Figure 2b also included only drops with radii greater than 20 μm, we thought it appropriate to directly compare these to the Andreas (1998) curves. We did so by using Edson et al. (2013, equation 22), which appears as equation 11 below, to convert the V(u*) s of Kudryavtsev to V(U)s.

\[ u^* = 0.062 \  U - 0.28 \] (11)

The small discrepancy between the Andreas (1998) and Kudryavtsev (2006) curves as they appear in our Figure 1 is probably attributable to Kudryavtsev using a slightly different U-to-u* conversion than that given by equation 11. The Kudryavtsev V(U) curve that we derived from his V(u*) plot is thus understandably only slightly different from the Andreas (1998) V(U) curve and will not be treated as an independent spume aggregate volume flux expression.

2.9 \( V_{\beta=1.2} \) and \( V_{\beta=0.2} \) Based on Field-Based and Laboratory-Based Results in Zhao et al. (2006)

The spray data sets used by these investigators, most of which included observations into the spume drop size range, were those reported in Toba (1961), Toba and Chaen (1969, 1973), Chaen (1973), Koga and Toba (1981), Koga (1986), and Sugioka and Komori (2005). Using these field and laboratory measurements, the authors were able to produce a spume drop production spectrum, which they described as “a similar droplet size spectrum to that of Monahan et al. (1986),” whose shape is invariant with wind speed, and “windsea Reynolds number \( R_B \).” This windsea Reynolds number is given by equation 12,

\[ R_B = C_D \ U^3 \beta \sqrt{g \nu} \] (12)

where \( C_D \) is the drag coefficient, \( \nu \) is the kinematic viscosity of air, \( U \) is the 10 m-elevation wind speed, and \( \beta \) is the wave age, as given by equation 13,

\[ \beta = g \omega_p \ U \] (13)
where $\omega_P$ is the angular frequency of the wind-wave spectral peak. While the shape of their spume drop production spectrum, which covers the drop radius range of 30–500 µm, is invariant with changes of $U_{10}$ and $R_B$, the amplitude of this spectrum, as can be seen from their equation (17), is both a function of the wind speed, $U_{10}$, and of the wave age, $\beta$, which in turn is both a function of the angular frequency of the wind-wave spectral peak, $\omega_P$, and of the wind speed. While these authors have demonstrated that $R_B$ is a much better descriptor of the spume drop production flux than is $U$, they do provide, in their Figure 8, a description of how the spume drop production flux varies with wind speed, for two values of wave age, $\beta$. This figure has enabled us to compute the spume drop volume flux, $V(U)$, for well-developed wind waves, corresponding to a $\beta$ of 1.2, and for young wind waves, where the value of $\beta$ is 0.2. The resulting two $V(U)$ curves are plotted in Figure 1.

We will include in our further considerations as a “typical” spume drop production function the Zhao et al. (2006) $V(U)$ curve they ascribed to a well-developed wind-wave field, one where the wave age, $\beta$, is equal to 1.2. We will not consider further the $V(U)$ expression which these authors associate with young wind waves, where $\beta$ has a value of 0.2, as this paper focuses mainly on the potential role of spume drops in air-sea gas exchange under fully developed seas.

2.10 $V(U)$ of Fairall and Banner Model as Described in Fairall et al. (2009)

In the Fairall et al. (2009, Figure 8, bottom) the authors have plotted a mass flux expression, $M(u^*)$, in g m$^{-2}$ s$^{-1}$, as a function of the friction velocity, $u^*$, m s$^{-1}$, which they describe as an updated “parameterization obtained from a physically based model” developed by Fairall and Banner. We converted six points on this $M(u^*)$ curve to $V(U)$ values using the $u^*$ to $U$ conversion of Edson et al. (2013) found in equation 11 above, assuming that the density of the spume drops could be well approximated by unity. The resulting $V(U)$ curve appears in Figure 1.
We note that this V(U) function varies approximately as U^{5.3}. In the absence of a full discussion by the authors of their rationale for this expression, we will not include this V(U) function in what follows.

2.11 \( V_A(U) \) Production Flux \( V_B(U) \) and \( V_B(U) \) Suspended Fraction Flux From Mueller and Veron (2009)

In this paper, the authors present a semiempirical derivation of the spume drop source function, which owes much to assumptions to the governing hydrodynamic mechanisms of drop formation. This derivation centers around their perception that such drops are formed from coherent aqueous ligaments formed via instabilities induced in wave crests under high wind conditions. The ligaments become separated from the bulk water and transform into globules. These globules, under the action of shear forces and turbulence, then eventually shatter into the spume drops. At ever higher wind speeds, the associated energy is available to shatter the globules into ever smaller spume drops. These authors provide two spume generation functions, the first of which describes the spume drops at their moment of production at the sea surface and the second of which describes that portion of this spume drop flux which is effectively transported upward to “where measurements are routinely made.” This second droplet flux they label “suspended.” They provide in their Figure 2d the \( \partial V/\partial D \) functions for both the spume drops produced and for the “suspended” portion of this production, at seven wind speeds, and for a fetch of 75 km. It is apparent from this figure that the peak in the \( \partial V/\partial D \) production curves falls at markedly smaller drop diameters as the wind speed increases; while the peak in the “suspended” portion of the production curves only shows a modest, if any, shift to smaller diameter drops for the very highest winds.
We have via graphical integration calculated the $V_A$ (total spume volume flux at the sea surface) and $V_B$ (suspended portion of spume volume flux) for winds up to 30 m s$^{-1}$ from the relevant curves in Mueller and Veron's Figure 2d, and plotted curves in our Figure 1. One notes from Figure 1 that the Mueller and Veron $V_A$ (total flux) decreases as wind speed increases. This is consistent with the behavior of the “source function” line on Mueller and Veron's Figure 4, a plot of mass flux versus friction velocity, for friction velocities above 0.35 m s$^{-1}$, i.e., for 10 m-elevation wind speeds above 7–10 m s$^{-1}$. In Figure 1, it is apparent that the Mueller and Veron $V_B$ (suspended portion of flux) increases rapidly with wind speed, in agreement with the behavior of the “suspended” spume flux curve on Mueller and Veron's Figure 4. Concerned that the hydrodynamic constraints imbedded in this model have forced a too extreme diminution of the characteristic drop volume with increases in wind speed, we will also set this “source” model aside.

2.12 $V(U)$ Expression Described in Andreas et al. (2010)

First introduced in Andreas (2002), the sea spray generation function described in this 2010 article, intended to cover drops with the radii at the time of their formation, $R_0$, ranging from 1.6 to 500 μm, was produced by combining the bubble-mediated drop generation function of Monahan et al. (1986) with the large drop generation function of Fairall et al. (1994). These two expressions are “merged in the radius range of 1.5–2.0 μm.” (The Monahan et al. (1986) function was selected as it “has been repeatedly proven to be accurate for predicting the production of [the] smaller droplets” and the Fairall et al. (1994) function was judged “to be the best available for larger droplets.”) These authors point out that both of these functions “have the same wind speed dependence.” In a subsequent paper, Jones and Andreas (2012) point out that this wind
dependence is the one that Monahan and O'Muircheartaigh (1980) ascribed to whitecap coverage. Since the shape of the resulting combined spray drop generation expression, \( \partial F/\partial R_0 \), is invariant with change of wind speed (Jones & Andreas, 2012), and the Monahan and O'Muircheartaigh (1980) whitecap coverage dependence on wind speed was a simple power law relationship, one can calculate the spray drop aggregate volume flux, \( V \), at one wind speed, say 10 m s\(^{-1}\), and then calculate \( V(U) \) for any \( U \) using equation 14, where \( U/10 \) is the ratio of the wind speeds.

\[
V(U) = (U/10)^{3.41} V(10) \tag{14}
\]

The Andreas et al. (2010) \( V(U) \) curve is plotted in Figure 1.

As with the case of the Fairall et al. (1994) \( V(U) \) expression, which also incorporated the whitecap wind dependence of Monahan and O'Muircheartaigh (1980) in both its bubble-mediated spray and spume production components, we will include the Andreas et al. (2010) \( V(U) \) expression as a lower bound expression for spume drop production.

2.13 \( V(U) \) Derived From “Equilibrium Assumption” \( \partial F/\partial R \) of Jones and Andreas (2012)

Jones and Andreas (2012) developed their \( \partial F/\partial R \) expression by combining two concentration functions with the assumption of a dynamic equilibrium. The concentration function found in Lewis and Schwartz (2004) was used for the droplets generated by bubble-mediated mechanisms. Jones and Andreas (2012) postulated another concentration function for primarily spume drops, along with the terminal fall velocities, \( v_g(R) \), for these drops of various radii. The assumption of a dynamic equilibrium states that the concentration in the lower MABL of drops of each radius were, over short periods, invariant with time. Jones and Andreas generated the \( \partial F/\partial R \) curves for several wind speeds shown in Figure 11 of their paper. The concentration
function for the bubble-derived drops varied as $U^2$ while the concentration function they used for spume drops varied as $U^4$.

By graphical integration of the area under the respective $(4/3) \pi R^3 \partial F/\partial R$ curves the associated $V(U)$ values were obtained and plotted in Figure 1. Note, these integrations were carried out from the $R$ value of 20 $\mu$m to the $R$ values at which the respective $\partial F/\partial R$ curves reached the right edge or bottom border of Jones and Andreas' Figure 11 since our focus is on the role of spume drops in air-sea exchange processes. Even though this expression incorporates a higher wind dependence for spume production than that assigned to this production element in the Andreas et al. (2010) model, this $V(U)$ expression falls below those we have already designated as “lower bound” expressions in the wind speed range for which it has been proposed (see Figure 1), and will not be considered further in what follows.

2.14 $V(U)$ Expression Based on Laboratory Results of Ortiz-Suslow et al. (2016)

Laboratory experiments were carried out in the University of Miami's Air-Sea Interaction Saltwater Tank by Ortiz-Suslow and colleagues to obtain the information needed to describe the spume drops production function at high wind speeds. The test section of this tank is 15 m long, 1 m wide, and 1 m high. The height of 1 m is divided between the air-filled head-space and the flume-space filled with sea water (Donelan et al., 2004). The initial water depth in the experiments of Ortiz-Suslow et al. was 0.42 m and thus the vertical dimension of the space filled with water and droplets was 0.58 m. The wind speed in this wind-wave flume was measured 0.20 m above the still water surface, and extrapolated up to the standard 10 m-elevation wind speed in the manner described in Donelan et al. (2004). These authors carried out direct measurements at five wind speeds of spume number concentration spectra at two reference levels in the tank head-
space, and the vertical gradients of the spume volume spectra were also determined. They then calculated from these findings, among other quantities, the spume drop volume production flux spectrum assuming a steady state between droplet production and droplet deposition back to the water surface. In their conceptual model they assumed that the theoretical spume drop source height was equivalent to the significant wave height. The significant wave heights measured in these experimental runs are listed in Table 1 of the Ortiz-Suslow et al. paper, and ranged from 29.2 to 37.7 mm. The equivalent 10 m-elevation winds for these experimental runs ranged from 36 to 54 m s\(^{-1}\). Their spume drop volume production spectra, \(\partial V(U)/\partial R\) for these five wind speeds are plotted in Ortiz-Suslow et al. (2016, Figure 8b). The V(U) values that appear in Figure 1 were obtained by graphically integrating their \(\partial V(U)/\partial R\) curves. Given the significant wave heights measured by these investigators (less than 40 mm), we conclude that these were very young wind waves. The marked difference in amplitudes between the Ortiz-Suslow et al. (2016) and Anguelova et al. (1999) V(U) curves (see Figure 1) may in part be due to a difference in the wave ages associated with these two tank studies. The impact of different wave ages on spume production is apparent from the relative position in Zhao et al. (2006, Figure 1a) V(U) curve for well-developed wind waves and the Zhao et al. (2006, Figure 1b) curve for young wind waves. The Ortiz-Suslow et al. V(U) expression will be omitted from further consideration, as was the Zhao et al. (2006, Figure 1b) expression.
Air-Sea Gas Transfer Via Spume Drops Compared to Bubble and Interfacial Air-Sea Gas Transfer

Before we embark on these comparisons, we should note that there are three complementary means by which spume drops can potentially function efficiently in enhancing air-sea gas exchange at high wind speeds. In most circumstances, two or more of these mechanisms work simultaneously on an airborne spume drop. In each of the following sections, we will set the boundary conditions such that only one of these mechanisms is in effect.

The first of these three roles played by spume drops we will designate the “geometrical mechanism”; by which we refer to the fact that even large spume drops individually have a relatively large surface-area-to-volume ratio, which when coupled with their enhanced ventilation while aloft in the MABL, makes them effective instruments for air-sea gas exchange.

The second means by which spume drops serve a role in enhancing air-sea gas exchange we will refer to as the “wet bulb mechanism.” This is in acknowledgment of the fact that a large spume drop will quickly, compared to its time aloft, adjust to a temperature close to the web bulb temperature associated with the MABLs air temperature and RH (Andreas, 1995). This rapid temperature adjustment will result in the spume drop either gaining gas from, or losing gas to, the MABL. (Since the wet bulb mechanism working alone results in the drop cooling, and since the solubility of most gases of interest increases as the droplet temperature decreases, the wet bulb mechanism usually fosters gas invasion to spume drops.)

The third means by which spume drops potentially enhance air-water gas exchange, we will refer to as the “delta T mechanism,” and refers to the fact that, absent of the “wet bulb effect,” a spume drop, initially at the sea surface temperature, will experience a fairly rapid adjustment to the temperature of the MABL.
Before we proceed to consider the effectiveness of each of these three mechanisms, it is important to stress that in each of the following sections we have set the relevant boundary conditions so that only the mechanism discussed in each section is operative. These boundary conditions are summarized in Table 1.

3.1 \( V(U):k(U) \) Ratios When Only the “Geometrical” Mechanism Is Operative

It is important to stress that the following discussion of the relative magnitude of the spume drop facilitated air-sea gas exchange to the interfacial (and bubble facilitated) air-sea gas exchange at various wind velocities is based on the \( V(U)/k(U) \) ratios, where \( k(U) \) is the air-sea interfacial gas exchange coefficient in equation 1, which is analogous to equation 2. But for the \( V(U)/k(U) \) ratios to accurately represent the ratio of the spume facilitated gas exchange to the interfacial air-sea gas exchange the geometrical mechanism must be paramount, i.e., the temperature of the spume drop must remain the same while it is airborne as it was when the drop left the ocean surface, and this requires that the temperature of the air and the temperature of the surface layer of the ocean must be nearly equal and the RH of the atmosphere must correspond closely to the saturation vapor pressure for sea water at that temperature. While these conditions may only occasionally be approximated at sea, our assumption of these conditions is warranted given the great range in the \( V(U) \) values as has been discussed earlier in the text. Typical MABL conditions would exhibit temperature gradients between air and water and RH influenced by regional air conditions.

We will begin this discussion by comparing the “spume drop gas transfer coefficients,” i.e., the \( V(U) \) expressions, identified above as “typical,” and as “upper” and “lower” bounds, with several of the more recently published \( k(U) \) expressions, i.e., the combined bubble-mediated and
interfacial gas transfer coefficients. In Figure 2 are plotted the five selected V(U) expressions. In this instance, they are expressed in μm s\(^{-1}\), as is appropriate for a gas transfer coefficient or “piston velocity” (*note*: \(10^3 \text{ mm}^3 \text{ m}^{-2} \text{ s}^{-1} = 1 \text{ μm s}^{-1}\)).

Two of the k(U) formulae plotted on this figure are the quadratic and cubic expressions for CO\(_2\) air-sea exchange described in Wanninkhof and McGillis (1999). A third k(U) formula for the air-sea exchange of CO\(_2\) (and gases of similar solubility) plotted in Figure 2 is the piecewise linear expression found in Liss and Merlivat (1986, Figure 1). These expressions were chosen as representing the current consensus as to the wind dependence of the air-sea CO\(_2\) transfer coefficient. (For a summary of the variety of k(U) power law expressions found in the literature the reader is referred to Monahan (2002, Figure 1).) The fourth k(U) expression plotted in Figure 2 was one derived for dimethyl sulfide, an amphiphilic gas for which bubbles, when present as they are at high wind speeds, markedly delay the gas transfer at the bubble surface, leading to a significant attenuation of the dimensionless Henry's law coefficient, as described in Vlahos and Monahan (2009, Figure 1), from which this k(U) expression has been taken. (The k(U) expressions for other such hydrophobic organic compounds are to be found plotted in Vlahos et al. (2011, Figure 3).)

Comparisons, in the form of simple ratios, of the spume contributions to air-sea gas exchange to the recognized bubble-mediated and interfacial air-sea gas exchange, for various wind speeds up to 40 m s\(^{-1}\), are provided in Table 2. This upper end of the range of wind speeds is chosen because this is the valid range for the measurements on which the expressions for k(U) and V(U) considered here are based. Given that spume drops are only produced in quantity when the wind speed is greater than 9 m s\(^{-1}\) (Monahan et al., 1986) it is not surprising that for winds of 15 m s\(^{-1}\) neither of the “typical” spume drop gas exchange coefficients, i.e., V(U)s, exceed 1% of
the amplitude of any of the four k(U)s plotted in Figure 2. Even the V(U) of Bortkovskii (1987) identified previously as the “upper bound” V(U) expression is less than 5% of the several CO2 k(U) values at the wind speed of 15 m s\(^{-1}\), and is 12.7% of the DMS k(U) at this wind speed.

### Table 2. Ratio of V(U\(_i\)) to k(U\(_i\))

<table>
<thead>
<tr>
<th>V(U(_i))/k(U(_i))</th>
<th>U (m s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Typical V(_1)/k \sim U^2 (Wanninkhof &amp; McGillis, 1999)</td>
<td>0.23%</td>
</tr>
<tr>
<td>Typical V(_2)/k \sim U^2 (Wanninkhof &amp; McGillis, 1999)</td>
<td>0.07%(^b)</td>
</tr>
<tr>
<td>Upper V(_3)/k \sim U^2 (Wanninkhof &amp; McGillis, 1999)</td>
<td>4.00%</td>
</tr>
<tr>
<td>Typical V(_1)/k \sim U^3 (Wanninkhof &amp; McGillis, 1999)</td>
<td>0.19%</td>
</tr>
<tr>
<td>Typical V(_2)/k \sim U^3 (Wanninkhof &amp; McGillis, 1999)</td>
<td>0.05%(^b)</td>
</tr>
<tr>
<td>Upper V(_3)/k \sim U^3 (Wanninkhof &amp; McGillis, 1999)</td>
<td>3.03%</td>
</tr>
<tr>
<td>Typical V(<em>1)/k(</em>{DMS}) (Vlahos &amp; Monahan, 2009)</td>
<td>0.77%</td>
</tr>
<tr>
<td>Typical V(<em>2)/k(</em>{DMS}) (Vlahos &amp; Monahan, 2009)</td>
<td>0.20%(^b)</td>
</tr>
<tr>
<td>Upper V(<em>3)/k(</em>{DMS}) (Vlahos &amp; Monahan, 2009)</td>
<td>12.7%</td>
</tr>
</tbody>
</table>

- \(^a\) Based on an extrapolation of power law fit to Zhao et al. (2006) data.
- \(^b\) Based on extrapolation of power law fit to Anguelova et al. (1999) data.

We need to take a moment here and explain why we are using at all wind speeds the same spume drop V(U) expressions for DMS as were used for CO2, while the k(U) for DMS is much reduced compared to the CO2 k(U) expressions for wind speeds of 10 m s\(^{-1}\) and higher. Vlahos and Monahan (2009) showed that this attenuation of the DMS k(U) compared to the k(U) for CO2 and other such gases has been attributed to the great number of small bubbles in the bubble
plume beneath a recently formed whitecap. These small bubbles sequester temporarily on their surfaces much of the DMS which otherwise would have been in solution at just the time when the rapidly rising larger bubbles were stirring the ocean surface above this plume. The mixing from the large bubbles forms, momentarily, a “low impedance vent” that facilitated the escape into the atmosphere of DMS in solution in the surface layer of the ocean. In contrast, spume drops are formed from the disruption of a wave crest before the wave breaks. And it is only when a wave breaks that it entrains large volumes of air, forming a whitecap and the dependent dense plume of bubbles. Thus, recognizing that, even in a storms tossed ocean, a wave rarely breaks where another wave has just broken, it can confidently be assumed that a typical spume drop contains few if any microbubbles, and thus the spume drop's exchange of DMS with the MABL will not be impeded by the mechanism outlined above.

When we look at the ratios of the various spume drop gas exchange coefficients to “conventional” gas exchange coefficients, i.e., the $V(U)/k(U)$ values, for a $U$ of 20 m s$^{-1}$ as they appear in Table 2, it is apparent that all but two of these ratios are markedly larger than these same ratios at the lower wind speed of 15 m s$^{-1}$. The two exceptions are those involving the spume drop gas exchange coefficient based on the spume drop volume production flux reported in Bortkovskii (1987). One of these ratios remained as it was for winds of 15 m s$^{-1}$, and one actually decreased in magnitude. This is because this spume production flux over the range of wind speeds (15–30 m s$^{-1}$) for which it was reported in Table 3.8 of Bortkovskii appears to vary as the square of the wind speed, as did one of the CO$_2$ exchange coefficients described in Wanninkhof and McGillis (1999), while the other CO$_2$ exchange coefficient described in this 1999 publication increases as the cube of the wind speed. In spite of the low wind dependence of the Bortkovskii spume drop volume production flux, it is noted that the ratio of the Bortkovskii
spume drop gas exchange coefficient to the DMS exchange coefficient does increase to 20.4% at this wind speed of 20 m s\(^{-1}\), due the “leveling off” of the DMS exchange coefficient at this wind speed as described in Vlahos and Monahan (2009).

Now when we go to the \(U = 30\) m s\(^{-1}\) column in Table 2, we see no gas exchange coefficient ratios listed for the amphiphilic gas DMS. This is because in their earlier paper the current authors did not extrapolate their DMS \(k(U)\) curve beyond a wind speed of 20 m s\(^{-1}\). It is interesting to note that if they had extrapolated their \(k(U)\) curve, which was nearly horizontal at 20 m s\(^{-1}\), to higher wind speeds then clearly \(V(U)/k_{DMS}\) ratios at 30 m s\(^{-1}\) would be markedly larger than they were at 20 m s\(^{-1}\), with the ratio of the Bortkovskii spume drop “piston velocity” to the DMS “piston velocity” reaching 46.3% at this higher wind speed. While such extrapolations are subject to uncertainty, this estimate suggests that further investigations of the role of the spume drop “geometrical” mechanism in fostering the air-sea exchange of DMS are warranted.

Since the two \(k(U)\) expressions from Wanninkhof and McGillis (1999) plotted in Figure 2 are both power law expressions, as are all five of the \(V(U)\) expressions plotted on this log-log graph, all seven of these curves appear as straight lines on this figure. It is thus tempting to extrapolate all of these expressions beyond the upper end of the range of wind speeds for which the original authors had \(k\), or \(V\), measurements from which they based these expressions. We have limited ourselves to extrapolating the \(V(U)\) expressions derived from Anguelova et al. (1999) and Zhao et al. (2006), which both are power laws, and the quadratic and cubic \(k(U)\) expressions of Wanninkhof and McGillis (1999) to a wind speed of 40 m s\(^{-1}\). The resulting \(V(U)/k(U)\) ratios are listed in Table 2.
Noting that while the wind dependence of the Bortkovskii (1987) V(U) expression plotted in Figure 2 is approximately that of $U^2$, all four of the other V(U) expressions have a wind dependence of greater than $U^3$, thus all but the Bortkovskii V(U) expression converge even further toward the magnitude of the k(U) expressions plotted on this figure as the wind speed increases beyond those listed in Table 2. The wind dependence of the Fairall et al. (1994) and the Andreas et al. (2010) V(U) expressions identified above as “lower bound” expressions reflect the wind dependence of whitecapping as determined by Monahan and O'Muircheartaigh (1980), i.e., are power law expressions of $U^{3.41}$ (see equation 6), and the “typical” V(U) expressions of Zhao et al. (2006) and of Anguelova et al. (1999) can be fitted, respectively, to power laws of the form $U^{-5.6}$ and $U^{-7.2}$. While we think it ill advised, if one were to extrapolate the “typical” V(U) expression of Anguelova et al. (1999) to beyond 40 m s$^{-1}$ it would intersect the Wanninkhof and McGillis (1999) $U^2$ k(U) expression at $\sim$40 m s$^{-1}$ and those authors' $U^3$ k(U) expression at $\sim$60 m s$^{-1}$.

Before we summarize our general conclusions, we should point out the two circumstances where the assumptions summarized in the above section lead to invalid conclusions as to the relative importance of spume facilitated and interfacial air-sea gas exchange. In each of these two cases, described in sections 3.2 and 3.3, spume drops could conceptually contribute more to the air-sea exchange of a particular gas than would the traditional interfacial exchange mechanism. The two spume drop mechanisms described in these sections are effective gas exchange mechanisms when the traditional interfacial mechanism is not in play, i.e., in the circumstance where the gas concentration in the lower MABL and in the sea surface layer are in equilibrium. (In this circumstance, the third spume drop mechanism, the geometrical one, is also inactive, as it too relies on a disequilibrium in gas concentration across the air-sea interface to be effective.)
3.2 The Case Where the Wet Bulb Mechanism Is Paramount

In this case the temperature of the ocean surface and of the lower MABL will be taken to be the same, and the concentration of our gas in solution in the surface layer of the ocean, and the gas concentration of the lower marine atmospheric boundary layer will be taken to be such that the terms in parentheses on the right-hand side of equations 1 and 2 sum to zero. This corresponds to no net exchange of this gas across the ocean-atmosphere interface via diffusion. And while spume drops thrown up from the sea surface in this instance will initially have the temperature of the oceanic surface layer, these very large drops will, as was mentioned in section 1.1, quickly cool to an evaporation equilibrium temperature closely equivalent to the wet bulb temperature for the given air temperature and RH (Andreas, 1995). The solubility of most of the atmospheric gases of interest increase as the drop's water temperature decreases. Noting that the spume drop will maintain this wet bulb temperature until it returns shortly to the sea surface, we are led to conclude that this relatively cool drop would experience a net invasion of gas during its relatively short time aloft, and would return its excess burden of gas to the sea surface when it splashes back down. Initial modeling of this “wet bulb” effect has been undertaken by the authors and indeed we find that even with no difference between the temperature of the air and the surface waters (see Table 1) a cooling effect is observed. Take, for example, a 100 µm droplet at a relative humidity of 80% and a salinity of 35 g/kg with air and sea temperatures being 15°C. Even with no air-water temperature difference the droplet rapidly cools in 0.20 s from 15 to 13.1°C, leading to a theoretical increase in the gas holding capacity of the as yet unevaporated droplet. The equilibrium of the radius takes more than two minutes (180.4 s) and is a prerequisite for the droplet to warm back to the air temperature. Thus, it is very likely that the droplet will return to the ocean in its cooled/higher gas content state.
This “wet bulb effect” would over time cause the surface layer of the ocean to become supersaturated with this gas compared to the concentration of this gas in the lower MABL, in those instances where the “wet bulb” temperature of each spume drop is significantly cooler that the temperature of the lower MABL. But spume drops, and the smaller bubble-generated spray drops, are only produced in quantity when the wind is high and the waves are well developed, and in this circumstance the RH of the lower MABL approaches 98.2%, the saturation vapor pressure for sea water at 35‰ salinity (and the saturation vapor pressure of a large spume drop of this same salinity), and the difference between the spume drop “wet bulb” temperature and the air temperature approaches zero. While a thorough modelling of this situation is recommended, the above discussion leads to the conclusion that when spume and spray concentrations in the MABL are large, the temperature difference between the spume drops and the atmosphere becomes negligible, and the “web bulb” gas exchange mechanism becomes ineffective. (We note that a similar asymmetry in the role of bubbles in the air-sea exchange of gases can, and does, lead over time to a supersaturation of the oceanic surface layer with such gases as nitrogen and oxygen as has been described in Woolf and Thorpe (1991) and Hamme and Emerson (2006).)

3.3 The Case Where the Delta-T Mechanism Holds Sway

In this case, the ocean surface temperature is taken to be significantly different from the temperature of the lower MABL. The RH of the lower MABL is assumed to be 98.2%, the saturation vapor pressure over sea water, and therefore the drop will not suffer significant evaporative cooling while it is airborne. We will further stipulate that the term in brackets on the right-hand side of equation 1 is zero, i.e., there is initially no interfacial air-sea gas exchange. And initially the right-hand side of equation 2 will also be zero, but very quickly after it is
injected into the atmosphere the spume drop's temperature will adjust toward the temperature of
the MABL (see Andreas, 1995, Figure 1, right-hand plot), and this drop will then be in
disequilibrium with the atmosphere and as a consequence will either gain or lose gas to the
atmosphere. If the gas in question is one where its solubility will increase as the drop's
temperature decreases, and if the air temperature is less than the surface water temperature, then
the drop will quickly cool and as it does so it will gain gas from the atmosphere and return to the
ocean surface with a higher concentration of this gas than when it left this surface, i.e., it will
facilitate gas exchange from the atmosphere to the ocean, and over time the ocean will become
supersaturated with this gas with respect to the atmosphere. If the air temperature is greater than
the surface water temperature then the subsequent warming of the drop will facilitate gas evasion
from the drop to the atmosphere. This particular mechanism for spume-mediated gas exchange is
currently being modeled by our research group, and the comprehensive results will appear in a
paper by Staniec et al. This model actually allows for a comparison of relative equilibration
times associated with both radius and temperature, when both this mechanism and the one
discussed in section 3.2 come into play. For example, a 100 µm radius drop at 97% humidity,
i.e., in an MABL that is slightly undersaturated, will generally reach its equilibrium temperature
in less than a second while the time that it takes to reach equilibration in regards to radius can be
on the order of hundreds of seconds. Take, for example, a 100 µm drop in 97% RH with the sea
surface temperature at 20°C and an ambient air temperature of 18°C. Such a drop will rapidly
cool to 17.89°C in 0.17 s, dropping past the ambient air temperature and increasing its theoretical
gas content. Meanwhile the equilibrium radius of about 89 µm will take this drop over 900 s to
reach and thus the drop is far more likely to fall back into the sea while still cooled (and with a
greater gas content) relative to both the atmosphere and ocean before it could reach its equilibrium radius and warm toward the ambient MABL temperature.

4 Conclusions

If the wind speed is less than 20 m s\(^{-1}\), and the gas transfer coefficient's wind dependence is between \(U^2\) and \(U^3\) (see Wanninkhof & McGillis, 1999), then it can, with a high degree of confidence, be concluded that the ratio of the “typical” spume gas transfer coefficient associated with the “geometrical” mechanism and the “conventional” transfer velocity for gases such as CO\(_2\) is less than 1%, and thus the spume contribution can, with confidence, be ignored. Even if an “upper bound” spume gas transfer coefficient (such as that derived from Bortkovskii, 1987) is substituted in this ratio in place of a “typical, conventional” coefficient the ratio for wind speeds of 20 m s\(^{-1}\) or less is still 4% or smaller, and the spume contribution to air-sea gas exchange need not be considered for most exchange flux calculations in this wind speed range.

If one is dealing with an amphiphilic gas such as dimethyl sulfide, and one adopts the DMS gas transfer coefficient proposed by Vlahos and Monahan (2009), one still finds for winds of less than 20 m s\(^{-1}\) the ratio of the “typical” spume gas transfer coefficient to the DMS transfer coefficient is 3% or less and thus again the spume contribution to air-sea DMS exchange can be set aside. But it should be noted that if the “upper bound” spume gas transfer coefficient derived from Bortkovskii (1987) is adopted, then the ratio of this coefficient to the DMS transfer coefficient reaches 20% at a wind speed of 20 m s\(^{-1}\). Thus, even in this wind speed range, more observational and modelling work needs to be carried out before a spume contribution to the exchange of DMS across the air-sea interface can be comfortably ignored. Certainly there is the
real possibility that at higher wind speeds the spume drop mechanism will contribute significantly to air-sea DMS exchange.

When it comes to higher wind speed ranges, the results tabulated in Table 2 suggest that more work must be carried out before the role of spume drops in the air-sea transfer of gases such as CO$_2$ can with confidence be assessed. Going beyond the wind speed range in Table 2, it will be noted without further comment that the ratio of the “typical” spume gas transfer coefficient based on Anguelova et al. (1999) to the cubic CO$_2$ gas transfer coefficient of Wanninkhof and McGillis (1999) reaches no less than 30% for winds of 50 m s$^{-1}$.

An inescapable conclusion of this study is that further field measurements under high wind conditions of spume drop concentrations in the lower MABL need to be made before the necessarily tentative conclusions of the current study can be confirmed or modified. These difficult field measurements should be supplemented with further detailed wind-wave flume measurements of spume drop generation and be constrained and informed by additional fluid mechanical modeling studies. The above comparisons of spume drop gas transfer and the “traditional” interfacial gas transfer associated with diffusion across the sea surface specifically only take into account the “geometrical” spume gas transfer mechanism. In most real word circumstances, all three spume drop mechanisms come into play. The wet bulb mechanism and the Delta-T mechanism each then will contribute or detract from the spume drop air-sea gas transfer associated with the geometrical mechanism, depending on whether the geometrical mechanism leads to gas evasion or to gas invasion, and on the sign of Delta-T.

The authors are currently conducting an assessment of the total spume drop contribution to air-sea gas exchange, i.e., the algebraic sum of the geometric, wet bulb, and Delta-T, components in various oceanic provinces.
Acknowledgments

The authors benefited greatly from their protracted collaboration with their late colleague Edgar L. Andreas on such topics as sea spray droplets and air-sea gas exchange. His insights into the microphysical processes of air-sea exchange will continue to be missed. All data used in this synthesis are available through the respective cited publications. The current authors' work at the University of Connecticut on spray-mediated air-sea gas transfer has been supported by NSF awards 13–56541 and 16–30846.

A Note For The Defense of the Dissertation

AS would like to acknowledge that a major component of this work was prepared by Ed C. Monahan and Penny Vlahos; particularly the examination of the various spray functions and the examination of the mechanisms. AS is specifically responsible for the examination of the droplet evolution. This paper is included in the dissertation due to its pivotal nature for moving forward with the AGES model (see Chapter 3) and for the sake of completeness.

Citations


Monahan, E. C. (2002). The physical and practical implications of a CO₂ gas transfer coefficient that varies as the cube of the wind speed. In E. S. Saltzman, M. Donelan, W. Drennen, & R.


Chapter 3. Sea Spray Gas Transfer: The role of sea spray in atmosphere-ocean exchange (in appeal for Nature Geosciences)

Abstract

Sea spray facilitates the movement of matter and energy between the ocean and the atmosphere. While many of its contributions to heat and momentum transfer are relatively well understood, the contribution to chemical exchange, particularly gas exchange remains less well known. This study provides a first estimation of sea spray gas exchange potential for five gases (He, Ne, Ar, O₂, and N₂) using a chemically modified microphysical model, the Andreas Gas Exchange Spray model (AGES). Results indicate that sea spray does not contribute appreciably to gas exchange of He and Ne except in extreme cases. However, for Ar, O₂, and N₂, at high wind speeds, sea spray could contribute significantly to gas flux and is on the same order of magnitude as the empirically constrained interfacial exchange. Sea spray, as a potential pathway for atmosphere-ocean gas exchange, may improve gas exchange predictions in the high wind scenarios that are particularly important in the Southern Ocean polar region.

Sea spray spans orders of magnitude in size and is most commonly categorized by its generation mechanism. Bubble mediated droplets include “film” and “jet” droplets; smaller droplets which result from air entrained by waves rising to the surface as a bubble plume and bursting at the interface to create film drops and ejecting jet droplets through the collapse of the bubble cavity¹,². These drops are important sources for marine derived atmospheric aerosols³,⁴. Bubble mediated droplets are generated at winds above 4 m·s⁻¹ where whitecapping begins and increase rapidly in number with wind speed⁵,⁶. These drops experience long residence times in the air due to their smaller size and have the potential to evaporate to completion with respect to
the relative humidity of the surrounding atmosphere\textsuperscript{7}. Thus, their role in air sea gas exchange is largely unidirectional, as a mechanism to transfer dissolved gases and volatile compounds back into the atmosphere.

Larger spray droplets include spume and splash droplets; the result of wind tearing off the crests of waves and wave spillover, respectively. These wave-mediated drops become prevalent in seas where wind speeds exceed 12 m·s\textsuperscript{-1} and have been characterized for their role in heat and moisture exchange\textsuperscript{8, 9}. Larger wave mediated droplets dominate the volume flux of water lifted into the air\textsuperscript{10} but generally experience higher settling velocities and therefore spend less time aloft. In extreme wind speeds, however (>18 m·s\textsuperscript{-1}), higher rates of production and increased time aloft could lead to a significant spray transfer of gases between the ocean and atmosphere.

Though the contribution of sea spray has long been recognized in transferring heat and momentum between the ocean and the atmosphere\textsuperscript{8}, the role of sea spray in other types of transfer is not broadly understood. For example, it is likely that spray contributes to the transfer of chemical compounds between the atmosphere and ocean, including gases and biogenic compounds dissolved in the surface microlayers\textsuperscript{11, 4, 12}. Such transfer could be particularly effective via large spray droplets due to the relative volume they contain however, currently, this contribution remains unknown. The discrepancy is generally due to the difficulty of performing in situ measurements, particularly at the high wind speeds required for reliable sea spray generation functions\textsuperscript{10}.

This analysis applies a microphysical model of droplet gas exchange for a subset of gases (He, Ne, Ar, O\textsubscript{2}, and N\textsubscript{2}) to representative ranges of temperature and wind speed across global sub-regions from 1981 to 2010 to assess the dominant direction of gas exchange through sea-spray (ocean to atmosphere or atmosphere to ocean) and to determine the potential contribution
of sea spray in comparison to other gas exchange mechanisms (see Supplemental Methods for model details). The results are coupled with representative sea-spray functions\(^\text{10}\) and sub-region wind patterns to assess the potential importance of sea spray in the exchange of these gases regionally, globally, and over time.

**Drop Size and Evolution**

Almost all sea spray drops undergo an initial cooling upon injection into the air associated with the exchange of sensible heat to reach the wet bulb temperature and start to evaporate\(^\text{10}\). This step will be referred to as the initial thermal equilibrium. The initial net flux of gases is *usually* from the air into the droplet as the gas becomes more soluble in the cooling water. The second step includes a subsequent radial decrease due to evaporation as the droplet evaporates to come into equilibration with the relative humidity of the air. This step will be referred to as the final radial equilibrium. The reduction in size/water content augments gas *evasion* from the drop to the air as it is coupled with the salinity increase in the droplet which reduces gas solubility. The second phase also includes heat exchange wherein the temperature of the droplet approaches the temperature of the air \(T_{\text{air}}\) (Figure 1). For a droplet where the temperature of the air \(T_{\text{air}}\) is less than or equal to the temperature of the surface water \(T_{\text{water}}\) from which the droplet is formed, the initial gas invasion is only reversed if the drop remains aloft enough to evaporate and “salt-out” the gas. The degree of evaporation is a function of drop size, relative humidity (RH) and temperature (T). The extent of gas invasion or evasion from the spray droplet varies with gaseous species.
Figure 1. Sea Spray Evolution The typical evolution of a sea spray droplet upon injection into the atmosphere. G represents a gas molecule, T, the temperature, R, the radius, and white dots represent the salt ions in solution.

Gas exchange potential is calculated here using Henry’s Law constants, which represent an equilibrium between the concentration of a gas in the air vs the concentration in the underlying water. The Henry’s Law constant is modified for the temperature and salinity and the gas concentration is subsequently calculated for each step in the droplet evolution (initial injection, thermal equilibrium, and radial equilibrium: see Supplemental Methods for further details).

Influence of $\Delta T_{\text{air-water}}$ (Air-Water Temperature Difference)

The role of wave mediated drops in air-sea gas exchange is bi-directional and primarily controlled by $\Delta T_{\text{air-water}}$ in the first step. For wave mediated drops where $T_{\text{air}} \leq T_{\text{water}}$, gas generally invades the drops and those that return to the surface ocean are enriched in dissolved gases and thus facilitate gas exchange from the air into the ocean. When $T_{\text{air}} > T_{\text{water}}$, the size of this temperature differential controls gas exchange. For $\Delta T_{\text{air-water}} \geq 2^\circ C$ there is enough heat transfer to the drop upon injection that there is no initial cooling and the gas flux is from the drop to the
air. As the drop warms and then evaporates to some degree, the flux of gas remains from drop to air.

**Influence of Gas Type**

Gases which are inert or non-reactive upon dissolution were chosen for this analysis including He, Ne, Ar, O\(_2\) and N\(_2\), in order to isolate the effects of physical-chemical, rather than chemical reaction parameters (i.e. those that are expected to react readily with water upon dissolution such as CO\(_2\)). The differences across gases are controlled by differences in chemical properties; primarily the solubility function and vapor pressure (see Table S1). The resulting K\(_{\text{Hi}}\) (Henry’s Law constant) is approximately 4x greater for the gases O\(_2\), N\(_2\), and Ar, versus He and Ne; driven primarily by the lower solubility of He and Ne. These gases are characterized as water-side controlled and sea spray offers an enhanced air-sea gas exchange route.

**Gas Exchange upon Initial Injection**

Combining both thermal and chemical properties, the gas exchange upon injection of a drop into the overlying air is estimated for a representative spay drop of 100 µm initial radius (Figure 2). The largest change in droplet dissolved gas concentration is for O\(_2\) followed by Ar and N\(_2\). This change is most pronounced when the air-water temperature gradient is large and the T\(_{\text{water}}\)\(>\)T\(_{\text{air}}\). The net evasion across all gases when T\(_{\text{air}}\)\(>\)T\(_{\text{water}}\) is slightly lower than might be expected in this first step as it is attenuated by the cooling resulting from injection so the droplet does not immediately reach the air temperature.
Figure 2. Air-Sea Temperature Differentials  The effect of air-sea temperature differentials on gas exchange associated with initial thermal equilibrium upon injection of a drop into air. A positive change is associated with invasion of gas to the drop while a negative change is evasion. Change in droplet concentration (y-axis) is with respect to the initial concentration of the gas in the droplet upon injection. Equal air and water temperatures still cause a cooling to the wet-bulb temperature which leads to an influx of gas.

Gas Exchange Associated with Radial Equilibration

The second step in typical droplet evolution is the reduction in radius associated with evaporation as the droplet remains aloft. This decrease in radius (r) results in two outgassing mechanisms that include a change in total volume and the resulting large increase in salinity proportional to $\Delta r^3$. The associated effects are modeled using the assumption that the droplet acts as a sphere and that solubility changes according to the Setschenow constant (which accounts for the effect of salt concentrations on $K_H$ and gas exchange)\textsuperscript{13}. The total amount of each gas evaded from the droplet can be traced to both of these factors (i.e., volume change and salinity change). The result is that reaching radial equilibrium is associated with a mass evasion of the gas. Total
volume of gas lost is generally ~95% of the initial dissolved gas volume in the droplet when the droplet achieves final radial equilibrium. We made a closer examination of the contributions of the reduction in water volume versus the “salting out” effect. We find that the evaporation mechanism appears to dominate the evasion of gas, with the reduction in volume alone able to account for the majority of the loss of gas. The salting out effect becomes more comparable to the evaporation effect as the droplet becomes more saline. For a 100 μm droplet, evaporation and salting out are contributing almost equally when the droplet radius reaches radial equilibrium around 50 μm. These mechanisms work in conjunction toward an equilibrium which designates the endpoint of the evasion.

Global Perspectives

The AGES model was coupled with global temperature distributions to evaluate regions where net invasion or net evasion for wave derived drops would dominate (see Supplementary Methods for a detailed description of the AGES model) (Figure 3). Regional climatological averages for 1981-2010 derived from air and sea surface temperatures isolated from the ICOADS (International Comprehensive Ocean-Atmosphere Data Set) indicate that for all global regions, the average air-sea temperature differentials result in an initial invasion of gas to the droplet\textsuperscript{14}. However, all drops that remain airborne long enough to experience some evaporation will experience evasion. Evasion is most pronounced in the Southern Ocean and the Subarctic. The West South Pacific region has a particularly large thermal equilibrium gas invasion due to the large average temperature differential between air and ocean. This gas invasion counters against the evading salting out and evaporation processes.
Bubble mediated drops (typically <80µm) will usually experience net evasion of gas regardless of temperature differentials. At higher wind speeds, however, (i.e. >18m·s⁻¹) wave mediated drops (typically larger) dominate the sea spray volume flux and begin to contribute significantly. Their absolute contribution will vary based on regional air-water temperature differences and droplet time aloft.

**Figure 3. Global Gas Exchange Potential Map** The percent change in gas volume (oxygen) of a droplet associated with the 100 µm radius droplet reaching final equilibration associated with both steps combined. Air and water temperatures used for analysis are averaged from 1981-2010 from ICOADS. Other gases are mapped in Supplemental materials (Figures S2-S5).

In assessing potential seasonal effects we find that January and July global averages do not show significant differences, particularly for the radial equilibrium where evaporative
processes have the major effect. Variations between January and July on regional scales are generally less than 10% and frequently in the range of 1-2%. Seasonal variation is most pronounced in the northern hemisphere where January air-water temperature differences tend to be consistently larger than July air-water temperature differences. Globally, January tends to have a slightly higher gas invasion associated with the initial thermal equilibrium, which can be attributed to a slightly higher air-water temperature difference, particularly in the northern hemisphere. Overall, global average air-water temperature differences tend to be less than 1.1°C.

*Contribution to Gas Exchange*

Using representative volumetric spray fluxes\textsuperscript{10,15}, we can calculate the relative contribution to gas flux for bubble and wave mediated droplets in mol m\textsuperscript{-2}s\textsuperscript{-1} (Figure 4). This is done by multiplying the potential gas exchange (as represented by its change in volume of gas contained) of a single droplet of a certain volume by the total volume of sea spray lifted into the air at a particular wind speed. While this provides a rough estimate of potential sea spray contribution, it does not account for the sea spray size spectrum which includes droplets both smaller and larger in volume. Bubble mediated droplets, which are typically much smaller, were assumed to evaporate completely, as an upper bound. Realistically, we do not expect that all droplets will reach total evaporation. Nevertheless, their relative contribution remains less than 1% of the interfacial flux at all wind speeds. Wave mediated droplets were considered based on initial thermal equilibrium as a lower bound and final radial equilibrium as an upper bound for potential gas flux. These bounds can then be compared to the interfacial flux by Stanley et al.\textsuperscript{16} who used models to separate the bubble mediated and interfacial fluxes from observations at the
Bermuda Atlantic Time Series (BATS). We compare our spray mediated fluxes to the interfacial flux calculated using the methods of Stanley et al.\textsuperscript{16}, in order to show the potential contribution of sea spray in the context of gas exchange with well understood mechanisms. As the interfacial flux relies on the difference between the actual water concentration and that at equilibrium we chose to use representative saturation anomalies of 1 and 2.5\%\textsuperscript{17}.

![Diagram](image)

**Figure 4. Gas Flux associated with Evolution of a Spray Droplet as a function of Wind Speed** The gas transfer in mol m\textsuperscript{-2}s\textsuperscript{-1} associated with total evaporation of smaller bubble mediated droplets (blue), initial thermal equilibrium (red), final radial equilibrium of wave
mediated droplets (purple) for He (a) and O\textsubscript{2} (b) at different wind speeds and the interfacial flux (green, teal) based on the diffusive flux equation of Stanley et al\textsuperscript{16}(equation 2). Arrows depict gas transfer from water to air (up) or air to water (down). Volume fluxes are calculated from Monahan et al\textsuperscript{10}. Note that concentrations are presented on a logarithmic scale. Percentages represent scale comparison of wave mediated droplets to interfacial flux.

For gases with lower Henry’s Law constants (Ne and He), the larger wave mediated droplets do not contribute to gas exchange in any appreciable way until you reach radial equilibrium, as they are relatively less water-side controlled. For gases with higher Henry’s Law constants (O\textsubscript{2}, N\textsubscript{2}) appreciable contributions emerge at thermal equilibrium above 20 m\cdot s\textsuperscript{-1}. Reaching radial equilibrium in very high wind speeds contributes on the same order of magnitude as the interfacial flux. Wave mediated droplets in wind speeds above 20 m\cdot s\textsuperscript{-1} have the potential to contribute to oxygen exchange on the same order of magnitude as the interfacial flux with an approximate contribution range of 10 to 100 % of the interfacial flux (Figure 4).

The droplet contributions in Figure 4 are intended to be a first estimate of the potential for sea spray to contribute to overall gas exchange. They are separated initially by type of droplet and secondly by steps in the droplet evolution. The bubble mediated droplets (blue bar), commonly referred to as film and jet droplets are assumed to reach total equilibrium as an upper bound for these droplets, though this still represents only a small fraction of the better constrained interfacial flux. Thus, we do not expect these to make great contributions to net gas exchange except in very extreme winds. Due to the nature of these calculations the estimates presented here are an upper bound, as they assume that the entire volume of water reaches total equilibrium. Wave mediated droplets in this calculation are separated by the degree of evolution they have undergone. In reality, some droplets only remain aloft long enough to undergo the initial thermal equilibrium; others may remain aloft long enough to undergo total or partial radial
equilibrium. Thus the total contribution of wave mediated droplets to gas exchange is a continuum between lifted droplets which only undergo thermal equilibrium, absorbing gas and transferring it into the sea surface, and those which remain aloft long enough to reach radial equilibrium and outgas into the atmosphere. Lower bound estimates\textsuperscript{10} of gas exchange which do not include the effects of the equilibration place the contribution of sea spray mediated gas exchange around 0.4-4\% of the interfacial flux at 20-30 ms\textsuperscript{-1}. This is remarkably consistent with the thermal equilibrium estimations made here and thermal equilibrium occurs quickly enough that we might expect all droplets to meet this condition.

These large droplet contributions could be particularly important in areas where wind speeds regularly reach greater than 20 m·s\textsuperscript{-1} (Figure 5) and in shorter lived high wind events. The exchange based on the droplet evolution is expected to augment that which can be represented by more traditional gas exchange calculations using gas transfer coefficients and the impact of the droplet surface area to volume ratio, such as that indicated in Monahan et al.\textsuperscript{10} This leads to an increase in the potential water to air exchange and a third spray component necessary to constrain gas flux in addition to interfacial and bubble gas exchange terms at these high wind conditions.
High wind events (>18 m·s\(^{-1}\)) occur 1-3% of the year in the tropics and anywhere from 2%-16% of the time in temperate and polar regions\(^\text{20}\). These events represent a small temporal fraction, but their possible contribution to gas exchange and therefore aerosol generation, though episodic, may be critical to understanding dynamic anomalies and generating improved predictive models, particularly for understanding gas transfer under high wind, storm conditions\(^\text{21}\). In areas where the average wind speed is greater than 18 m·s\(^{-1}\), such as portions of the Southern Ocean, the exchange of gases due to sea spray has the potential to be on the same order of magnitude as the interfacial flux. Transfer of gases via sea spray is a potentially important mechanism in such areas, as increased winds keep spume droplets aloft longer, allowing them to outgas to the atmosphere rather than carrying gases back into the ocean. The Southern Ocean, in particular, as an area of both high average wind speeds and long fetch, likely is impacted by gas exchange via sea spray. As the Southern Ocean represents a well-known carbon sink, it is imperative that we understand the gas exchange mechanisms at work here.
In addition, long term climate trends predict increasing wind speeds, particularly in extreme weather phenomena like cyclones and hurricanes\textsuperscript{24}. Increased sea spray generation and increased time aloft would enhance the outgassing of the surface ocean via spray droplets. This spray-induced gas exchange likely acts in direct opposition to ocean supersaturation of gases through entrained air from wave breaking.

The analysis here is based on a representative droplet radius and this approach has identified the relevant wind speeds in which the gas exchange of sea spray becomes important. These results can help inform future studies that address gas exchange across a range of droplets sizes applied to higher resolution and region specific wind speeds.

Acknowledgements
The authors would like to acknowledge Edgar Andreas for the creation of the original program\textsuperscript{25} upon which this model was built and without which this work could not be accomplished. Work was funded through NSF Grants #13-56541 and 16-30846

Citations


Supplemental

Figure S1. Global Regions The global regions used for this study (adapted from Emery and Meincke¹).

Table S1. Henry’s Law Constants² @ 25 °C, 0 g/kg

<table>
<thead>
<tr>
<th>Gas</th>
<th>Henry's Law Constant (K_H) (mol L⁻¹ Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>3.8x10⁻⁹</td>
</tr>
<tr>
<td>Ne</td>
<td>4.5x10⁻⁹</td>
</tr>
<tr>
<td>Ar</td>
<td>1.4x10⁻⁸</td>
</tr>
<tr>
<td>O₂</td>
<td>1.2x10⁻⁸</td>
</tr>
<tr>
<td>N₂</td>
<td>6.4x10⁻⁹</td>
</tr>
</tbody>
</table>
Methods

Microphysical Model

The Andreas$^3$ microphysical model for the evolution of sea spray droplets was adapted to include a chemical thermodynamic component for gas exchange. This model is intended to calculate the evolution of a single droplet using a representative initial radius (100 µm), the average temperatures of air and water, salinity, relative humidity (considered here to be 80%) and barometric pressure (1 atm). The Andreas model is based on a two-step process; a change to an initial thermal equilibrium represented by a change in temperature, followed by a change in radius until the droplet reaches radial equilibrium with the relative humidity of the air. The initial thermal equilibration involves heating or cooling of the droplet based on the ocean-atmosphere temperature differential. This is followed by evaporation of the droplet to the radial equilibrium dictated by the relative humidity and temperature of the surrounding air. The first step (heretofore referred to as the initial thermal equilibrium) is relatively rapid, requiring on the order of 0.1-5 seconds for droplets between 50 and 500µm. The second step is more involved, requiring 200 to 2,000 seconds to reach the droplet’s final radial equilibrium depending on the initial radius at the time of formation and the relative humidity. Sea spray droplets come into equilibrium with the surrounding relative humidity and temperature which determines their final radius and water content. The droplet is unlikely to evaporate completely unless it is exposed to very low relative humidities due to the phenomenon known as efflorescence$^4$. As a sea spray droplet is exposed to lower and lower relative humidities it becomes more likely to crystallize (super saturated with salt, etc) but the general efflorescence RH for NaCl is around 40-45% RH which is unlikely to occur over the ocean. That is to say there is a sort of “nucleation” activation that must occur for a droplet to transition to a single crystalline particle and that without some
sort of trigger for that nucleation or exposure to very low RH, droplets can remain in an unstable, but liquid state for time periods up to weeks\textsuperscript{4}. This means that we must calculate gas exchange using both steps; the initial thermal equilibrium and the final radial equilibrium.

\textit{Chemical Modifications}

This model was modified to include terms for calculating the change in gas concentration associated with the two-step process. The modifications were based on the Henry’s Law constant and adjusted dynamically using the Van’t Hoff equation and gas specific Setschenow constants\textsuperscript{5} (Table S1) to account for dynamic temperature and salinity changes. Base values for Henry’s Law constant are included in Table S1\textsuperscript{2}. These represent only starting values at 25°C and a salinity of 0 which are always modified for the actual temperature at each step in the droplet evolution. Concentrations are then adjusted for the effect of salinity using the Setschenow constant. Each gas has associated coefficients which account for their individual temperature dependence. Transfer of the gases through the droplet and across the droplet-air interface is considered to be instantaneous with respect to the other timescales associated with thermal and radial equilibration according to the model of Andreas et al\textsuperscript{6}.

The starting values of the Henry’s Law constant were modified first with the van’t Hoff equation (1) to calculate the equilibrium water concentration associated with the change in temperature due to the droplet evolution.

\[ K_{\text{Ht}} = K_{\text{Hi}} \exp \left( \frac{-\Delta H}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right) \]

This returns a Henry’s Law constant for the temperature of the droplet at each specific moment in its evolution. The first temperature shift is considered to be from an initial
temperature of the surface water to the thermal equilibrium temperature upon injection which is
generally lower than the initial water temperature due to the latent heat of evaporation.
Temperature of the droplet was considered to have reached the air temperature when the droplet
stopped evaporating during the final radial equilibration. However these Henry’s Law constants
do not account for the effect of the salinity on the droplet gas content. The temperature-modified
Henry’s Law constant was used to calculate the concentration of the gas in water assuming
equilibrium with the air. Average atmospheric concentrations of the representative gases were
used for the air concentration across the regions.

After the temperature effect was established, the Setschenow constant was used to further
modify the concentration to reflect changes due to salinity upon evaporation. Starting salinity
values across all regions were taken from Emery and Meincke\(^1\) (Table S2). Evolution of salinity
due to evaporation was calculated according to the change in radius associated with achieving
radial equilibrium. The adjusted Henry’s Law constant was used to calculate the concentration of
gas in the droplet at final radial equilibrium. In order to ascertain the influence of the reduced
volume of the droplet, the volume of gas was calculated by using the final radius indicated by the
original Andreas model to calculate a droplet volume. These concentrations were then modified
by the Setschenow constant using the approach of Masterton et al. Setschenow effects use the
equation;

$$\log \frac{S_0}{S} = k_s \times c$$

Where S is the solubility at a particular salt content, S\(_0\) is the solubility in pure water, ks
is the Setschenow constant and c is the concentration of salt. Masterton modifies this dependence
to the form

$$\log \frac{B_0}{B} = k_s \times I$$
So that the dependence is on the ionic strength, I. B is the Bunsen solubility which is reported in volume of gas per volume of solution which can easily be converted in both cases to a concentration in mol/L. The Setschenow constant, ks, is calculated according to the experimental temperature dependences reported in Masterton and the ionic strength is calculated using chlorinity derived from the reported salinity. The concentration in the water according to the temperature modified Henry’s Law constant is adjusted as above and combined with the droplet volume, and the molar mass and density of the dissolved gas to ascertain the volume of gas dissolved in the droplet.

Setschenow constants were calculated using the methods given by Masterton\textsuperscript{5}, which accounts for temperature dependence. The microphysical model was initially created to calculate the time needed for the changes in temperature and radius associated with the evolution of a sea spray droplet. The resulting temperatures and salinities were used to calculate the solubility of gases within the droplet where invasion or evasion of gas to the atmosphere is considered to be instantaneous relative to the preceding changes in temperature\textsuperscript{7}. This combined physical-chemical model is referred to as the Andreas Gas Exchange Spray model (AGES).

*Regional Data Analysis*

In order to achieve a representative gas exchange contribution, the AGES model was adapted to regional temperature and salinity conditions using a representative 100 µm droplet.
### Table S2. Region, average air T°C, average water T°C, and salinity

<table>
<thead>
<tr>
<th>Region</th>
<th>T&lt;sub&gt;air&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;water&lt;/sub&gt; (°C)</th>
<th>S (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antarctic Surface</td>
<td>2.69 ±3.02</td>
<td>2.68 ±2.96</td>
<td>34.5</td>
</tr>
<tr>
<td>Arabian Sea</td>
<td>24.76 ±2.66</td>
<td>25.65 ±2.27</td>
<td>35.85</td>
</tr>
<tr>
<td>Atlantic subarctic</td>
<td>1.02 ±3.99</td>
<td>4.46 ±2.82</td>
<td>35.95</td>
</tr>
<tr>
<td>Bengal Bay</td>
<td>27.09 ±0.98</td>
<td>27.87 ±1.02</td>
<td>35.05</td>
</tr>
<tr>
<td>East N Atlantic Central</td>
<td>14.22 ±5.73</td>
<td>15.5 ±5.22</td>
<td>31.5</td>
</tr>
<tr>
<td>East N Pacific Central</td>
<td>22.39 ±4.43</td>
<td>23.15 ±4.36</td>
<td>36.15</td>
</tr>
<tr>
<td>East N Pacific Transition</td>
<td>17.95 ±6.23</td>
<td>18.69 ±6.34</td>
<td>34.8</td>
</tr>
<tr>
<td>East S Pacific Central</td>
<td>23.82 ±2.84</td>
<td>23.99 ±3.08</td>
<td>34.7</td>
</tr>
<tr>
<td>East S Pacific Transition</td>
<td>19.13 ±2.03</td>
<td>18.95 ±2.11</td>
<td>35.2</td>
</tr>
<tr>
<td>Indian Equatorial</td>
<td>27.32 ±0.95</td>
<td>27.9 ±1.01</td>
<td>33.1</td>
</tr>
<tr>
<td>Indonesian Upper</td>
<td>27.84 ±0.91</td>
<td>28.65 ±0.88</td>
<td>34.7</td>
</tr>
<tr>
<td>Pacific Equatorial</td>
<td>26.93 ±1.29</td>
<td>27.48 ±1.64</td>
<td>34.6</td>
</tr>
<tr>
<td>Pacific subarctic</td>
<td>1.23 ±4.68</td>
<td>4.37 ±2.65</td>
<td>34.05</td>
</tr>
<tr>
<td>S Indian Central</td>
<td>22.37 ±3.17</td>
<td>22.81 ±3.13</td>
<td>35.25</td>
</tr>
<tr>
<td>S Atlantic Central</td>
<td>24.35 ±2.90</td>
<td>24.7 ±2.89</td>
<td>35.15</td>
</tr>
<tr>
<td>Subantarctic surface</td>
<td>12.41 ±3.85</td>
<td>12.11 ±3.90</td>
<td>35.1</td>
</tr>
<tr>
<td>West N Atlantic Central</td>
<td>17.66 ±7.21</td>
<td>19.74 ±6.16</td>
<td>34.9</td>
</tr>
<tr>
<td>West N Pacific Central</td>
<td>20.52 ±7.56</td>
<td>22.51 ±6.12</td>
<td>34.75</td>
</tr>
<tr>
<td>West S Pacific Central</td>
<td>15.5 ±10.18</td>
<td>25.71 ±3.64</td>
<td>34.3</td>
</tr>
</tbody>
</table>

Global temperature data was separated into regions according to surface ocean salinity and temperature ranges which approximate individual water masses<sup>1</sup>. Data was acquired from the International Comprehensive Ocean-Atmosphere Data Set (ICOADS) through the National Ocean-Atmosphere Administration (NOAA) Earth System Research Laboratory (ESRL) for long term averages of air and sea surface temperature from 1981-2010<sup>8</sup>. Input for relative humidity was set at a representative value (80%)<sup>4</sup>. Barometric pressure was assumed to be 1 atm. Average wind speeds across the global oceans for Figure 5 were acquired from the QuickSCAT satellite<sup>9</sup> for the purpose of illustrating areas where sea spray gas flux might be relevant. Wind speeds of
10, 20 and 30 m·s$^{-1}$ were only used for scaling up (Figure 4) sea spray volume fluxes assuming a representative sea spray size of 100 µm radius.

Data for air and surface water temperatures was processed in ArcGIS using raster and netCDF processing tools and divided into the sub-regions outlined by Emery and Meincke$^1$ in order to be averaged (Figure S1). Standard deviations were also calculated and included in Table S2. January and July air and sea surface temperatures were compiled from the beginning and end of the temporal range for the long term average and averaged into regions in the same manner. Most of the conclusions presented here are based on the long term average rather than the seasonal data.

Scaling

A limitation of the current AGES model is that the model is intended for calculating the evolution of one single droplet at a time. Likewise, the modifications made to the AGES model for gas exchange are limited to calculating the gas concentrations in a single droplet. In order to ascertain an estimate of the global relevance, scaling up was necessary. Scaling of the droplet gas exchange to global relevance was accomplished by taking a 100 µm droplet as representative and scaling it through the use of a sea spray generation function which calculates the volume of water lifted per meter squared of ocean surface according to the wind speed. Thus, we assessed the volume of water lifted as if it were composed entirely of 100 µm radius droplets. We expect this number to act as a first estimate, as the large number of available sea spray generation functions and spectra of droplet sizes will be addressed in a future publication in appropriate detail. We
used the volume flux from Monahan et al\textsuperscript{10} based on the number flux of Anguelova et al\textsuperscript{11} as it falls squarely within in the typical range of the literature sea spray generation volume fluxes\textsuperscript{10}.

The 100 µm droplet has been used as a bellwether of sorts for sensible heat fluxes associated with sea spray droplets in the literature\textsuperscript{12} and thus we felt that it was an appropriate starting point for our own scaling estimates. The volume of a 100 µm droplet was multiplied to reach the total volume flux (ie the volume of water lifted per meter squared) associated with each of three wind speeds (10, 20, and 30 m·s\textsuperscript{-1}). This gave us the scaling factor which could then be used for scaling the gas exchange. The volume flux was further separated into the volume lifted that could be associated with bubble mediated droplets (film and jet) and the volume lifted associated with wave mediated (spume) droplets. As the volume flux is a sea spray \textit{generation} flux, and therefore representative of the amount and size of droplets produced from the sea surface, the initial radius of the droplet was used for calculating the scaling factor.

The gas exchange associated with each type of spray droplet was multiplied by this same factor. We assumed total evaporation for the gas exchange associated with bubble mediated (colloquially jet and film) droplets, thus all of the initial gas in the droplet was released into the atmosphere. This represents an upper bound for bubble mediated droplets and is not intended as an estimate of what actually occurs in the atmosphere. For the wave mediated droplets the gas exchange was divided into the thermal equilibrium step and the radial equilibrium step. The timescales associated with the thermal equilibrium are typically under 2 seconds; thus we can assume that most droplets will reach this first step and absorb gases due to their lowered temperature. This represents a lower bound for wave mediated droplet contributions to gas exchange. The radial equilibration often takes hundreds to thousands of seconds and therefore is unlikely to occur to completion across all drop sizes except in cases of high wind speeds that
advect droplets considerably. The gas exchange associated with this step therefore represents an upper bound for the contribution of wave mediated sea spray. It must also be noted that these exchanges are in opposing directions; therefore further work on understanding exactly how long droplets remain aloft would be necessary to make an absolute determination of the sea spray contribution to overall gas exchange. However, we consider these bounds a reasonable first estimate.

The interfacial fluxes were calculated from equation 2 of Stanley et al. This diffusive flux uses the Schmidt number (calculated from Wanninkhof), the wind speed squared and the difference in the equilibrium and actual concentration of the gas in water to estimate the diffusive flux. We used representative saturation anomalies of 1% and 2.5% which represent the range across large portions of the ocean.

Table S3. Diffusive/Interfacial flux calculated from Stanley et al (mol m$^{-2}$ s$^{-1}$)

<table>
<thead>
<tr>
<th>$U_{10}$ (m·s$^{-1}$)</th>
<th>Interfacial (1%)</th>
<th></th>
<th>Interfacial (2.5%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>O$_2$</td>
<td>He</td>
<td>O$_2$</td>
</tr>
<tr>
<td>10</td>
<td>2.92E-12</td>
<td>2.36E-07</td>
<td>7.30E-12</td>
<td>5.90E-07</td>
</tr>
<tr>
<td>20</td>
<td>1.17E-11</td>
<td>9.45E-07</td>
<td>2.92E-11</td>
<td>2.36E-06</td>
</tr>
<tr>
<td>30</td>
<td>2.63E-11</td>
<td>2.13E-06</td>
<td>6.57E-11</td>
<td>5.31E-06</td>
</tr>
</tbody>
</table>
Figure S2. Global Map of Helium Gas Exchange. Potential gas exchange associated with a 100 µm sea spray droplet presented as the percentage of the initial gas volume lost to the atmosphere if the droplet reaches final radial equilibrium.

Figure S3. Global Map of Neon Gas Exchange. Potential gas exchange associated with a 100 µm sea spray droplet presented as the percentage of the initial gas volume lost to the atmosphere if the droplet reaches final radial equilibrium.
Figure S4. Global Map of Argon Gas Exchange. Potential gas exchange associated with a 100 μm sea spray droplet presented as the percentage of the initial gas volume lost to the atmosphere if the droplet reaches final radial equilibrium.

Figure S5. Global Map of Nitrogen Gas Exchange. Potential gas exchange associated with a 100 μm sea spray droplet presented as the percentage of the initial gas volume lost to the atmosphere if the droplet reaches final radial equilibrium.
Citations


8. Data: ICOADS data provided by the NOAA/OAR/ESRL PSD, Boulder, Colorado, USA, from their Web site at http://www.esrl.noaa.gov/psd/


Chapter 4. Scaling Up Sea Spray (in preparation for JGR)

Abstract:

Gas exchange across the ocean-atmosphere boundary has increasingly been characterized as taking place via a variety of mechanisms. These mechanisms include the well understood interfacial exchange due to concentration gradients, air entrainment by breaking waves, and the ensuing bubble plumes which are injected to depth. In opposition to the air into water transfer of bubble injection is the water to air transfer of sea spray. Where bubbles represent parcels of air injected into the ocean; sea spray represents water injected into the air. These transfers of matter and energy have implications for the transfer of gases as well. Here we use a selection of sea spray volume generation functions and spray droplet size spectra, combined with a microphysical droplet model (AGES), to more accurately depict the potential transfer of gases due to the creation and evolution of the sea spray droplet. We find that application of a variety of volume flux indicates that the total potential contribution of sea spray to gas exchange varies by several orders of magnitude but may represent anywhere from 3 – 100% of the interfacial flux at wind speeds greater than 20 m·s⁻¹. Conservative estimates with a number flux give a lower bound of sea spray gas exchange which confirms that spray is likely to be most impactful in high wind speed environments. More work is needed on integrating time aloft trajectories in high wind events with sea spray generation to robustly constrain sea spray mediated gas exchange.

Introduction

Sea spray maybe considered analogous yet in direct opposition to the bubble plumes which form the current focus of atmosphere-ocean gas exchange studies (Stanley et al., 2009, Deike et al., 2017, Emerson and Bushinsky, 2016). These bubble plumes are formed by waves breaking and entraining air into the ocean surface. In effect, they are parcels of air which have been injected into the ocean surface and have been characterized as transferring gas into the ocean as they are pressurized and/or dissolved (Stanley et al., 2009). Sea spray represents water which has been injected into the air via either the breaking of those bubbles at the surface or the tearing of wave crests due to wind action. If the bubble plumes represent an injection of air and therefore gases into the ocean it is reasonable to assume that sea spray may also act to carry gases between the ocean and the atmosphere (Figure 1).
Figure 1. Sea spray represents a mirror to the action of bubble plumes entrained by breaking waves

Previous work on this topic has ascertained that, at first estimate, gas exchange via sea spray has the potential to be considered on the same order of magnitude as the interfacial or diffusive exchange (Staniec et al., 2020, Chapter 3). However, these estimates work with a single sea spray generation function and do not include a droplet size spectrum or number flux. In those studies a single droplet size and a representative sea spray volume flux were used to ascertain the relative contributions of the droplet evolution. These contributions represent an upper limit for sea spray for that generation flux. Here we use a variety of representative sea spray generation fluxes and droplet size spectra to ascertain the range of values that might be expected from gas exchange via sea spray. The purpose of this manuscript is to clearly present uncertainties of gas exchange via sea spray and to more closely represent a realistic spectrum of sea spray droplets.

Existing sea spray generation fluxes have been formulated using experimental, observational, and modeling data. The two major types of generation flux representations are volume and number fluxes. Volume fluxes calculate the amount of water lifted as sea spray per meter squared of ocean surface, usually as a function of wind speed (Monahan et al., 2017). Number fluxes count the number of droplets of a particular size which are lifted and are visualized as a unique spectrum at each wind speed. These general sea spray generation fluxes can be used to give the rate at which droplets are produced (Andreas, 1998). They are often
interchanged using the droplet radius and an assumption that the droplets are generally spherical (Andreas, 1998).

Monahan et al (2017) recently published a review of these functions to identify those which may be considered reasonable and representative. They came to the conclusion that there were three fluxes which represented upper bounds, lower bounds, as well as “average” fluxes drawn from Bortkovskii et al (1987), and Fairall et al (1994), and Anguelova et al (1999) respectively. The fluxes were converted to volume fluxes for the purposes of comparison. It is these three volume fluxes which will form the basis of this analysis. Two representative number fluxes are then applied to further refine the gas exchange estimates to be more representative of in situ sea spray and more precisely compare time aloft to degree of gas exchange per drop size.

**Methods**

Based on two step evolution of a single sea spray droplet, the gas exchange potential of a single droplet was calculated using Henry’s Law constants based on the AGES model (for more detail on AGES model see Staniec et al., 2020, Chapter 3 in this dissertation) (Figure 1a). The equilibrium gas concentration for a droplet is calculated at its thermal and radial equilibration steps using Henry’s Law constants modified for the temperature and Setschenow constants for the salinity effect.
Figure 2. Schematic of the methods used to calculate gas exchange. a) The droplet evolution is modeled as two-step process and the accompanying changes in temperature, salinity, and radius are used to calculate the amount of gas exchanged in each step. b) Using a representative droplet or series of droplets, the gas exchange potential associated with each step is multiplied to meet the volume of water lifted in a series of sea spray volume fluxes. c) A number flux is modeled and the gas exchange potential for each droplet size is multiplied by the number of droplets produced.

This is then multiplied by the volume of the droplet at that step in the evolution. The volume of gas present in the droplet can then be calculated using the molar mass and density. The gas exchange is considered as the difference in the gas content of the droplet at equilibrium at each step in the evolution. The flux for a single droplet is then scaled to a series of sea spray generation incremental volume fluxes as presented in (Chapter 3) (Figure 1b) and using two incremental number fluxes (Andreas, 1998, Zhao et al., 2006) (Figure 1c). Scaling using a
number flux is accomplished by multiplying the gas exchanged by a single droplet by the number of droplets lifted.

**Gas Exchange Potential**

The AGES model is based on Andreas’ (2013) microphysical model of the evolution of a sea spray droplet after it is ejected from the sea surface. The droplet undergoes a two-step process wherein the droplet changes temperature and then the droplet undergoes evaporation before reaching the temperature of the air. The droplet undergoes a series of changes in temperature, radius, and salinity, all of which affect the dissolved gases in the droplet itself (Figure 2). Using Henry’s Law constant and adjusting it for temperature and salinity the concentration of the gas in the droplet could be calculated by assuming it comes into equilibrium (Staniec et al., 2020, Chapter 3). This process is considered instantaneous with respect to the changes in temperature and water content that the droplet is undergoing (Andreas et al., 2017). The volume of gas in the droplet can then be calculated from the size of the droplet and the density of the gas.

The droplet gas exchange was separated into the exchange associated with the initial thermal equilibrium and that associated with the final radial equilibrium as they are generally in opposing directions and represent different timescales during which the droplet must be held aloft.

Generally, the cooling associated with the initial thermal equilibrium means that the droplet absorbs gas in the first few seconds after it is ejected from the wave. Once aloft the droplet will begin evaporating in seconds though the relative humidity is the major determinant in this. The drop will continue to evaporate until it reaches radial equilibrium which may occur on second to minute timescales depending on the droplet radius and environmental conditions. The reduction in water content also causes an out-flux of gas from the droplet due to a combination of the reduction in droplet size and the “salting-out” effect as the drop becomes hypersaline.
Scaling Up Using a Volume Flux

In order to scale the droplet to environmental relevance, a series of volume fluxes were added to the AGES model. The first estimate was based on a 100µm droplet due to its previous use for examining sensible heat fluxes from sea spray (Andreas, 2008). Dividing the volume of water lifted at a particular wind speed by the volume of water in a 100µm droplet gives the factor by which the gas exchange potential of a single droplet should be multiplied to estimate the gas exchange associated with sea spray at that wind speed.

The volume fluxes chosen here include the Bortkovskii (1987) flux (B87) (Equation 1), Anguelova et al (1999) flux (A99) (Equation 2), and the Fairall (1994) flux (F94) (Equation 3). The potential gas exchange of a single droplet was scaled to various well known spray volume fluxes by dividing the volume of water lifted at a particular wind speed by the volume of the chosen droplet size using the initial radius of the droplet as these are considered “generation” fluxes. This gives the factor by which the volume of gas exchanged for each step could be multiplied and then was converted to moles to give a flux of gas in mol m\(^{-2}\) s\(^{-1}\). The sea spray volume fluxes were fitted to power law wind speed dependent regressions which are appended below (Equations 1 to 3). The ranges of wind speed for which this model is valid are 15-30 ms\(^{-1}\) for the B87 volume flux (V), 18-25 ms\(^{-1}\) for the A99 and 5-30 ms\(^{-1}\) for the F94. Wind speed here is \(U_{10}\) or the wind speed reported at 10 m above the sea surface in ms\(^{-1}\). These algorithms are considered accurate within the reported ranges and fit to the volume flux data within \(r^2>0.96\).

The volume flux figures may be found in chapter 2 of this dissertation.

(1) \[ B87: V=3.55\times10^{-5}\times U_{10}^{2} \]

(2) \[ A99: V=2.01\times10^{-13}\times U_{10}^{7.62} \]
These fluxes are best fit to the available data in Monahan (2017) Figure 1 and represent the upper, average, and lower bound of the volume fluxes. The model allows for the approximation of a size spectrum by choosing the percentage of the volume flux that will be represented by a certain radius droplet. For example, it may be considered that 50% of the flux is attributed to 100µm droplets. In this case the volume flux will be halved and then divided by the volume of the initial droplet. Please note that these gas exchanges represent droplet reaching total equilibrium and do not account for the time aloft as drops fall back into the ocean. Partial equilibrium is not considered here though it is touched on in the number flux discussion. The overall gas exchange upon reaching radial equilibrium will be the same for all droplet sizes as the volume of water lifted acts in the same way albeit at different timescales. Calculations of different droplets will return the particular timescales and gas exchange proportions associated with that droplet size.

**Scaling Up using a Number Flux**

The second attempt at scaling up the sea spray gas exchange flux is made using two representative number fluxes, the Andreas (1998) and the Zhao et al., (2006). Number fluxes are generally reported in m$^{-2}$ s$^{-1}$ µm$^{-1}$ which gives a number of droplets generated per m$^2$ per second per increment of radius (usually 1µm). This means that the gas exchange associated with any specific droplet size can be calculated by using the number flux to generate a number of droplets at a particular wind speed and multiplying the gas exchange potential of that droplet by that number.
The Andreas (1998) flux was chosen for this calculation due to its explicit set up in the manuscript which allowed for a straightforward translation into the model and because the shape of its related volume flux captures the expected change in contribution that is associated with the larger vs the smaller droplets with larger droplets contributing more and more at higher wind speeds. This number flux is based on a scaling of an empirically derived generation flux by Smith et al. (1993) which has been modified to come into line with the well-known Monahan (1986) function and extrapolated to spume using data from Wu et al. (1984). This is done with the caveat that the extrapolation to larger size spume drops has been questioned due to the nature of the Smith et al (1993) measurements used to constrain it, which were collected far away from the site of spray production. This flux is chosen for its longevity in the literature and the fact that it generally falls in the center of the various generation fluxes in magnitude. This function is cited in most reviews of the sea spray generation flux (Andreas, 2002, Veron, 2015, and Monahan et al., 2017) and falls reliably near the center of the range of spray generation functions reported. When compared to the other fluxes in Monahan et al., (2017) (Chapter 2 of this dissertation) it may be considered a conservative (lower bound) estimate.

The Zhao et al. (2006) model was chosen because Monahan et al. (2017) identifies it as an average flux and because it is derived from field and lab measurements. We choose to use the developed wave age of 1.2 because we expect spray to contribute more in the case of developed seas. This number flux is relatively unique in that it uses Reynolds number rather than wind speed as its environmental parameter but the Reynolds number can be tied back to $U_{10}$. This number flux is generally an order of magnitude larger than the more conservative Andreas (1998) flux.
Results

*Volume Fluxes*

This study shows that the choice of sea spray generation flux has a great impact on the potential for sea spray droplets to enhance air-sea gas flux. The fluxes vary by over an order of magnitude based on the choice of flux. These differing fluxes give us a first look at the wide range of potential impacts spray could have on total gas flux budgets. Likely, the greatest source of uncertainty in the contribution of sea spray to gas exchange is the sea spray generation function. This is true for many processes in the ocean, including momentum, sensible heat, and latent heat particularly with regards to sea spray’s role in large storm systems (Veron, 2015, Bao et al 2011, Wu et al., 2015). We provide a range of sea spray generation fluxes in an attempt to characterize the sea spray contribution within this uncertainty.

Using wind speeds from 10 to 30 ms\(^{-1}\) we plot the various sea spray gas exchanges for different volume fluxes against representative interfacial fluxes calculated from Stanley et al., (2009) at 1 and 2.5% saturation anomalies (Figure 3).
The range of spray generation fluxes and therefore the range of potential contributions to air-sea gas exchange by sea spray droplets spans orders of magnitude. Over the wind speed range from 10 to 30 m s$^{-1}$ there is a 2-3 order of magnitude change in the gas exchange, with the Bortkovskii showing the smallest change and Anguelova and Fairall showing larger changes. The interfacial flux shows a 2 order of magnitude range over the same wind speed range. The Anguelova estimates span the range from the lower bound Fairall to the upper bound Bortkovskii as the wind speed increases. It is worth noting that Fairall and Bortkovskii are the results of mathematical analysis and modeling while Anguelova reports from experimental data. The thermal fluxes are less than the interfacial flux for all estimates though they can represent a non-negligible fraction of the flux for gases like oxygen. We compare two gases He, a small noble gas, and O$_2$, a non-noble but unreactive to dissolution gas which is environmentally important. Helium fluxes are much smaller than oxygen fluxes due to both the lesser environmental
concentration and differences in solubility which manifest in different Henry’s Law constants and temperature dependences. Helium spray fluxes also generally represent a smaller proportion of their interfacial flux. Carbon dioxide, a climatically relevant gas, is more likely to resemble oxygen in its physical chemical behavior though the reactions of the carbonate system are likely to complicate its exchange.

In places where high wind speeds are common or in storm events, sea spray likely contributes to the gas exchange across all generation functions. Despite their sporadic nature, storm conditions cannot be discounted as non-important to our understanding of global climate, especially as the IPCC (2014) predicts an increase in storms and storm conditions as we move into the future. Hurricanes and tropical cyclones in particular are known to act as transports from warmer tropical oceans to higher latitudes and to be instrumental in the global heat budget, despite their relative rarity. Many places in the ocean only experience tropical cyclones at a rate of 0.2-3 storms per year and they occur disproportionately in the Northern hemisphere (Knapp et al., 2010). The Southern Ocean experiences average wind speeds of 20 ms$^{-1}$, meaning that spray droplets may be contributing to gas fluxes a large portion of the time (QuickScat). Storm conditions are known to contribute to loadings of nutrients, and to be instrumental in the heat balance of the global atmosphere.

**Number Fluxes**

Two representative number fluxes (Andreas, 1998, Zhao et al., 2006) are applied to get a better understanding of how each part of the sea spray spectrum impacts the overall gas exchange. Applying a number flux is especially important for future work in order to discern how long droplets of different sizes stay aloft and use that to ascertain whether certain droplets are ingassing or outgassing, and how far they move along in their evolution before re-entering the sea.
surface. Ongoing work on the time that a drop spends aloft can then be compared to the spectrum to ascertain what percentage of the overall flux could occur in the allotted time period. The difference in the gas flux attributable to sea spray is largely dependent on the size of the droplets as that controls how long it takes a droplet to reach the temperatures and radii that control their gas exchange.

Plotting the gas exchange associated with each droplet size gives us a spectrum of the contribution of individual droplet sizes to the overall gas exchange (Figure 4).

**Figure 4.** Amount of gas exchanged by radius of droplet: Calculated by multiplying the gas exchange at each droplet size by the number of droplets predicted by Andreas (1998) and Zhao et al. (2006) number flux.

Using the number flux we see that much of the gas flux would be carried by the droplets in the middle of the spume size range, 100-200 μm radius with the upper and lower ends of the spectrum tapering off relatively quickly. This makes theoretical sense as smaller droplets will carry less gas and there are fewer of the larger droplets.
Discussion

If sea spray generation acts as in Bortkovskii (1987) (upper limit) then even the relatively small thermal flux that is achieved by all drops may be on the same order of magnitude as the interfacial flux above 15 ms\(^{-1}\), depending on the gas (Table 1). Lower bound estimates indicate that the wind speed must be above 20 ms\(^{-1}\) for sea spray gas fluxes to represent a reasonable percentage of the typical interfacial flux (Table 1). In the case of the upper bound Bortkovskii fluxes, gas exchange for both helium and oxygen in droplets reaching radial equilibrium are on the same order of magnitude as a representative interfacial flux (Stanley et al., 2009) calculated at a saturation anomaly of 2.5%. Gas exchange associated with thermal equilibrium, which occurs on much shorter timescales (Figure 3) is negligible for helium but represents a reasonable percent of the interfacial flux for oxygen. Using the average Anguelova or lower bound Fairall sea spray generation fluxes introduces the threshold of 20 ms\(^{-1}\) wind speed to reach above 3% of the interfacial flux. The Fairall estimates are more conservative and therefore indicate that a potential contribution at high wind speeds is not unreasonable.

In order to truly ascertain the contribution of sea spray to gas exchange we need more consistent sea spray generation fluxes at higher wind speeds as most generation fluxes are capped at wind speeds of 30 ms\(^{-1}\) and there is reasonable evidence that higher wind speeds may lead to a shift in the spray formation regime (Veron, 2012).

Table 1. Percentage of the Interfacial Flux represented by Sea Spray gas exchange at 20 ms\(^{-1}\) wind speed

<table>
<thead>
<tr>
<th></th>
<th>He Thermal</th>
<th>He Radial</th>
<th>O(_2) Thermal</th>
<th>O(_2) Radial</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bortkovskii</td>
<td>0.4-1%</td>
<td>80-199%</td>
<td>11-28%</td>
<td>137-342%</td>
</tr>
<tr>
<td>Anguelova</td>
<td>0.04-0.1%</td>
<td>9-23%</td>
<td>1-3%</td>
<td>16-40%</td>
</tr>
<tr>
<td>Fairall</td>
<td>0.02-0.4%</td>
<td>3-8%</td>
<td>0.4-1%</td>
<td>5-13%</td>
</tr>
</tbody>
</table>
While spume production is largely known to be the canonical tearing off of droplets from the wave crest, there may be more complex mechanisms at higher wind speeds such as the “ligament-tearing” reported by Veron (2012) and the “bag breakup” reported by Troitskaya (2017). These methods of spume drop formation involve the lifting of larger ligaments or sheets of water which then shatter or fragment into myriad smaller droplets. This has implications for the potential of droplets to contribute to gas exchange, as smaller droplets reach equilibrium more quickly and thus are more likely to in or out-gas before re-entering the sea surface.

Time aloft is exceedingly important to understanding both the direction and the magnitude of the sea spray contribution to gas exchange. The droplet is assumed to reach gas equilibrium on shorter timescales than the thermal or radial equilibrium (Andreas et al, 2017) but the temperatures and water content which drive the gas exchange must be reached in order for the exchange to be completed. The thermal and radial equilibrium also generally cause gas exchange in opposing directions. This means that the number of droplets of a particular size drives how much of the gas exchange is happening and what direction it is going in. Smaller droplets will reach thermal or radial equilibrium more quickly and thus may outgas completely. Larger droplets will take longer and thus may only reach thermal equilibrium or partial radial equilibrium in the time they are aloft. Studies of time aloft are ongoing. Andreas (1990, 2010) made a first estimate of this time aloft by calculating the terminal fall velocity of a droplet and using the significant wave height to calculate how long it would take a droplet to re-enter the sea surface (approximately 10 seconds or less for droplets larger than 20 µm radius). These could be used as a lower limit of time aloft assuming a one-dimensional vertical trajectory. Of course, this neglects the effects of turbulence and wind which in some cases may be a valid assumption (Lewis and Schwartz, 2004). Recent modeling efforts have attempted to elucidate the effect of
turbulence (Mueller and Veron, 2014) at least on the smaller wave scale and find that most droplets still do not stay aloft for very long (ie at 30 ms\(^{-1}\) wind droplets greater than 80 µm will not stay aloft more than 10 seconds).

It seems intuitive, and indeed it has been a longstanding assumption that larger droplets do not remain aloft for very long, and thus may not contribute greatly to gas exchange. According to Mueller and Veron (2014), the residence time of most droplets remains well below 100 seconds even in very high winds (approx. 60 seconds in 30 ms\(^{-1}\)). This is long enough to reach thermal across all droplet sizes but droplets over 100 µm initial radius will only partially evaporate before re-entering the sea surface and not completely reach radial equilibrium (Figure 5).

Using the number flux and the calculated times to equilibrium we can calculate a potential flux associated with all the droplets which reach their equilibrium in less than 100 s by calculating the gas exchange associated with each droplet size in 1 µm radius increments and summing those gas exchanges across the range of droplets that reach equilibrium. This includes all droplet sizes for the thermal equilibrium and up to 80µm for radial equilibration. Using the Andreas (1998) model at 20 ms\(^{-1}\) both steps represent less than 1% of the equivalent interfacial

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**Figure 5.** Time to equilibrium according to Andreas microphysical model.
flux. At 30 ms\(^{-1}\), these contributions go up by an order of magnitude and may represent 1-2\% of a representative 1\% saturation anomaly interfacial flux. These are conservative estimates due to the fact that the Andreas (1998) model is at the lower bound defined by Monahan et al., 2017. Using the Zhao et al (2006) flux we find higher estimates of contribution, on the order of 4-23\% of the interfacial flux at 30 ms\(^{-1}\).

Droplets may reach a reasonable percentage of their evaporation in the time aloft and outgas accordingly and this model does not explicitly include that percentage of the gas flux. However the net flux may be smaller than this due to the opposing nature of the thermal equilibrium flux vs the radial equilibrium flux. At a conservative estimate, using a number flux, it appears that sea spray gas exchange is likely to be of the most importance at high wind speeds where it compares to the interfacial flux.

This analysis is complicated by several factors. For example, the model of time aloft focuses on the effect of small-scale turbulence only and neglects large scale atmospheric structures that might lift larger droplets. It is, in fact, a stated weakness of the Mueller and Veron (2014) model that it does not capture large scale turbulence, particularly at high wind speeds. Hurricanes, for example, generally have a lifting effect on the air and moisture produced. Nor does it consider that the droplet is evaporating while aloft and radially dynamic. Additionally, for droplets 500 \(\mu\)m radii, the spherical assumption begins to fail and turbulence leads to shattering or fragmenting while aloft, which may shift the radial size distributions to favor smaller drops and more exchange. There is some evidence that sea spray generation mechanisms at high wind speeds may favor this sort of shattering (Veron, 2012, Troitskaya et al., 2017) such that high wind speeds may generate a large number of smaller droplets which can in or outgas more quickly as well as remain aloft via turbulence more easily. Very small spray droplets have been
known to have residence times in the marine boundary layer of days or weeks (Lewis and Schwartz, 2004).

**Conclusions**
The variation in sea spray generation fluxes makes it difficult to constrain the potential contribution of sea spray to gas exchange over the ocean. Here we present three representative volume generation fluxes to represent the upper, average, and lower bounds of sea spray mediated gas exchange. These fluxes indicate that, particularly at wind speeds above 20 ms\(^{-1}\), the magnitude of sea spray gas exchange can represent a significant fraction of the interfacial flux or even exceed it. This implies that gas exchange is most likely important in high wind speeds and storm events. More robust understanding of sea spray generation, particularly at high wind speeds is necessary to fully constrain this flux.

Examining two separate number fluxes indicates that different size droplets likely contribute in different amounts to the exchange of gases. Different drop sizes have different timing for reaching equilibrium with the air and thus may contribute in different magnitudes and directions. Initial comparisons to a time aloft indicate that the contribution from spray is most important at very high wind speeds. However, estimates of time aloft in storm systems and better parameterization of the number and size of droplets produced are necessary to fully constrain the contribution of sea spray to gas exchange.

**Citations**
Andreas, E.L. Thermal and Size Evolution of Sea Spray Droplets; CRREL Rep. 89-11; U.S. Army Cold Regions Research and Engineering Laboratory: Hanover, NH, USA, 1989; 37p


Overarching Conclusions

This dissertation has examined dissolved gases in a variety of contexts with the intent of elucidating how anticipated climate change might be expected to impact gas reservoirs and fluxes. Chapter one finds that the temperate LIS, coastal estuarine system experiences increases in temperature greater than that of the open ocean and that this rise in temperature can be correlated with a corresponding reduction in dissolved oxygen. This result highlights the importance of long term time series for understanding and illustrating theoretical considerations and for managing coastal systems. By examining dissolved oxygen we can get a glimpse of how other gases may respond. Managing dissolved gases in the future will require knowledge of the fundamental large scale physical impacts of climate change, including temperature, to maintain resilience in coastal water systems.

Sea spray has been examined in a theoretical sense to understand its potential as a carrier of dissolved gases. Using an established model of the evolution of a sea spray droplet and combining it with well understood chemical parameterizations we can arrive at the conclusion that the sea spray droplet not only evolves in its gas content throughout its evolution while aloft but that scaling indicates, at high enough wind speeds, when the number and volume flux increase non linearly, sea spray gas exchange may be on the same order of magnitude as the interfacial flux. The large variety of sea spray generation fluxes means that this work is ongoing as uncertainties in the generation flux directly translate to uncertainties in the contribution of sea spray. The size of the droplets and the time held aloft will play a pivotal role in how much sea spray can contribute to gas exchange. This is because smaller droplets will reach their thermal and radial equilibrations faster and are therefore more likely to contribute to this exchange in their entirety. Large droplets may shred apart in higher winds (Mueller and Veron, 2009) due to
the mechanism by which they are formed (generally sheets or ligaments which are unstable). If
the droplet spectrum in high winds does shift to smaller droplets because of this fragmentation
effect, it would allow them to in or outgas on shorter timescales and increase their contribution to
gas exchange. Future work must include a stronger understanding of how spray is lifted and
carried in high wind systems. Such a result is unsurprising in the greater context of sea spray
studies; it has been shown that sea spray likely impacts tropical cyclone formation through
impacts on the drag coefficient, and that it may contribute to heat and momentum fluxes (Veron,
2015).

**Future Work**

One of the fundamental requirements to advance our understanding of sea spray moderated gas-
exchange is more observations at high wind speeds to improve our understanding of the
incremental spray number flux (dF(R)/dR) and incremental spray volume flux (dV(R)/dR) at
these extremes. The difficulty in making these observations remains a challenge. Recent reviews
have pointed to the potential of remote sensing and eddy covariance as well as establishing
scaling parameters for experimental data (Meskhidze et al., 2013). This becomes more of a
priority as coupled air-sea exchange models advance and such data will be critical to
understanding exchange in important areas such as the Southern Ocean and in complex storm
systems which are predicted to increase in intensity.

The contribution of sea spray is also fundamentally linked to the time a droplet spends aloft.
Comparison of the number and size of droplet to the time they spend aloft will allow us to make
a nuanced estimation of sea spray gas exchange as droplets require time to equilibrate and
exchange gas. Most of the improvements could be termed “refining.” Thus there is a need to nest
the sea spray model within an air-sea interaction model that can predict sea spray time aloft in very turbulent systems.

The ultimate purpose of this model is for use in larger scale systems, to reduce uncertainties, particularly in the estimations associated with gas exchange in tropical cyclones.

Finally the model has been designed for gases that do not react upon dissolution in seawater. The model should be expanded to gases such as CO$_2$ that undergo various disproportionate reactions once dissolved in water. This will further improve our understanding of reactive and other climate relevant gases.

Citations

