7.1 PERSPECTIVES ON ESTIMATING THE SPRAY-MEDIATED FLUX OF GASES ACROSS THE AIR-SEA INTERFACE

Edgar L Andreas NorthWest Research Associates, Inc.; Lebanon, New Hampshire

1. INTRODUCTION

The air-sea interface is often multiply connected. Ocean water in the form of spray droplets exists in the near-surface air, and air in whitecap bubbles exists in the near-surface ocean. Each of these air-water interfaces exchanges properties between the air and water just as the actual sea surface does.

I have spent a lot of time trying to understand how spray droplets enhance the air-sea transfers of sensible and latent heat (e.g., Andreas 1992; Andreas and DeCosmo 2002; Andreas et al. 2008). Whitecap bubbles, on the other hand, do not seem able to also enhance air-sea heat and moisture transfer (Andreas and Monahan 2000). Meanwhile, air-sea interaction specialists and ocean chemists have been studying how bubbles affect air-sea gas exchange (e.g., Thorpe 1982; Merlivat and Memery 1983; Monahan and Spillane 1984; Wallace and Wirick 1992; Keeling 1993; Woolf 1993; Vlahos and Monahan 2009).

To my knowledge, however, no one has investigated how or whether spray droplets affect air-sea gas transfer, although Fairall et al. (2000) speculated that sea spray may be an even more efficient agent for air-sea gas transfer than bubbles.

In this paper, I therefore open this discussion of how to quantify the role of spray droplets in airsea gas transfer. I hypothesize that gases can cross the air-sea interface by three distinct routes: through *interfacial* exchange that is controlled by molecular processes right at the air-sea interface, by *spray*-mediated exchange that is controlled by microphysical processes at the surface of sea spray droplets, and by *bubble*-mediated exchange.

Because, as I will explain, these three gas exchange routes do not obey the same scaling, separating their contributions using data analysis alone is not possible. Instead, as I have done in my work on spray-mediated heat fluxes, only with theoretical models for each transfer route can we sort out from measured gas fluxes how much each route contributes to the total air-sea flux. Here, I will set down theoretical equations for these routes, highlight the different scaling relations that each obeys, and suggest the potential importance of spray-mediated gas transfer.

2. GENERAL CONSIDERATIONS

Microphysical modeling underlies my approach to understanding spray-mediated transfer (Andreas 1989, 1990, 1992. 1995, 1996; Andreas and DeCosmo 1999). Figure 1 shows a sample of this modeling for a typical spray droplet that is created from seawater with a temperature (Θ_s) of 20°C and has an initial radius (r_0) of 100 µm.

Figure 1 depicts the time evolution of this 100 μ m droplet's temperature, radius, and salinity when it is ejected into near-surface air of 18 °C and relative humidity 90%. Both the temperature and the radius of the droplet follow approximately exponential decays; we can therefore characterize these evolution curves with temperature (τ_T) and radius (τ_r) e-folding times and the associated equilibrium temperature (T_{eq}) and radius (r_{eq}). That is, until temperature (T) and radius (r) reach equilibrium, these evolution curves are well represented by

$$\frac{T(t) - T_{eq}}{\Theta_s - T_{eq}} = exp(-t/\tau_T), \qquad (2.1)$$

$$\frac{r(t) - r_{eq}}{r_{o} - r_{eq}} = \exp(-t/\tau_{r}), \qquad (2.2)$$

where t is the time since formation.

In particular, because ocean spray droplets are saline, they do not evaporate entirely as freshwater droplets would. Instead, as the pure water evaporates and if the relative humidity is 75% or higher, the droplets concentrate salt until they reach an equilibrium radius, r_{eq} . Figure 1 also

Corresponding author address: Dr. Edgar L Andreas, NorthWest Research Associates, Inc., 25 Eagle Ridge, Lebanon, NH 03766-1900; e-mail: <u>eandreas@nwra.com</u>.



FIG. 1. Microphysical modeling of the temperature, radius, and salinity evolution of a spray droplet. The droplet formed with an initial radius (r_0) of 100 μ m from seawater with temperature (Θ_s) 20 °C and salinity (S) 34 psu. It was flung into air at temperature (T_a) 18 °C and relative humidity (RH) 90%. The barometric pressure was 1000 mb. T_{eq} and r_{eq} are equilibrium temperature and radius that the droplet evolves to; τ_T and τ_r are the respective e-folding times that quantify these evolution rates.

shows how the salinity of the droplet builds up as the droplet evaporates. If the relative humidity is less than 75%, seawater droplets will evaporate all their water if given enough time and leave just salt particles (e.g., Twomey 1953, 1954; Tang and Munkelwitz 1993; Pruppacher and Klett 2010, Table 4.3).

The e-folding times τ_T and τ_r in Fig. 1 quantify the time required to reach equilibrium. These times and the equilibrium properties T_{eq} and r_{eq} all depend on environmental conditions: sea surface temperature (the initial droplet temperature) and salinity, air temperature, and relative humidity.

The e-folding times, especially, also depend strongly on initial droplet radius. I have made many such calculations as in Fig. 1 (e.g., Andreas 1990, 1995; Andreas et al. 2008) and find that the curves and, thus, τ_T and τ_r slide to the left on the

time axis in Fig. 1 for smaller droplets and to the right for larger droplets. τ_T and τ_r , nevertheless, always maintain the relative separation shown in Fig. 1, where τ_r is three orders of magnitude longer than τ_T (e.g., Andreas 1992; Andreas et al. 1995; Andreas and DeCosmo 2002).

Presumably, the same droplet size range that is relevant for spray-mediated heat and moisture exchange is relevant for spray-mediated gas exchange. But not only is the size range relevant but also the rate at which droplets of a given radius are produced. We quantify this rate as the spray generation function—denoted dF/dr₀ (e.g., Monahan et al. 1986)—which predicts the number of droplets with initial radius r₀ produced per square meter of sea surface per second per micrometer increment in droplet radius and has units m⁻² s⁻¹ µm⁻¹. Because the volume of water



FIG. 2. A candidate spray generation function expressed as a volume flux, $(4\pi r_o^3/3)dF/dr_o$, for droplets of initial radius r_0 . U_{10} is the wind speed at 10 m above the sea surface. Nominal size ranges for the three primary droplet classes—film, jet, and spume (Monahan et al. 1986)—are noted. This function comes from Fairall et al. (1994) and is the one that Andreas (2002) has judged most reliable in the important spume range.

produced rather than simply the number of droplets is the important quantity for any spraymediated flux, we usually want to know the volume flux, $(4\pi r_0^3/3) dF/dr_0$.

Figure 2 shows my candidate for the spray generation function (Andreas 2002; Andreas et al. 2010). The figure also indicates the nominal size ranges for the three main classes of spray droplets—the film and jet droplets that bubbles bursting in whitecaps produce and the spume droplets created when the wind tears water off the wave crests.

In my studies of spray-mediated heat and moisture transfer, spume droplets, which contain most of the spray volume (Fig. 2), also account for most of the heat and moisture transfer. Still, the film and jet droplets play a significant role. In general, droplets with r_0 from 1 to 500 μ m are the most important for spray-mediated transfer. For 1 μ m droplets, τ_T is of order 10⁻⁴ s; for 500 μ m droplets, τ_T is about 5 s. τ_r is typically three orders of magnitude longer than τ_{T} . That is, spraymediated sensible heat transfer-the transfer associated with the droplet's temperature change-is very fast while the spray-mediated moisture flux (the latent heat flux)-the transfer associated with radius change—is much slower.

As a point of reference for these microphysical time scales, I also estimate a droplet's residence time in air as (Andreas 1992)

$$\tau_{f} = \frac{H_{1/3}}{2u_{f}(r_{0})}.$$
 (2.3)

Here, $H_{1/3}$ is the significant wave height; $H_{1/3}/2$ is therefore the significant wave amplitude. Also, $u_f(r_0)$ is the terminal fall speed of droplets with initial radius r_0 . In words, (2.3) estimates a droplet's residence time as if it were a ballistic projectile created at the wave crest—where spume droplets, at least, are created—that falls back into the ocean at mean sea level.

For $H_{1/3}$, I usually use the algorithm from Andreas and Wang (2007) that predicts $H_{1/3}$ simply as a function of the square of the 10 m wind speed. If a more sophisticated model for $H_{1/3}$, such as WAM or WAVEWATCH, is available, by all means use its value for $H_{1/3}$.

Fall speeds, u_f in (2.3), range from 0.0013 m/s for 1 μ m droplets to 4 m/s for 500 μ m droplets. Because H_{1/3} may range from, say, 1 to 8 m for wind speeds from 0 to 25 m/s, large droplets have residence times of a few seconds while small droplets can remain suspended for hours.

Figure 3 summarizes some generalities we can now make about spray-mediated gas transfer simply from the microphysical modeling of droplet evolution and the constraints on residence time.

For conceptual ease, we can separate droplets into just two classes: small droplets and large droplets. Small droplets are those with long residence times such that they reach radius equilibrium before falling back into the sea. Large droplets, on the other hand, will probably reach temperature equilibrium because the sensible heat transfer for all droplets of interest is very fast, but most will fall back into the sea before reaching radius equilibrium. These are the so-call reentrant droplets (Andreas and Emanuel 2001) that do not have time to evolve fully to their natural equilibrium.

Droplet radius alone does not distinguish small and large droplets. Increasing wind speed increases residence time through its influence on wave height [see (2.3)]. Therefore, the cutoff radius between small and large droplets increases with wind speed.

In most open ocean conditions, both classes of spray droplets evaporate and thus concentrate



FIG. 3. Gas transfer processes near the air-sea interface. The figure depicts three routes for gas transfer: the *interfacial* route that is controlled by the sea-air difference in the partial pressure of the gas, Δp ; *bubble*-mediated transfer; and *spray*-mediated transfer, in which droplet size is a crucial parameter.

salt, as Fig. 1 shows. The Setchenow salting-out relation (e.g., Riley and Chester 1971, p. 106) therefore means that any gas becomes less soluble in an evaporating droplet. In other words, other things being equal, spray droplets tend to expel more gas than the ocean would if the air-sea partial pressure difference Δp is positive or to take up less gas than the ocean would if Δp is negative.

Moreover, if the relative humidity is less than 75%, the nominal deliquescence point for saline droplets, small droplets will evaporate to dry salt particles and thereby give up all their water and all of their gas regardless of the sign of the sea-air partial pressure difference. This behavior has no analog for normal gas transfer right at the air-sea interface, which simply follows Δp .

Finally, because spray droplets are so small that we need microphysics to quantify transfer to

and from their surfaces (Andreas 1989, 1990; Pruppacher and Klett 2010, Chapters 13 and 17), we can presume that surface curvature will play a role in spray-mediated gas transfer. For example, water vapor transfer at a droplet's surface is controlled, in part, by the Kelvin effect (e.g., Bohren and Albrecht 1998, p. 240f.) whereby water molecules are less tightly held to a droplet as the droplet's radius decreases. But an offsetting effect for water vapor and also other gases is that the relative thickness of the "jump" layer around a droplet increases as the droplet radius decreases. Because the kinetic theory of gases controls transfer between the atmospheric reservoir and a droplet through this layer, the effective molecular diffusivity in this layer decreases with decreasing radius. In effect, the molecular transfer of gas molecules to or from a

droplet's surface slows with decreasing radius.

In the next section, I will elaborate on these processes and provide some quantitative estimates of their effect on spray-mediated gas transfer.

3. MATHEMATICAL FORMULATION

A typical parameterization for the total air-sea flux of a gas is (e.g., Merlivat and Memery 1983; Asher et al. 1996; McNeil and D'Asaro 2007; Vlahos et al. 2011)

$$\mathbf{F}_{g,T} = \mathbf{k} \left(\mathbf{C}_{W} - \mathbf{K}_{H}^{*} \mathbf{R} \boldsymbol{\Theta}_{s} \mathbf{C}_{a} \right). \tag{3.1}$$

In this, k is the transfer or piston velocity; C_w , the gas concentration in the near-surface seawater; C_a , the gas concentration in the near-surface air; R (=8.31447 Jm⁻¹K⁻¹), the universal gas constant;

 $\Theta_{s},$ the seawater temperature in kelvins; and $K_{H}^{^{\star}},$

the Henry's law coefficient (Bohren and Albrecht 1998, p. 233ff.; Pruppacher and Klett 2010, Table 17.14). The superscript * denotes a coefficient that can include the effects on solubility of gases that dissociate in water into ions (Pruppacher and Klett 2010, p. 747). Also in (3.1), $K_{\rm H}^{\star} R \Theta_{\rm s}$ is dimensionless; hence, if $C_{\rm w}$ and $C_{\rm a}$ are in mol m⁻³, $F_{\rm g,T}$ has units of mol m⁻² s⁻¹.

Equation (3.1) is often written in terms of partial pressure (e.g., Wanninkhof and McGillis 1999), where, from the ideal gas law,

$$p_{q} = R\Theta C_{q}. \qquad (3.2)$$

 p_g is then the partial pressure of the gas, C_g is its concentration, and Θ is its temperature. I prefer (3.1), however, because the concentration gradient that drives the gas flux is, to me, more analogous to the temperature and specific humidity gradients that drive the interfacial air-sea sensible and latent heat fluxes.

The Henry's law coefficient depends on both temperature and salinity and is unique for each gas. Typically, it is written as (e.g., Weiss 1970, 1974; Wanninkhof 1992; Warneck and Williams 2012, p. 289ff.)

$$ln(K_{H}^{*}) = A_{1} + A_{2}/\Theta + A_{3}ln\Theta + S(B_{1} + B_{2}\Theta + B_{3}\Theta^{2}).$$
(3.3)

Here, again, Θ is the temperature in kelvins, S is the salinity of the solution in psu, and the As and Bs are constants for a particular gas.

From (3.3), the derivative of $K_{\rm H}^{\star}$ with respect to temperature is

$$\frac{1}{K_{H}^{*}}\frac{\partial K_{H}^{*}}{\partial \Theta} = -\frac{A_{2}}{\Theta^{2}} + \frac{A_{3}}{\Theta} + S(B_{2} + 2B_{3}\Theta). \quad (3.4)$$

Because for ocean and near-surface air temperatures the terms on the right side of (3.4) sum to a negative number, the solubility of a gas decreases as the temperature increases.

Likewise, the derivative of (3.3) with respect to salinity is

$$\frac{1}{K_{H}^{*}}\frac{\partial K_{H}^{*}}{\partial S} = B_{1} + B_{2}\Theta + B_{3}\Theta^{2} . \qquad (3.5)$$

Again, the sum on the right is negative for normal ocean conditions; the solubility of a gas decreases as the salinity of the solution increases. This behavior is known as the Setchenow salting-out effect (e.g., Weiss 1971).

These two influences compete when our subject is spray-mediated gas transfer. As Fig. 1 shows, a newly formed spray droplet cools quickly to a temperature that is less than the air temperature and usually less than the sea surface temperature. This tendency would make the droplet a more accommodating reservoir for dissolved gas than is the sea underneath it.

But as time passes and the droplet begins evaporating, it concentrates salt and now becomes a less hospitable environment for dissolved gas. The relative importance of these two processes will depend on air temperature and humidity, gas concentrations in the air and ocean, and the droplet's residence time in air.

Many attempts to parameterize air-sea gas transfer are based on measurements of $F_{g,T}$, C_w , and C_a and then an empirical fit to wind speed of the resulting k values (e.g., Wanninkhof 1992; McGillis et al. 2001; Donelan and Wanninkhof 2002; Ho et al. 2006). Thirty years ago, though, Thorpe (1982) and Merlivat and Memery (1983) hypothesized that bubbles could be effective agents for air-sea gas exchange (see also Monahan and Spillane 1984; Memery and Merlivat 1985; Woolf and Thorpe 1991; Wallace and Wirick 1992; Keeling 1993).

The obvious mechanism for bubble-mediated

gas exchange is the additional air-water contacts that bubbles provide; but Monahan and Spillane (1984) hypothesized that bubbles bursting in whitecaps also disrupt the aqueous boundary layer—the primary resistance to interfacial air-sea gas transfer (e.g., Liss and Merlivat 1986; Donelan and Wanninkhof 2002)—and thereby provide a conduit for interfacial gas transfer.

Because the interfacial and bubble-mediated routes by which gases cross the air-sea interface have different dependencies on wind speed, researchers found it necessary to develop unique, theoretically based parameterizations for each (e.g., Merlivat and Memery 1983; Woolf 1993, 2005; Fairall et al. 2000; Hare et al. 2004; Stanley et al. 2009; Vlahos and Monahan 2009; Vlahos et al. 2011). As a result, the transfer velocity in (3.1) is commonly written as the sum of transfer velocities for the interfacial (k_{int}) and bubble-mediated (k_b) fluxes:

$$\mathbf{k} = \mathbf{k}_{\rm int} + \mathbf{k}_{\rm b} \,. \tag{3.6}$$

There are many candidate expressions for both k_{int} and k_b . For k_{int} , at least, I prefer the suggestion by Woolf (2005) that

$$k_{int} = 1.6 \times 10^{-4} \, u_{*} \left(600 \, / \, \text{Sc} \right)^{1/2}$$
. (3.7)

Woolf based this algorithm on theoretical arguments and experimental data from Jähne et al. (1987; cf. Kraus and Businger 1994, p. 163). In (3.7), u_{\star} is the friction velocity in air, and both u_{\star} and k_{int} are in m/s, Sc is the Schmidt number in seawater of the gas of interest, and 600 is the Schmidt number of CO₂ in seawater at 20°C.

I gravitated to (3.7) for parameterizing the interfacial flux because, with (3.7) in (3.1), the interfacial gas flux will go linearly with u, and scale with the air-sea constituent gradient, as do the interfacial latent and sensible heat fluxes (Andreas et al. 2012, Appendix). This similarity makes good physical sense.

The point of this paper, however, is to add a spray-mediated flux $(F_{g,sp})$ to (3.1). That is, with (3.6), (3.1) becomes

$$F_{g,T} = (k_{int} + k_b) (C_w - K_H^* R \Theta_s C_a) + F_{g,sp}. \quad (3.8)$$

In other words, I hypothesize that gases can cross the air-sea interface by three distinct routes (Fig. 3): directly at the interface and via air bubbles and spray.

Andreas and Monahan (2000) evaluated a similar hypothesis with regard to the sensible and That is, in addition to the latent heat fluxes. interfacial and spray routes by which heat and moisture cross the sea surface (Andreas and DeCosmo 2002; Andreas et al. 2008), they also computed the bubble-mediated heat and moisture They found, however, these bubblefluxes. mediated fluxes to be negligible even for winds up to 40 m/s. It would, thus, not be unreasonable to expect the spray-mediated gas transfer to be comparable to or larger than the bubble-mediated gas transfer. In fact, it is probable that many of the empirical k_b values include the unrecognized effects of spray-mediated transfer.

By analogy with my work on spray-mediated heat and moisture transfer (e.g., Andreas 1989, 1990), I adapt the microphysical equations in Pruppacher and Klett (2010, p. 759ff.) to treat gas transfer to and from saline sea spray droplets. The essential equation is

$$\frac{dm_{g}}{dt} = -4\pi r D'_{g} \left[\frac{C_{d}(t)}{K_{H}^{*}(t)RT_{d}(t)} - C_{a} \right]. \quad (3.9)$$

Here, m_g is the mass of a particular gas in a droplet of radius r, and t is time; hence, dm_g/dt is the rate of change of that mass. Also in (3.9), $T_d(t)$, $C_d(t)$, and $K_H^*(t)$ are the droplet temperature, gas concentration in the droplet, and Henry's law coefficient, all of which are functions of time. The gas in these very small droplets is assumed to be well mixed (Pruppacher and Klett 2010, p. 760).

Lastly in (3.9), D'_{g} is the modified molecular diffusivity in air of the gas of interest:

$$D'_{g} = \frac{D_{g}}{\frac{r}{r + \Delta_{g}} + \frac{D_{g}}{r \alpha_{g}} \left(\frac{2\pi M_{g}}{R T_{a}}\right)^{1/2}}.$$
 (3.10)

Here, D_g is the molecular diffusivity of the gas in air, a function of pressure and temperature (Andreas 2005); M_g is the molecular weight of the gas; T_a is the temperature of the ambient air; Δ_g is the thickness of the gas "jump" layer, which is approximately the mean free path of air molecules, ~10⁻⁷ m (Pruppacher and Klett 2010, pp. 505, 760); and α_g is the mass accommodation



FIG. 4. Schematic of gas transfer processes near the air-sea interface and the gas concentration gradients that force them. Interfacial gas transfer is forced by $C_w - K_H R \Theta_s C_a$ [equation (3.8)], as is bubble-mediated gas exchange. Spray-mediated transfer, in contrast, is forced by $C_d / K_H R T_d - C_a$ [equation (3.11)], the concentration gradient across the jump layer around spray droplets.

coefficient, which is the ratio of the number of gas molecules that stick to a water surface compared to all those that impinge on that surface (Bohren and Albrecht 1998, p 187f.). For now, I take $\alpha_g = 0.036$, the value of the water vapor accommodation coefficient (Andreas 1989, 2005; Pruppacher and Klett 2010, Tables 13.1 and 17.18; cf. Lamb and Verlinde 2011, p. 334).

Equations (3.8), (3.9), and (3.10) highlight fascinating differences between interfacial and spray-mediated gas transfer. While the interfacial and bubble-mediated transfers are assumed to be controlled by molecular diffusion on the aqueous side of the air-water interface (Donelan and Wanninkhof 2002)—as evidenced by the $C_w - K_H^* R \Theta_s C_a$ term in (3.8)—gas transfer to and from spray droplets is limited by how rapidly gas molecules can cross the jump layer around a droplet (Fig. 4). In this layer, which extends from r to r + Δ_g , the kinetic theory of gases explains the rate of transfer because distances are so small that the air no longer behaves as a continuous fluid.

First, the $C_d/K_H^*RT_d - C_a$ term in (3.9) is the concentration gradient between the gas in air at the droplet's surface that is in equilibrium with the droplet (i.e., $C_d/K_H^*RT_d$) and the gas in air beyond the jump layer (i.e., C_a). The assumption is that transfer across the droplet's interface is so fast that the air in contact with the interface always has a concentration given by Henry's law equilibrium with the gas in the droplet.

Second, the $(2\pi M_g/RT_a)^{1/2}$ term in (3.10) is

 $4/v_g$, where v_g is the average speed of an ideal gas molecule according to the Maxwell-Boltzmann speed distribution (Bohren and Albrecht 1998, p. 60ff.). This velocity across the jump distance Δ_g is how gas molecules impact or escape from the droplet's surface.

In (3.9), the instantaneous mass of the gas of interest in the droplet is $4\pi r^3 C_d/3$. Hence, we can rewrite (3.9) as

$$\frac{dC_{d}}{dt} = -\frac{3D_{g}'}{r^{2}} \left(\frac{C_{d}}{K_{H}^{*}RT_{d}} - C_{a} \right). \quad (3.11)$$

Although a droplet's radius, temperature, and Henry's law coefficient will all be changing with time along with the gas concentration, for the sake of demonstration, I assume that all the quantities in (3.11), with the exception of C_d , are constants. Equation (3.11) then has the solution

$$C_{d}(t) = K_{H}^{*}RT_{d}C_{a} + (C_{w} - K_{H}^{*}RT_{a}C_{a})exp\left(\frac{-3D'_{g}t}{r^{2}K_{H}^{*}RT_{a}}\right).$$
(3.12)

In this, C_w is again the gas concentration in bulk seawater and is assumed to be the initial concentration in all droplets.

Equation (3.12) suggests that the gas concentration in a droplet will decay (or increase, depending on the sign of $C_d/K_H^*RT_d - C_a$) exponentially over an e-folding time of (cf. Lamb and Verlinde 2011, p. 506f.)

$$\tau_{g} = \frac{r^{2} K_{H}^{*} R T_{a}}{3 D'_{g}}.$$
 (3.13)

Figure 5 shows calculated values of the modified diffusivity D'_g for an ideal gas, helium, and for a gas that reacts with water, carbon dioxide. For comparison, the plot also shows the modified molecular diffusivity of water vapor in air, which figures crucially in the radius evolution depicted in Fig. 1 (cf. Andreas 1989, 2005). Figure 5 implies that, for helium transfer, droplets with radii above 20 μ m behave as planar surfaces. But, for the transfers of carbon dioxide and water vapor, only droplets larger than 300 μ m behave as planar surfaces. That is, in general, we must



FIG. 5. Modified molecular diffusivities for carbon dioxide and helium in air as computed from (3.10). For comparison, the plot also shows the modified diffusivity of water vapor. The air temperature is 18 °C and the barometric pressure is 1000 mb, as in Fig. 1.

account for surface curvature and non-continuum exchange.

With the D_g^{\prime} values from Figure 5, I can estimate e-folding times given by (3.13) for the spray-mediated exchanges of carbon dioxide and helium for comparison with the time scales for temperature and radius evolution shown in Fig. 1. For 100- μm droplets in air at 18 °C, I calculate τ_g for carbon dioxide and helium to be, respectively, $1.9{\times}10^{-4}\,s$ and $4.7{\times}10^{-6}\,s$.

Remember, these are crude estimates because I derived them under the assumption that droplet temperature, radius, and salinity were held constant. But if fully coupled microphysical modeling proves these τ_g values to be in the right ballpark, the assumption of constant droplet conditions is accurate because these time scales are so short that droplet temperature and radius have not yet changed (see Fig. 1). Apparently, gas transfer mediated by even fairly large spray droplets is extremely fast.

To find the spray-mediated gas flux required in (3.8), we must integrate the contributions over all droplet radii. This integral is

$$F_{g,sp} = \int_{r_{min}}^{r_{max}} \left[m_{0} - m_{g} \left(r_{0}, \tau_{g}, \tau_{f} \right) \right] \frac{dF}{dr_{0}} dr_{0} . \quad (3.14)$$

Here, m_0 is the mass of gas in droplets of initial radius r_0 and is $4\pi r_0^3 C_w/3$. The magnitude of

 $m_g(r_0, \tau_g, \tau_f)$ comes from numerically solving (3.9) simultaneously with comparable equations for droplet temperature and radius evolution (e.g., Andreas 1989, 1990). Again, $m_g(r_0, \tau_g, \tau_f)$ is specific to droplets of initial radius r_0 and represents the mass of gas in these droplets at the instant they fall back into the sea or are suspended but in equilibrium. The interplay between τ_g and τ_f determines these two limits. From Fig. 2, we see that r_{min} and r_{max} are nominally 0.5 µm and 500 µm.

In words, $m_0 - m_g(r_0, \tau_g, \tau_f)$ is the gas exchanged by each droplet of initial radius r_0 . dF/dr₀ is the rate at which droplets of this size are produced. Hence, $F_{g,sp}$ has units of mol m⁻² s⁻¹ when we integrate over all droplet sizes.

4. SUMMARY

This is an admittedly preliminary study of spray-mediated air-sea gas transfer. Air-sea gas transfer is a complex problem, and I have tried to highlight that complexity in anticipation of a more thorough study. In particular, different physical and chemical processes come into play with spray-mediated transfer than with interfacial and bubble-mediated transfer. Figure 4 summarizes these transfer processes.

To recap, the temperature of a newly formed spray droplet decreases, and its salinity increases. The Henry's law coefficient is therefore not constant as droplets evolve. For interfacial and bubble-mediated transfer, in contrast, the ocean surface temperature and salinity vary only diurnally or seasonally.

Relative humidity in the near-surface air determines the equilibrium size of spray droplets and therefore has a first-order effect on spraymediated transfer. But relative humidity has negligible effect on interfacial and bubblemediated gas transfer.

Spray-mediated transfer increases approximately as the cube of the wind speed because dF/dr_0 is approximately cubic in wind speed. Bubble-mediated transfer is also cubic in wind speed because it follows whitecap coverage. Interfacial transfer, on the other hand, is approximately linear in wind speed.

The slow step in spray-mediated gas transfer is molecular diffusion across the jump layer in the air surrounding spray droplets. The slow step in interfacial transfer is molecular diffusion through an aqueous boundary layer at the surface of the ocean; in bubble-mediated transfer, through the aqueous boundary layer surrounding the bubbles.

Finally, the direction of interfacial and bubblemediated gas fluxes follows the sign of the sea-air difference in partial pressure, Δp . With the spraymediated fluxes, it is unclear without further study whether Δp or its sign is meaningful because, for example, some droplets sizes in some conditions can accomplish sea-to-air gas transfer regardless of the sign or magnitude of Δp .

In closing, I hope it is by now obvious that we cannot find the ultimate solution to parameterizing air-sea gas transfer from just flux measurements and a parameterization like (3.1) that is based on interfacial scaling (cf. Andreas 2011). Because interfacial exchange, bubble-mediated exchange, and spray-mediated exchange all follow different scaling relations, we must develop theoretically based parameterizations for each route and test these combinations against measurements, which provide only the total gas flux.

5. ACKNOWLEDGMENTS

I would like to thank Penny Vlahos and Ed Monahan for advice on this topic and Jeff Hare for providing the seed in 2008 that started my thinking about spray-mediated gas transfer. Emily Moynihan of BlytheVisual prepared Figs. 3 and 4. The Office of Naval Research supported this work with awards N000-11-1-0073 and N000-12-C-0290.

6. REFERENCES

- Andreas, E. L, 1989: Thermal and size evolution of sea spray droplets. *CRREL Report 89-11*, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 37 pp.
- Andreas, E. L, 1990: Time constants for the evolution of sea spray droplets. *Tellus*, **42B**, 481–497.
- Andreas, E. L, 1992: Sea spray and the turbulent air-sea heat fluxes. *J. Geophys. Res.*, **97**, 11,429–11,441.
- Andreas, E. L, 1995: The temperature of evaporating sea spray droplets. *J. Atmos. Sci.*, **52**, 852–862.
- Andreas, E. L, 1996: Reply. *J. Atmos. Sci.*, **53**, 1642–1645.
- Andreas, E. L, 2002: A review of the sea spray generation function for the open ocean. *Atmosphere-Ocean Interactions, Volume 1*, W. A. Perrie, Ed., WIT Press, Southampton,

U.K., 1–46.

- Andreas, E. L, 2005: Handbook of physical constants and functions for use in atmospheric boundary layer studies. *M-05-1*, U.S. ERDC/CRREL Monograph Army Cold Regions Research and Engineering Laboratory, Hanover, NH, 42 pp.
- Andreas, E. L, 2011: Fallacies of the enthalpy transfer coefficient over the ocean in high winds. *J. Atmos. Sci.*, **68**, 1435–1445.
- Andreas, E. L, and J. DeCosmo, 1999: Sea spray production and influence on air-sea heat and moisture fluxes over the open ocean. *Air-Sea Exchange: Physics, Chemistry and Dynamics*, G. L. Geernaert, Ed., Kluwer, Dordrecht, The Netherlands, 327–362.
- Andreas, E. L, and J. DeCosmo, 2002: The signature of sea spray in the HEXOS turbulent heat flux data. *Bound.-Layer Meteor.*, **103**, 303–333.
- Andreas, E. L, and K. A. Emanuel, 2001: Effects of sea spray on tropical cyclone intensity. *J. Atmos. Sci.*, **58**, 3741–3751.
- Andreas, E. L, and E. C. Monahan, 2000: The role of whitecap bubbles in air-sea heat and moisture exchange. *J. Phys. Oceanogr.*, **30**, 433–442.
- Andreas, E L, and S. Wang, 2007: Predicting significant wave height off the northeast coast of the United States. *Ocean Eng.*, **34**, 1328–1335.
- Andreas, E. L, J. B. Edson, E. C. Monahan, M. P. Rouault, and S. D. Smith, 1995: The spray contribution to net evaporation from the sea: A review of recent progress. *Bound.-Layer Meteor.*, **72**, 3–52.
- Andreas, E. L, P. O. G. Persson, and J. E. Hare, 2008: A bulk turbulent air-sea flux algorithm for high-wind, spray conditions. *J. Phys. Oceanogr.*, **38**, 1581–1596.
- Andreas, E. L, K. F. Jones, and C. W. Fairall, 2010: Production velocity of sea spray droplets. *J. Geophys. Res.*, **115**, C12065, doi:10.1029/2010JC006458.
- Andreas, E. L, L. Mahrt, and D. Vickers, 2012: A new drag relation for aerodynamically rough flow over the ocean. *J. Atmos. Sci.*, **69**, 2520–2537.
- Asher, W. E., L. M. Karle, B. J. Higgins, P. J. Farley, E. C. Monahan, and I. S. Leifer, 1996: The influence of bubble plumes on airseawater gas transfer velocities. *J. Geophys. Res.*, **101**, 12,027–12,041.
- Bohren, C. F., and B. A. Albrecht, 1998:

Atmospheric Thermodynamics. Oxford University Press, New York, NY, 402 pp.

- Donelan, M. A., and R. Wanninkhof, 2002: Gas transfer at water surfaces—Concepts and issues. *Gas Transfer at Water Surfaces*, M. A. Donelan, W. M. Drennan, E. S. Saltzman, and R. Wanninkhof, Eds., American Geophysical Union, Washington, DC, 1–10.
- Fairall, C. W., J. D. Kepert, and G. J. Holland, 1994: The effect of sea spray on surface energy transports over the ocean. *Global Atmos. Ocean Syst.*, **2**, 121–142.
- Fairall, C. W., J. E. Hare, J. B. Edson, and W. McGillis, 2000: Parameterization and micrometeorological measurement of air-sea gas transfer. *Bound.-Layer Meteor.*, **96**, 63– 105.
- Hare, J. E., C. W. Fairall, W. R. McGillis, J. B. Edson, B. Ward, and R. Wanninkhof, 2004: Evaluation of the National Oceanic and Atmospheric Administration Coupled-Ocean Atmosphere Response Experiment (NOAA/COARE) air-sea transfer gas parameterization using GasEx data. J. Geophys. Res.. 109. C08S11. doi:10.1029/2003JC001831.
- Ho, D. T., C. S. Law, M. J. Smith, P. Schlosser, M. Harvey, and P. Hill, 2006: Measurements of air-sea gas exchange at high wind speeds in the Southern Ocean: Implications for global parameterizations. *Geophys. Res. Lett.*, 33, L16611, doi:10.1029/2006GL026817.
- Jähne, B., K. O. Münnich, R. Bösinger, A. Dutzi, W. Huber, and P. Libner, 1987: On the parameters influencing air-water gas exchange. *J. Geophys. Res.*, **92**, 1937– 1949.
- Keeling, R. F., 1993: On the role of large bubbles in air-sea gas exchange and supersaturation in the ocean. *J. Mar. Res.*, **51**, 237–271.
- Kraus, E. B., and J. A. Businger, 1994: *Atmosphere-Ocean Interaction, 2nd Edition.* Oxford University Press, New York, 362 pp.
- Lamb, D., and J. Verlinde, 2011: *Physics and Chemistry of Clouds*. Cambridge University Press, Cambridge, U.K., 584 pp.
- Liss, P. S., and L. Merlivat, 1986: Air-sea gas exchange rates: Introduction and synthesis. *The Role of Air-Sea Exchange in Geochemical Cycling*, P. Buat-Ménard, Ed., D. Reidel, Dordrecht, The Netherlands, 113– 127.
- McGillis, W. R., J. B. Edson, J. E. Hare, and C. W. Fairall, 2001: Direct covariance air-sea CO₂

fluxes. *J. Geophys. Res.*, **106**, 16,729–16,745.

- McNeil, C., and E. D'Asaro, 2007: Parameterization of air-sea gas fluxes at extreme wind speeds. *J. Mar. Syst.*, **66**, 110– 121.
- Memery, L., and L. Merlivat, 1985: Modelling of gas flux through bubbles at the air-water interface. *Tellus*, **37B**, 272–285.
- Merlivat, L., and L. Memery, 1983: Gas exchange across an air-water interface: Experimental results and modeling of bubble contribution to transfer. *J. Geophys. Res.*, **88**, 707–724.
- Monahan, E. C., 2002: The physical and practical implications of a CO₂ gas transfer coefficient that varies as the cube of the wind speed. *Gas Transfer at Water Surfaces*, M. A. Donelan, W. M. Drennan, E. S. Saltzman, and R. Wanninkhof, Eds., American Geophysical Union, Washington, DC, 193–197.
- Monahan, E. C., and M. C. Spillane, 1984: The role of oceanic whitecaps in air-sea gas exchange. *Gas Transfer at Water Surfaces*, W. Brutsaert and G. J. Jirka, Eds., D. Reidel, Dordrecht, The Netherlands, 495–503.
- Monahan, E. C., D. E. Spiel, and K. L. Davidson, 1986: A model of marine aerosol generation via whitecaps and wave disruption. Oceanic Whitecaps and Their Role in Air-Sea Exchange Processes, E. C. Monahan and G. Mac Niocaill, Eds., D. Reidel, Dordrecht, The Netherlands, 167–174.
- Pruppacher, H. R., and J. D. Klett, 2010: *Microphysics of Clouds and Precipitation, 2nd Revised Edition.* Springer, Dordrecht, The Netherlands, 954 pp.
- Riley, J. P., and R. Chester, 1971: *Introduction to Marine Chemistry*. Academic Press, London, U.K., 465 pp.
- Stanley, R. H. R., W. J. Jenkins, D. E. Lott III, and S. C. Doney, 2009: Noble gas constraints on air-sea gas exchange and bubble fluxes. *J. Geophys. Res.*, **114**, C11020, doi:10.1029/2009JC005396.
- Tang, I., and H. R. Munkelwitz, 1993: Composition and temperature dependence of the deliquescence properties of hygroscopic aerosols. *Atmos. Environ.*, **27A**, 467–473.
- Thorpe, S. A., 1982: On the clouds of bubbles formed by breaking wind waves in deep water and their role in air-sea gas transfer. *Phil. Trans. Roy. Soc. London*, **A304**, 155–210.

- Twomey, S., 1953: The identification of individual hygroscopic particles in the atmosphere by a phase transition method. *J. Appl. Phys.*, **24**, 1099–1102.
- Twomey, S., 1954: The composition of hygroscopic particles in the atmosphere. *J. Meteor.*, **11**, 334–338.
- Vlahos, P., and E. C. Monahan, 2009: A generalized model for the air-sea transfer of dimethyl sulfide at high wind speeds. *Geophys. Res. Lett.*, **36**, L21605, doi:10.1029/2009GL040695.
- Vlahos, P., E. C. Monahan, B. J. Huebert, and J. B. Edson, 2011: Wind-dependence of DMS transfer velocity: Comparison of model with Southern Ocean observations. *Gas Transfer at Water Surfaces 2010*, S. Komori, W. R. McGillis, and R. Kurose, Eds., Kyoto University Press, Kyoto, Japan, 455–463.
- Wallace, D. W. R., and C. D. Wirick, 1992: Large air-sea gas fluxes associated with breaking waves. *Nature*, **356**, 694–696.
- Wanninkhof, R., 1992: Relationship between wind speed and gas exchange over the ocean. *J. Geophys. Res.*, **97**, 7373–7382.
- Wanninkhof, R., and W. R. McGillis, 1999: A cubic relationship between air-sea CO₂ exchange and wind speed. *Geophys. Res. Lett.*, **26**, 1889–1892.
- Warneck, P., and J. Williams, 2012: The Atmospheric Chemist's Companion. Springer, Dordrecht, The Netherlands, 436 pp.
- Weiss, R. F., 1970: The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Res.*, **17**, 721–735.
- Weiss, R. F., 1971: The effect of salinity on the solubility of argon in seawater. *Deep-Sea Res.*, **18**, 225–230.
- Weiss, R. F., 1974: Carbon dioxide in water and seawater: The solubility of a non-ideal gas. *Marine Chem.*, **2**, 203–215.
- Woolf, D. K., 1993: Bubbles and the air-sea transfer velocity of gases. *Atmos.-Ocean*, **31**, 517–540.
- Woolf, D. K., 2005: Parametrization of gas transfer velocities and sea-state-dependent wave breaking. *Tellus*, **57B**, 87–94.
- Woolf, D. K., and S. A. Thorpe, 1991: Bubbles and the air-sea exchange of gases in nearsaturation conditions. *J. Mar. Res.*, **49**, 435– 466.