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Article

Eight categories of air-water gas transfer

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Abstract: The air-sea transfer of gases is important within climate physics, biogeochemistry and the control of pollutants. A two-layer model of transfer directly across the sea surface underpins most discourse, but an expanding literature also features transfer mediated by "suspended fragments", either bubbles in the upper ocean or drops and aerosol in the lower atmosphere. Here, we describe a categorization of process that elucidates departures from two-layer theory and is a starting point for quantification. Six distinct phenomena are identified that cause a transfer of gas across an interface such as the sea surface. A total of eight categories are identified. Each category has a distinct scaling with respect to the properties of the gas and this is key to the relative importance of different categories and processes. Transfer through sea spray can be an exchange process, but the evaporation of sea spray is more effective and is an ejection process. The reactivity of carbon dioxide in aqueous solution enhances the effect of spray. Exceptional levels of sea spray generation and evaporation are required to be significant for most gases, but moderate levels are sufficient for carbon dioxide and the most soluble pollutants.

Keywords: gases; solubility; carbon dioxide; urea; exchange; transfer; ejection; injection; air-sea; bubbles; drops; aerosol; spray

1. Introduction

The sea surface is a key boundary in the earth system. While volatile gases are more easily transferred than non-volatiles, diffusive processes on either side of the sea surface can limit some transfer between atmosphere and ocean and is often a convenient surface at which to calculate fluxes. The transfer of gases between a liquid and gaseous medium is usually described by a two-layer model [1,2]. This model typically implies that transfer rates of soluble gases is controlled by processes in a gaseous boundary layer, while the liquid boundary layer dictates poorly soluble gases. For each case, a "bulk equation" is used to describe the net transfer of a gas based on the product of a concentration difference and a transfer velocity. Various formulae exist for the estimation of transfer velocity; in the case of air-sea transfer usually incorporating a dependence on wind speed, and mostly using semi-empirical parametrizations derived from measurements in flux experiments. At the same time, the transfer velocities are calculated from those flux measurements based on the structure of the bulk equation, and implicitly the two-layer model. A key insight here is that with a few exceptions, the validity of the two-layer model is a hidden assumption within studies of air-water gas transfer.

The first motivation for this paper is to explore cases where a two-layer model is incomplete and to set a framework for assessing the importance of the complications. There are known complications for a "broken surface", for example where bubbles and sea spray are produced by breaking waves at the sea surface [3]. The effect of bubbles in the surface ocean [4,5] and other water bodies [6] is well recognized. The effects of spray and aerosol have been discussed [7,8] but primarily relating to large spray droplets and their contribution to the exchange of poorly soluble gases. A second motivation is to take forward understanding of the role of spray in air-water gas transfer.

The methodology consists firstly of analytical and logical categorization of processes; secondly, a derivation of basic scaling rules for each category and infer when each category will be relatively important; and finally, quantify as far as practical the importance of spray to the air-water transfer of gases. The results provide some support for a spray effect for carbon dioxide and highly soluble gases. The discussion explains why there are many unanswered questions with respect to spray-mediated transfer and identifies some key research priorities.

2. Materials and Methods

This is a theoretical study. Calculations are based on equations described in this and following sections and mostly based on published equations.

The first part of the analysis is to consider different ways a gas can be transferred between atmosphere and ocean (or any pair of liquid and gaseous reservoirs) given that fragments of either reservoir can be entrained into the other reservoir (air bubbles into the upper ocean, drops or particles into the lower atmosphere), in addition to the simple diffusive transfer across two boundary layers either side of the sea surface [2]. Another key distinction is between the different critical processes that apply to poorly soluble gases and soluble gases; this follows from the two-layer theories [1,2], where while any gas needs to traverse two layers, for almost all gases the traverse of only one layer is critical. Another distinction for transfer mediated by a fragment is to distinguish between transfer where the gas is equilibrating across the surface of a fragment of fixed size, and transfer driven by shrinkage of the fragment. A final distinction, which applies solely to spray-mediated transfer of poorly soluble gases, is to recognize when it is necessary for the fragment to be torn from within the reservoir rather than drawn from the absolute surface.

The distinctions in the first part are motivated by the implied governing equations which differ for the eight categories identified. In the second part of the analysis, these equations are inspected to infer the key scaling of each type of transfer. Two types of scaling are considered. Firstly ("Scaling 1"), identifies a proportionality to the concentration in the dissolved phase (water), or as a free gas (air), or a variable combination (complex). Secondly ("Scaling 2"), identifies whether the net transfer scales with the "difference" in concentration across the critical layer, or the "absolute" concentration in the fragment at generation. Scaling occurs in different permutations across the eight categories.

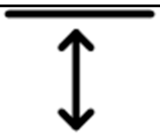
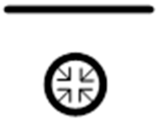
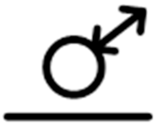
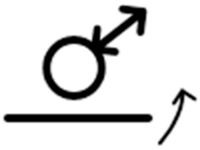
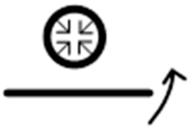
A final scaling relates to the vigor of each process; for example, the amount of wind-driven stirring, or the production rates of bubbles or spray. A rich if incomplete literature exists on these processes and resulting transfer rates, and the method here is limited to an unsystematic but careful review of what is already known and critical gaps relating to spray-mediated transfer.

3. Results

Table 1 provides a summary of results from the two main parts of the analysis. Eight distinct categories are identified. These categories are represented by glyphs in a column of Table 1, with a detailed explanation of each in the next sub-section below. Five categories are relevant to poorly soluble gases (broadly as defined by Liss and Slater [2]), while three are relevant to soluble gases. As explained in the preceding section, scaling refers to which medium (water or air) is relevant, and whether "difference" in concentration across a layer or "absolute" content of a fragment in that medium is relevant. Formulae for each category are presented in the second sub-section below. A final sub-section presents quantification in the general case of atmosphere-ocean exchange and in a few special cases. The treatment of direct (Categories 1 and 2) and bubble-mediated transfer (Categories 3 and 4) is brief and largely a review of existing studies. The research on spray-mediated transfer is more original but depends on some existing studies.

Table 1. Categorizations of air-water gas transfer.

Category	Glyph	Relevance	Scaling 1	Scaling 2
1		poorly soluble	water	difference

				
2		soluble	air	difference
3		poorly soluble	complex	difference
4		poorly soluble	air	absolute
5		soluble	complex	difference
6		poorly soluble	complex	difference
7		soluble	water	absolute
8		poorly soluble	water	absolute

3.1. Categories

3.1.1. Category 1

The first two categories follow from a two-film theory originating in chemical engineering [1] and later applied to air-sea exchange [2]. In the original two-film model [1], each layer required molecular diffusion across the film. In recent decades, a more nuanced description has emerged where there is a gradual progression between molecular diffusion very close to the surface and turbulent transfer further from the surface (a two-layer model). While transfer directly between atmosphere and ocean always requires transit across the two boundary layers either side of the sea surface, usually one or other is limiting. The first category is where diffusion across a thin boundary layer immediately below the sea surface limits gas exchange between atmosphere and ocean. For most important gases including carbon dioxide and oxygen, this is recognized as the primary model for air-sea gas exchange [2] and is the basis for most estimates of air-sea gas transfer. The original film model implies a film thickness of typically ~30 μm thick [9] but modern understanding implies a curved profile [10] with most of the concentration change associated with an atmosphere-ocean disequilibrium within 100 μm of the surface [11].

3.1.2. Category 2

The second category also follows from the two-layer model but identifies transfer across the atmospheric boundary layer above the sea surface as limiting. In the case of soluble gases, e.g., sulfur dioxide [2], it is the boundary above the sea surface that controls transfer rates, and calculations are based on models of molecular and turbulent transfer above the sea surface, with key dependences on wind speed and atmospheric stability.

3.1.3. Category 3

The third and fourth categories are features of bubble-mediated transfer. Here, bubbles inject fragments of the atmosphere into the upper ocean and gas is exchanged between the bubble and the surrounding water. Bubble-mediated transfer should only be effective for poorly soluble gases for two reasons. Firstly, the initial content of the bubble should be drawn from very close to the surface, where for a soluble gas the content will already be in equilibrium with the ocean. Secondly, since bubbles have a volume-limited atmospheric capacity for each gas, it is quite ineffective even for some poorly soluble gases and should be wholly ineffective for more soluble gases.

Category 3 considers the function of a bubble to be an additional surface between atmosphere and ocean. Whereas in Category 1, transfer requires transit across a thin boundary layer below the sea surface; for Category 3, transfer must be completed by crossing a thin liquid boundary layer surrounding the bubble. Note also that while stirring across the sea surface boundary layers is by the action of the wind, a rising bubble is essentially “self-ventilating” with transfer across its liquid boundary dependent on the flow induced by its motion relative to the surrounding water [12]. Categories 1 and 3 do not interfere with each other and both contribute to the exchange of poorly soluble gases between atmosphere and ocean [13]. Their relative importance depends on the surface area of all bubbles relative to sea surface area, and on the efficiency of transfer across each boundary layer (which are of similar order for the sea surface and a typical rising bubble [12]).

3.1.4. Category 4

Category 4 considers the effect of a bubble shrinking, and in some cases dissolving entirely, as a result of the loss of air from a bubble and compression of the bubble, resulting in injection of gas [4,14]. For nitrogen and oxygen, which dominate the content of air, there is some feedback between this category and exchange in Category 3. For other gases, there is a clear distinction between the exchange in response to the air-sea disequilibrium of the trace gas and an expulsion of the trace gas from the bubble driven by its compression and the loss of nitrogen and oxygen. Very rarely, a near-surface bubble can grow over its lifetime due to supersaturation of nitrogen and oxygen in the surface ocean, but shrinkage is normal. An injection of each gas into the ocean is implied by the reduction in volume through the lifetime of a bubble while maintaining the same gas concentration in the bubble and is identified as the Category 4 effect. If the bubble entirely dissolves, then the entire original content of every bubble is injected into the ocean as a Category 4 effect and there is no Category 3 effect.

3.1.5. Category 5

The remaining four categories describe spray-mediated transfer of gas, which is a relatively unresearched area of air-sea gas exchange. Categories separate soluble and poorly soluble gases [2] and exchange and ejection effects giving 4 permutations in all. Spray-mediated transfer is partly analogous to bubble-mediated transfer but with some interesting differences. Category 5 is a relatively straightforward analogy to Category 3 [15]. In Category 5, we identify an exchange of a soluble gas across the surface of spray, in parallel to direct exchange across the air-side boundary layer above the sea surface (Category 2). A simplification is to assume that crossing the boundary layer outside a spray fragment bypasses entirely the main boundary layer; which might not be correct and results in overestimate of the additional exchange.

3.1.6. Category 6

Category 6 considers a similar event to Category 5 but with a complication. In Category 6, poorly soluble gases are the application, and it is necessary to consider if the waterside boundary below the sea surface has been bypassed. In simple terms, it is necessary to know if the fragment originates very close to the sea surface or is torn from within the upper ocean. In the first case, there is no Category 6 contribution. In the second case, there is an effect and an additional contribution to the exchange of a poorly soluble gas [15].

3.1.7. Category 7

Categories 7 and 8 are ejection processes. A soluble gas (Category 7) or a poorly soluble gas (Category 8) can be ejected from the ocean through the evaporation of spray. At typical ocean salinities and humidities, the smaller aerosol particles will equilibrate with the ambient humidity to a brine particle of approximately half the original radius, typically excluding 90% of the moisture and gases originally within the original seawater fragment. At ocean salinities but low humidities, a dry particle stripped of moisture and gases can result. For lower salinity waters (e.g. Great Lakes [16]) only tiny dry aerosol will remain. In analogy to a bubble that completely dissolves, if only a dry fragment remains then there is no exchange, only ejection. There is an interesting feature for reactive gases that if internal processes allow conversion to the simple dissolved gas, then all the non-volatile forms can also be ejected.

Category 7 applies specifically to soluble gases. The dynamics of transfer is simple in this case, as internal mixing is generally sufficiently effective that loss of water vapor and the trace gases through diffusion outside the particle is rate limiting. For extremely soluble gases the loss of the gas is slower than the loss of water vapor and it is plausible to end with a brine drop highly supersaturated in the gas, which confuses the simple ideal of Category 7. If an extremely soluble gas is fully ejected, then evaporating spray is a very efficient way to remove these gases from the ocean.

3.1.8. Category 8

Category 8 refers to the ejection from the ocean of a poorly soluble gas by evaporating spray. It relates to Category 7 for ejection, as Category 6 relates to Category 5 for exchange. The source of the spray is important as in Category 6, but in this case, there is an ejection process irrespective of the source. If the water comes from the absolute surface, then there will be no exchange (Category 6) but there will be an ejection from a shrinking particle (Category 8). If the water comes from deeper, then there will be both exchange and ejection.

3.2. Scaling Formulae

3.2.1. Category 1

Categories 1 and 2 refer to the standard exchange of gases across a surface between a gaseous and liquid reservoir [1,2]. Category 1 applies to the case where exchange is limited by processes in the liquid reservoir, as applies to most gases of interest in the ocean [2].

For unreactive gases, the solubility determines whether Category 1 or Category 2 applies. Reactivity in water can also have an effect [2]. There are numerous definitions of solubility and volatility in the literature and it is important to be clear and consistent in use. For gas exchange, the relative concentration in dimensionless units is most practical. Therefore, we use a dimensionless

Henry's law solubility, H, an abbreviation of H_s^{cc} recommended by IUPAC [17]. Where gases are reactive in water, it is important to distinguish between an intrinsic solubility, H, of the exact species and an effective solubility H_{eff} that includes allied species in the aqueous phase. Reactivity has a complicated effect that depends on the relative value of reaction times and gas diffusion time scales. In the case of carbon dioxide, ignoring reaction is usually adequate, but an important exception arises for spray. For carbon dioxide, we will use H_{eff} if it is likely that all components of the carbonate system are transferred, H otherwise. In seawater, dissolved carbon dioxide is less than 1% of the total concentration of related species; typically, about 0.5% implying $H_{eff}/H = 200$ [18]. In what follows, any effect of reactivity is neglected unless stated.

For Category 1, an equation for the net flux, F_1, can be written:

$$F_1 = K_w\,(C_w - C_a\,H), \tag{1}$$

where C represents concentration, and a subscript of "w" or "a" represents the liquid and gaseous reservoir. A transfer velocity, K_w, is used to describe the efficiency of the exchange and here carries a "w" subscript to emphasize that it depends here on waterside processes. The dependence of K_w and analogous constants on environmental conditions will be summarized in the next subsection. A key thing to note here is that Equation 1 implies proportionality of flux to a difference in concentration on the waterside, and that scaling is recorded in Table 1.

3.2.2. Category 2

Category 2 applies to soluble gases, and the equation for flux can be written:

$$F_2 = K_a\,(C_w/H - C_a), \tag{2}$$

where the dependence in this case on difference in concentration on the airside is apparent. The transfer velocity, K_a, will depend on the airside environment.

3.2.3. Category 3

Category 3 and Category 4 concern bubble-mediated air-sea gas transfer [4,12]. Both categories are only significant to poorly soluble gases and are relatively ineffective for a few of those. Category 3 is closely analogous to Category 1 direct air-sea exchange of gases, and we can write a similar equation for the flux, F_3, associated with this pathway:

$$F_3 = K_b\,(C_w - C_a\,H), \tag{3}$$

where we introduce another waterside transfer velocity, K_b, to represent the efficiency of this pathway. Category 3 differs from Category 1 in the dependence of this transfer velocity on solubility. The partial pressure of each within a bubble and the concentration at its surface will change through exchange with the surrounding water and this will occur quicker for more soluble gases. As a result, the pathway is less effective for soluble gases and the sensitivity is complex, not simply proportional to the original waterside gradient. The complexity will be explained in the next subsection where we consider the area and volume of bubbles in the upper ocean. This category is similar to Categories 1 and 2 in being driven by an effective difference in concentration.

3.2.4. Category 4

Category 4 relates to the injection of a gas into the ocean by a shrinking bubble. It may be understood most easily for the total dissolution of a bubble, where it is apparent that a part of the atmosphere has been transferred to the ocean, with a scaling to the absolute airside concentration and independent of the waterside concentration. (There is a complication for nitrogen and oxygen since their waterside concentration affects the evolution of each bubble). The more common case of a bubble surfacing with a smaller volume than its initial volume is less obvious, but it is practical to calculate a transfer that would occur with only a change of bubble volume and no change in partial pressure and define that as the Category 4 transfer. The scaling of the injection flux, F_4, follows simply from the insight that there is proportionality both to the change in volume (at sea level pressure) and the concentration in the atmosphere:

$$F_4 = - \Delta V\, C_a, \tag{4}$$

where ΔV is the loss in volume and the sign is consistent with a flow from water to air being positive. The scaling is distinct from Category 1 and Category 3, with a proportionality to absolute airside concentration. The scaling implies that relative to Categories 1 and 3, Category 4 is most important for the least soluble gases. The scaling also implies that where atmosphere and ocean are very close to equilibrium and net fluxes in Categories 3 and 4 are small, a substantial injection flux is maintained by Category 4 and may exceed the exchange fluxes.

3.2.5. Category 5

Categories 5 – 8 concern spray-mediated fluxes whose scaling is relatively unexplored, though there are some interesting models and observations. The research here places spray-mediated transfer in the context of the more frequently studied fluxes and may form a base for more detailed study. We begin with considering spray as a pathway for exchange, in analogy to Category 3 of bubble-mediated exchange; and conclude with considering spray as a pathway for ejection from the ocean, in analogy to Category 4 for injection by bubbles.

One challenge is to model the transfer between each particle and the surrounding air. The fundamentals of this modelling have been laid by Andreas and collaborators [19,7]. A few time scales emerge for processes within, at the surface, and outside the drop. Over the full range of gas solubilities, the situation is complicated. For soluble gases, the crossing of an airside boundary layer outside of the particle is limiting, in a mixed analogy to the direct transfer of soluble gases (Category 2) and the bubble-mediated transfer of poorly soluble gases (Category 3).

Category 5 for exchange of soluble gases mediated by spray is analogous to the exchange of poorly soluble gases mediated by bubbles, but it is more complicated. The simple part is writing a basic flux equation for this category, which is very similar to the equation for Category 2, the direct exchange of soluble gases across an airside boundary layer:

$$F_5 = K_s\, (C_w / H – C_a), \tag{5}$$

where K_s is a transfer velocity for spray-mediated exchange. It is apparent that there is a scaling to the difference in concentration across the main airside boundary layer. However, there is a caveat to even this simple equation; it is not clear that the concentration far outside a spray particle will be simply “C_a”, the concentration beyond the airside boundary layer, since the spray may be within the boundary layer. (The COARE model [10,20] defines a thin diffusive sublayer and a thicker, turbulent sublayer, each significantly influencing gas transfer).

Just as the concentration just outside a bubble will converge on that far outside, the same will occur for gases in a particle; with the same effect of suppressing further net transfer. The effect of this is to reduce the effectiveness of Category 5 for the less soluble gases and smaller particles and introduce a complex scaling as recorded in Table 1. Setting aside the complications above, the most important question is whether spray provides sufficient additional surface area, relative to the sea surface, since this is a necessary though not sufficient condition for a substantial effect. That will be considered in a later section from knowledge of air-sea spray fluxes.

3.2.6. Category 6

Category 6 is the process by which an exchange of poorly soluble gases is achieved through spray-mediated transfer. Physically, Category 6 differs from Category 5 only by the additional requirement for a poorly soluble gas that spray is torn from below the surface. If we accept that it occurs then Equation 5 applies again, but it is useful to rewrite it to ease comparison to the exchange of poorly soluble gases directly and by bubble-mediated transfer:

$$F_6 = K_s / H\ (C_w - C_a\ H), \tag{6}$$

where the definition of K_5 is retained from Equation 5. It is apparent that a contribution K_s/H to the transfer velocity of poorly soluble gases is implied, additional to the direct and bubble-mediated contributions (K_w and K_b). From Equation 6, an inverse proportionality of this transfer velocity to solubility is implied but this is often not correct for two reasons. Firstly, among poorly soluble gases it is likely that internal processes within the particle limit the rate of exchange reducing the magnitude and dependencies of K_5. Secondly, concentration will change for the less soluble gases and smaller particles as the particle approaches equilibrium with the distant atmosphere. Sufficient solubility (or reactivity) can provide sufficient capacity to maintain a steady concentration in the particle. Note that for carbon dioxide, the timescale of convergence may be set by the total concentration of carbonate species if the internal timescales of the carbonate system are shorter. As for Category 7, the scaling is described as “complex” and “difference”.

3.2.7. Categories 7 and 8

Category 7 and Category 8 depend on water fragments losing capacity as they evaporate. The same formulae apply for both, apart from some complication from the sourcing of the spray from the sea surface. There is a parallel to shrinking bubbles, but with complications for sea spray, since the changes in temperature and salinity of an evaporating brine particle are important to the dynamics of both evaporation [19] and gas solubility [8]. The effect of changes in temperature and salinity on solubility will be discussed later, but in this subsection, formulae for a constant solubility in a shrinking liquid particle will be presented. For both categories, the primary effect should be captured by considering the loss of a gas implied by a reduced volume at a fixed concentration and the effect can be written as:

$$F_7 = F_8 = \Delta V_s\ C_w, \tag{7}$$

where ΔV_s is a loss in volume of spray through evaporation. Noting that in this case, C_w may refer to the total concentration of related species, and the scaling suggests Category 7 is an indefinitely increasing contribution to the transfer of soluble gases as solubility rises and will be enhanced for a gas with rapid, reversible reactions. Scaling for both categories is to “water” and “absolute”.

There is a complication for poorly soluble gases since if the material in the spray is drawn from very near the surface it will carry a concentration $C_w' = C_a\ H_{eff}$ rather than simply C_w and Equation 7 is modified to:

$$F_8 = \Delta V_s\ C_w', \tag{8}$$

and intermediate values may apply depending on the source material. In any case, there is an ejection.

It may be noticed that if water is lost from the upper ocean by evaporation of drops as described, the concentration of the gases in the upper ocean is unchanged. Nevertheless, there is an ejection and an upward flux. If the water budget is balanced by gas-free fresh water, then an undersaturation of the gas results in total.

3.3. Quantification

3.3.1. Popular Parameterizations for Poorly Soluble Gases

The calculation of air-sea fluxes of poorly soluble gases is a major scientific activity that usually requires a description of the transfer velocity, K_w, as part of the calculation implied by Equation 1. Most calculations simply assume control by a waterside boundary layer and neglect the additional relevant processes relevant to poorly soluble gases that we have identified (categories 3, 4, 6 and 8). Calculations can also contain error; for example relating to the handling of temperature [21]. At the same time, K_w is typically sourced for Equation 1 through a parametrization of K_w based on a limited number of gas flux experiments. In those experiments, K_w is determined through Equation 1. The parametrization derives from those experimental values together with theory, such as an assumed dependence on the properties of the dissolved gas (e.g. molecular diffusivity) and environmental conditions (e.g. an assumption that wind speed is an adequate predictor without reference to sea state). Inevitably, these experiments are affected by the other processes such that a measured or calculated flux is often ambiguous and not simply the direct flux across the waterside boundary layer. Though we should accept the limitation of existing parametrizations of K_w, they do provide a useful reference to evaluate the likely significance of transfer by categories 3, 4, 6, and 8.

Most historical parametrizations are based on experiments with trace gases of relatively little direct interest, notably a pairing of helium and sulfur hexafluoride [22,23]. Other parametrizations are directly for a gas of actual interest, for example, dimethyl sulfide or carbon dioxide. The different approaches now provide a reasonably consistent view of how the transfer velocity of carbon dioxide varies with wind speed. While parametrizations vary and there is evidence of other factors such as sea state [24], a quadratic expression [25] gives useful reference values to compare to quantitative estimates by various mechanisms (and within categories):

$$K_w = 0.251 <U^2> (Sc_w/660)^{-0.5}, \quad (9)$$

where K_w is the transfer velocity in cm/h, $<U^2>$ is averaged square wind speed and Sc_w is the Schmidt number in water. For example, the formula implies a transfer velocity of ~25 cm/h at 10 m/s wind speed, which can be a starting point for assessing the significance of bubble-mediated and spray-mediated mechanisms in moderate-to-strong winds.

Among other estimates of transfer velocity, another that is useful for distinguishing between the various mechanisms for poorly soluble gases are various measurements for dimethyl sulfide, a few coincident to those for carbon dioxide [13]. There are a number of fits to the DMS data, but they all represent a more linear relationship to wind speed than Equation 9 and are typified by [26]:

$$K_w\,[DMS] = (2.1\,U - 2.8)\,(Sc_w/660)^{-0.5}, \quad (10)$$

which implies a linear relationship of transfer velocity to wind speed. Dimethyl sulfide is one of the most soluble gases classified as poorly soluble and less likely than less soluble gases to be transferred through bubbles. Therefore, a common interpretation [26] of the empirical relationships represented by Equations 9 and 10 is that Category 1 transfer is linear in wind speed in moderate and strong winds and the non-linearity observed for carbon dioxide and helium is a result of a Category 3 bubble-mediated contribution to wind speed. From Equations 9 and 10, it can be provisionally inferred that bubble-mediated transfer contributes 5cm/h or more to the transfer velocity at wind speeds of 10m/s, rising rapidly at higher wind speeds. A study of concurrent transfer velocities [13] suggests a stronger bubble-mediated effect. There is a strong inference that Category 1 transfer is insufficient to fully explain observed carbon dioxide fluxes, but assigning the excess to any specific mechanism is less certain.

3.3.2. Parametrizations for Soluble Gases

Apart from water vapor, which should be treated as a special case [27], there are relatively few measurements of soluble “gas phase controlled” gases, on which to base parametrization of K_a for soluble gases [28]. Fortunately, improved methods have yielded measurements for gases predominantly controlled on the airside [29]. Since an airside influence is also evident, especially for acetone, there is an experimental validation of the two-layer model within a single study with realistic if imprecise values of over a range of wind speeds.

As for K_w in the previous subsubsection, an experimental determination of K_a may often be interpreted as measuring direct transfer (Category 2 in this case) but might also evidence other categories of transfer; for example, through an unexpected non-linearity in wind speed, or exceptional transfer in special conditions. The published measurements for methanol [] are sufficient to infer an approximate relationship for Category 2 transfer:

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$$K_a \sim 300\ U, \tag{11}$$

where the transfer velocity is in cm/h and wind speed in m/s. There should be a sensitivity to the Schmidt number in air, Sc_a; however different models suggest various relationships to molecular diffusional resistance and turbulent resistance [20,28] and no attempt is made here to generalize the expression for methanol ($Sc_a = 1.09$). The relationship is only approximate but at a minimum it gives reference values for Category 2 transfer. Models [20] imply that transfer should rise slightly faster than linear in wind speed, while the measurements of methanol suggest some suppression at high wind speeds. That comparison argues against a spray-mediated enhancement of exchange (Category 5) but could be consistent with evaporating spray ejecting gases (Category 7) since the total flux was downward, if the spray flux was sufficient, but on a first analysis this seems unlikely [30].

3.3.3. Quantification of Bubble Fluxes

The importance of bubble-mediated gas fluxes depends on the number and characteristics of bubbles. A detailed prediction of the gas fluxes from the characteristics of a bubble distribution requires numerical simulation [14] but some useful constraints follow from relatively simple characteristics [12] as follows.

For exchange by bubbles (Category 3), the net transfer can be constrained by both an “area” and “volume” parameter. If the original air-water concentration difference is maintained, then the gas transfer rate depends on an integration of transfer velocities over the surface of all bubbles. If we define “j” as an average “individual bubble transfer velocity” then:

$$K_b < j\ A_b, \tag{12}$$

where K_b is the contribution of bubble-mediated exchange to the transfer velocity, and A_b is the average surface area of subsurface bubbles over a suitable period. In the ocean for bubble clouds produced by breaking waves, small bubbles of the order of one meter deep contribute a large part of A_b. Measurement of these bubbles by acoustic methods is practical and inversions of field acoustic data suggest that bubble area will rise steeply with wind speed, equaling sea surface area for wind speeds ~15 m/s [31]. Combining this with standard expressions for j, the observations suggest a substantial contribution of K_b to K_w for wind speeds of 10 m/s and greater. However, there is evidence [32,33] that bubbles can be stabilized, lowering the value of j.

Note also that Equation 12 is an inequality, since if the concentration difference outside of a bubble reduces then the contribution of a bubble to exchange is reduced. Another inequality can be written by calculating the value of K_b if every bubble entering the water has equilibrated with the upper ocean before surfacing:

$$K_b < V_b / H, \tag{13}$$

where V_b is the rate at which air is flushed through the surface ocean, a volume per unit time. Note the sensitivity to solubility in Equation 13; this inequality is most relevant to the more soluble among the poorly soluble gases, such as carbon dioxide and dimethyl sulfide. Most of the flushing in the ocean is through depths of ~0.1 m which makes measurement of the relevant bubbles difficult. Also, estimating the “volume rate” is harder than measuring the volume of suspended bubbles and requires numerical simulation [5,14]. Note also that the bubbles flushed through the near surface within a few seconds are less likely to be stabilized than bubbles residing for several minutes, such that “j” in Equation 12 is likely to be close to theoretical values [5,12]. To date, evidence does support a sufficient volume flux and suspended area to support substantial values of K_b for most poorly soluble gases including carbon dioxide [5], but field data is scant and further understanding of processes such as stabilization are required.

For Category 4, as defined by Equation 4, we expect an injection of gas that is related to the loss of volume of the bubbles. Note the inverse relationship to solubility. It is useful to stratify data on the evolution of bubbles by depth of penetration. A very small volume flux of small bubbles penetrating deep into the upper ocean will lose a large fraction of their volume (some dissolving entirely) and though the volume flux is small, Equation 4 implies the injection rate for very low solubilities will be high. A larger volume flux sweeping rapidly through the near surface will lose a smaller fraction of its volume, but the volume lost may be greater than for the deep bubbles. Early research [4,34] focused on the smaller bubbles and suggested a substantial injection of very poorly soluble gases, supporting an asymmetry in air-sea gas exchange and sustained supersaturations. Those studies also implied that the injection process was largely irrelevant to carbon dioxide. However, when the larger bubbles sweeping through the near surface are simulated [5], the results imply a substantial asymmetry for carbon dioxide.

3.3.4. Quantification of Spray-Mediated Fluxes

Most of the preceding material is unoriginal and is largely included to explain the challenge presented in estimating spray-mediated fluxes. Less is known about spray compared to bubbles and on investigating the necessary steps to simulate the resulting gas fluxes, it is apparent that this is a more challenging undertaking than for bubble-mediated fluxes. Some recent results suggest a significant effect [35] and theoretical studies [19,7,8] have made a good start to providing an explanation. This study has tried to set a sound foundation for future progress and in this subsubsection, quantification is begun.

Quantification of air-sea spray-mediated gas fluxes may be achieved by estimating the sea spray source function and simulating the dispersion and evolution of the spray in the lower atmosphere. Necessarily, any quantification depends on the choice of sea spray generation function. The source functions of both the spray produced by bursting bubbles and the spume generated by direct tearing of the sea surface by strong winds are relevant. Both source functions are uncertain. A full model should also capture both the processes of transfer for water vapor and gas between individual particles and the atmosphere and the chemical response of a dissolved gas within a brine particle to heat exchange and the loss of moisture. Even if chemistry such as the changing solubility of the gas is neglected, as in 3.2.5-3.2.7, modelling of sea spray effects is quite daunting. Other applications of interest include water masses of very low salinity, e.g. Great Lakes [16]. Freshwater lakes present a different but interesting problem, especially for ejection of gases, since the remnant aerosol is smaller and chemically different from brine particles and ejection is likely to be total.

As explained already, a strong distinction should be made between exchange and injection or ejection; while noting that an enhancement or suppression of exchange may be reported using standard analyses, when in fact the explanation may be bubble-mediated injection or spray-mediated ejection.

Spray-mediated exchange as defined for Category 5 and Category 6 is quite analogous to the bubble-mediated exchange (Category 3). One important similarity is that in both gases the enhancement of exchange velocity can be limited by the suspended area or the volume flux of bubbles or spray. Therefore, we can usefully identify the analogies of Equations 12 and 13 as applying to spray:

$$K_s < j_s \, A_s, \tag{14}$$

where the contribution of spray to the airside transfer velocity, K_s, is limited by the total surface area of the suspended particles, A_s, and

$$K_s < V_s \, H_{eff}, \tag{15}$$

Implying a limit from the volume flux of spray cycled through the lower atmosphere. Note that the implied limits on contribution to a waterside transfer velocity are K_s/H as described in Equation 6, or $< j_s A_s/H$ and $< V_s$.

The ejection flux has been described in Equations 7 and 8 and can be translated to a geophysical flux by defining ΔV_s as the rate of volume loss from spray per unit sea surface area as it is cycled through the lower atmosphere. That loss is closely related to the direct contribution of spray to

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evaporation rates and latent heat fluxes. For a reactive gas, the ejection will include all soluble forms, not just the dissolved gas itself. That raises the efficiency of the ejection mechanism by a factor H_{eff}/H.

In the next subsubsections, evaporative fluxes and the sea spray source function provide constraints on the contributions of sea spray to air-sea gas exchange and ejection.

3.3.5. Constraint by Evaporative Fluxes

Evaporation and air-sea heat fluxes at the sea surface are important and well-studied parts of the earth system, therefore it is sensible to use them as firm constraints on estimates of gas exchange, and especially, gas ejection. There are complications, notably relating to the distinction between the latent heat and sensible heat directly lost from drops and the change in these air-sea heat fluxes arising from spray, which are summarized now.

A conceptual view of moisture and heat fluxes [27] describes air-sea heat fluxes above a "droplet evaporation layer" as resulting both from fluxes at the sea surface and transfers of moisture, latent heat and sensible heat between spray particles and their immediate surrounding. Since spray is interacting with the atmosphere anywhere within the "layer", the humidity and temperature profiles are more complicated than simply the result of a surface flux and ordinary boundary layer dynamics; instead, the profiles will be distorted by transfers to and from the spray. As a result, it is not possible to interpret measured total heat fluxes and evaporation rates as the sum of a direct flux that is roughly linear in wind speed and a more non-linear contribution mediated by spray [27]. However, we can reasonably assume that both in general and specific cases, the measured evaporation must exceed the moisture loss from the spray, and this constrains ΔV_s.

The loss of water from the global ocean is estimated as 4.13×10^5 km^3/yr [36] or approximately 1.31×10^7 m^3/s. Averaged over the surface of the ocean, an average of ~3.6×10^{-8} m/s (0.013 cm/h) is implied. This value can be compared to approximate values of K_w (25 cm/h) and K_a (3000 cm/h) at a wind speed of 10 m/s as described earlier. By reference to Equations 7 and 8, and the text of the previous subsubsection, it is evident that near-average evaporation cannot generally support ejection fluxes that are substantial relative to standard net transfer of gases. One exception is if the gas is very close to saturation, since then the absolute ejection of material may be significant relative to the net flux driven by disequilibrium [8]. A second exception is for the ejection of a very soluble gas since the ejection rate is proportional to solubility. A third exception is if the gas is reactive such that its concentration in all dissolved forms exceeds its concentration as a simple dissolved volatile. The third exception is relevant to carbon dioxide, since an evaporating drop should eject all species of the dissolved carbonate system, not just the part that was dissolved carbon dioxide at generation.

The general principles described above can be applied to specific studies of air-sea gas fluxes. A 9-year coastal study [35] provides a large carefully analyzed data set of carbon dioxide fluxes with a reported influence of evaporation. The original analysis was centered on a standard calculation of transfer velocity as implied by Equation 1, with anomalies in that calculated transfer identified with specific conditions. The analysis in this paper implies that an influence of evaporation should be interpreted as low humidity promoting evaporation of spray and ejecting all parts of the carbonate system from the drying particles. The main factors producing anomalies are ambiguous as many factors covary seasonally at the site (stronger winds, higher waves and cold dry air are all more likely in the winter). However, the original study is qualitatively consistent with evaporation driving ejection as it identifies positive anomalies of calculated transfer velocity with fairly low relative humidity, high enthalpy flux, a moderate supersaturation of carbon dioxide, high significant wave heights and strong winds; all of which are consistent with spray generation and a relatively large contribution from evaporation of the spray. The sign and strength of supersaturation is highly significant as follows:

- When the water is supersaturated, a high ejection rate will be interpreted as a positive anomaly in transfer velocity;
- When the water is undersaturated, a high ejection rate will be interpreted as a negative anomaly in transfer velocity;

- Ejection rates are proportional to the absolute concentration, while the direct flux is proportional to the difference in concentration, implying a relatively large effect of ejection on calculated transfer velocity for near-saturation conditions.

The third point above implies that it is unfortunate that the original analysis method excluded data where the partial pressure difference was <50 µatm (<12.5% for 400 µatm partial pressure in the atmosphere) since the effect of ejection on net flux may be most evident near equilibrium. However, it also explains why the largest positive anomalies were found for supersaturations of 50-100 µatm. The original study reported fairly similar average transfer velocities including an average value of ~25 cm/h at a wind speed of 10m/s, but with positive and negative anomalies of ~25 cm/h at moderate-to-high wind speeds. The new analysis here focusses on calculating the necessary evaporation and latent heat flux necessary to give an anomaly of 25 cm/h at a wind speed of 10 m/s, as a "reality check" on whether this mechanism is a viable explanation for the observations. The calculations of both exchange and ejection use a specific definition of solubility "H_s^{cp}" to calculate concentration, C from partial pressure, p, though this vanishes in the ratio of ejection and exchange unless the effective solubility for spray, $H_{eff,}$ differs from the standard solubility for direct exchange, H:

$$\text{Net Flux (Category 1 Exchange)} = K_w\, H_s^{cp}\, \Delta p, \quad (16)$$

$$\text{Ejection} = p_w\, H_{eff,s}^{cp}\, \Delta V, \quad (17)$$

Implying:

$$\text{Ejection/Exchange} = (p_w/\Delta p)\,(\Delta V/Kw)\,(H_{eff}/H). \quad (18)$$

The final ratio is written as the product of three ratios. In Table 2, the evaporation rate necessary for the ejection to equal the direct exchange (doubling or cancelling the direct flux) is calculated for K_w = 25 cm/h with a constant value of p_a = 400 µatm and various values of p_w and H_{eff}/H. Since the original study also reports enthalpy fluxes, the latent heat flux implied by the evaporation is also calculated using a value for latent heat of vaporization of 2.3 x 10^9 Jm^{-3}.

Table 2. Spray evaporation rate and latent heat flux required for ejection to equal direct exchange[1].

p_w (µatm)	$p_w/\Delta p$	H_{eff}/H	ΔV (cm/h)	ΔV ($x10^{-8}$ m/s)	H_L (Wm^{-2})
600	3	200	0.042	12.4	285
600	3	100	0.083	24.8	570
600	3	1	8.333	2480.2	57044
500	5	200	0.025	7.4	171
500	5	100	0.050	14.9	342
500	5	1	5.000	1488.1	34226
450	9	200	0.014	4.1	95
450	9	100	0.028	8.3	190
450	9	1	2.778	826.7	19015
350	-7	200	0.018	5.3	122
350	-7	100	0.036	10.6	244
350	-7	1	3.571	1062.9	24447
300	-3	200	0.042	12.4	285
300	-3	100	0.083	24.8	570
300	-3	1	8.333	2480.2	57044
200	-1	200	0.125	37.2	856
200	-1	100	0.250	74.4	1711
200	-1	1	25.000	7440.5	171131

[1] For a poorly soluble gas at a nominal wind speed of 10m/s and transfer velocity of 25 cm/h.

The values in Table 2 should be considered in the context of global evaporation rates (averaging ~3.6 x 10^{-8} m/s or 0.013 cm/h) and latent heat fluxes (order of 100 Wm^{-2}) and the local conditions of the original study [35]. Partial pressure values of 200 μatm and 600 μatm were quite typical for summer and winter conditions respectively, though values nearer equilibrium were also fairly common. Most estimates of enthalpy flux were less than 100 Wm^{-2} and never exceeded 200 Wm^{-2}. None of the inferred values of evaporation rate or latent heat flux for H_{eff} = H are remotely plausible. For a poorly soluble and unreactive gas comparable ejection and net exchange are only plausible within order of 0.1% of saturation. Ejection is a plausible explanation for the large anomalies in calculated K_w for H_{eff}/H = 200 and within 25% of equilibrium, and marginally plausible for either H_{eff}/H = 100 or further from equilibrium. However, the plausibility carries the requirement that a large fraction of the evaporation and enthalpy flux is associated with spray.

For soluble gases, a substantial contribution of ejection by spray requires the contribution to flux, $F_7 = \Delta V_s C_w$, to be comparable to the net exchange with a K_a of order of 3000 cm/h (at a wind speed of 10m/s). On one hand, since $K_a/K_w > 100$ a factor ~100 greater ejection is required for a soluble gas. On the other hand, the ejection flux scales with solubility. It is inferred that if $H_{eff}/H > 100$ is necessary for a poorly soluble, then $H_{eff} > 10^4$ is necessary for a soluble gas (H_{eff} = H for a soluble but unreactive gas). The proportionality to solubility implies that the ejection must eventually be dominant at the highest solubilities.

3.3.6. Constraint by Sea Spray Generation Fluxes

Sea spray generation functions (SSGFs) describe the size-dependent generation of spray at the sea surface []. The smaller spray particles (< 20 μm initial radius, representing a true aerosol) are mostly associated with bubbles bursting at the sea surface and the production of jet drops and film drops, with jet drops dominating for an original radius > 4 μm. Larger film drops and jet drops will be produced with substantial numbers up to 500 μm initial radius [37]. Other large spray droplets (spume) are associated with a direct "tearing" of material from the sea surface [38]. One challenge is that it can be difficult to interpret measured droplets of 10-100 μm as specifically spume or bubble-related, since while a rapid rise in numbers is associated with wind speeds above 8-10m/s as spume drop generation initiates [19] that might also be interpreted as increased suspension of larger jet drops as turbulence increases. Terminal fall velocities imply particles with radii up to 8-10 μm will likely remain airborne for minutes or more, while turbulence associated with a moderate-to-high wind speed may extend the range of suspended particles up to ~40 μm radius [19].

A SSGF defines generation in terms of a flux (rate of emission) per unit radius, df/dr, which has a complex and uncertain shape, but over a very large range of initial radius, 0.1 μm – 1mm, the coarse feature is ~ r^{-n} where n mostly varies between 1 and 2. That shape implies how number, surface area and volume flux are distributed across the size range. The number, surface area and volume suspended is very sensitive also to the suspension time, which will be far greater for the smaller particles.

The smaller particles (aerosol) dominate numbers and will typically be aloft long enough to equilibrate to the surrounding humidity. The smallest particles will also dominate surface area, but their volume flux will limit the associated gas exchange. For a typical relative humidity of 80%, the equilibrium radius, r_{80}, at oceanic salinities is approximately half the original ocean and approximately 90% of the original water and capacity for dissolved gases is lost (the latter varies by gas according to the effect of salinity and temperature on the solubility). For these conditions, the ejection of most gases should parallel the loss of water (as implicit in the definition of Categories 7 and 8). However, for extremely soluble gases it is possible that a very gas-rich brine particle could remain long after the equilibrium size is reached, since the time scale for the gas equilibration exceeds that for water vapor at the highest solubilities. For lower humidities where the particle effectively dries out, the total ejection of gas is certain unless it is reactive on the dry remnant.

Volume flux at the sea surface is skewed to large particles. Large particles (drops) – whether produced by bursting bubbles or by tearing (spume) – are not a true aerosol and may soon fall back to the sea surface. Spume is mostly associated with very strong wind speeds as the threshold for tearing is high, though generation at moderate-to-high wind speeds is possible especially from very steep waves. At sufficiently high wind speeds (far beyond any threshold for a generation mechanism), the same energetic arguments apply to all types of generation and imply a cubic dependence on wind speed. However, many drops will not remain aloft long enough to shrink far. Therefore, it is difficult to relate a volume flux at generation to the rate of evaporation and gas ejection for larger drops. A higher fraction of drops will remain aloft in the highly turbulent conditions of very strong winds. Substantial contributions to total evaporation and enthalpy flux are generally predicted only for extreme conditions such as tropical cyclones [27,38], and not widely proposed for moderate-to-strong winds.

SSGFs have converged slightly over the decades and a physical understanding of the jet and film drop production has advanced [37] but there remains a very large uncertainty for both the aerosol and the larger drops [38–40], up to about a factor of ten in each case. Meanwhile, there is also an uncertainty of suspension in the range of r_{80} from 8-100 μm and a sensitivity of suspension to humidity. The evaporation of sea spray is non-linear in humidity with the time scale of radius equilibration reducing with increasing humidity [19] at the same time the equilibrium radius reduces. It is very unlikely that a drop of initial radius 100 μm will equilibrate at high humidities before falling back to the surface, but at low humidities where it rapidly dries to 25 μm radius, the likelihood is far greater.

Estimates of the mass or volume flux of particles with r_{80} below a threshold vary between models and strongly with the threshold value [37,39]. Values of volume flux can be calculated from published models of df/dr, or estimated global values [39,40]. For example, various values of the “global dry SSA mass production”, expressed as $G \times 10^{12}$ kg yr^{-1} can be used to estimate a volume flux at emission for a wind speed of 10 m/s of $V = 5 \times 10^{-11}$ G m/s. (It is assumed that the emission at a wind speed of 10 m/s will be a factor of three greater than the global average, the dry density of salt is 1.22×10^{3} kg m^{-3}, the original radius is a factor of 4 greater than the dry diameter). Values for a maximum r_{80} of 8-10 μm imply values of V and ΔV of 1-5 $\times 10^{-10}$ m/s, while a relative outlier value of G = 118 [41] for a maximum r_{80} of 41 μm implies $V = 0.6 \times 10^{-8}$ m/s, which is an order of magnitude less than the lower values of ΔV in Table 2. It is apparent that relatively high values of SSGF are necessary to support an ejection hypothesis for large anomalies in carbon dioxide at moderate-to-high wind speeds.

4. Discussion

Four categories have been identified in total for direct and bubble-mediated transfer, but this discussion only considers them to provide context for the spray-mediated categories.

Four categories of spray-mediated transfer have been identified, all of which are worthy of study but not equally. The potential for the suspension and evaporation of large drops to contribute substantially to the air-sea transfer of a few unreactive and poorly soluble gases in very strong winds has been described by other authors [8]. The present study is an investigation of whether and how spray-mediated transfer can ever be important in moderate-to-high winds. The strongest motivations arise from field measurements where the ocean appears to be a source of a highly soluble gas even though that gas is under-saturated in the upper ocean [42], and where strong evaporation is associated with large anomalies in the calculated transfer velocity of carbon dioxide [35].

The categorization is useful to focus on some key characteristics. One distinction is between soluble and poorly soluble gases, as defined by the controlling phase for direct transfer. A complication for poorly soluble gases is that the mechanism differs if the original material in the spray is drawn from beneath the waterside boundary layer, but in practice that is only unlikely for film drops [7] (p.14). A more important point is that any spray-mediated transfer needs to be compared to that expected from direct transfer, which differs for the two sets. The second distinction is between “exchange” and “ejection”. Ejection needs to be identified as such, since traditional calculations of transfer velocity obscure the nature of both bubble-mediated (exchange plus injection) and spray-mediated (exchange and ejection) transfer and may lead to poor extrapolation to regional and global fluxes. Bubble-mediated exchange and injection are of comparable significance [5,13]. Empirical evidence and the characteristics and scaling of spray-mediated transfer suggest that ejection is more important than exchange for spray-mediated transfer, as argued below.

Exchange can be limited both by the finite surface area of the suspended particles (Equation 14) and by the finite volume flux of material (Equation 15). Both are important constraints that suggest that spray-mediated exchange may be modest. For the areal limitation, the values of j_s (effective transfer velocity at the surface of an individual particle) relative to typical values of K_a (~ 3000 cm/h) is also important. In general, calculation of j_s is complicated [7], but for sufficiently soluble gases, diffusion outside the particle is limiting, implying $j_s \cong D'/r$ where D_a' is a "modified" molecular diffusivity in air (typically 1-2 x 10^{-5} m^2/s) and r is the instantaneous radius, implying very large values of j_s for small values of r. For most particle sizes and gases of interest, the limit by surface area and j_s is relatively unimportant and the limit by volume flux is more meaningful. Comparing the limit on exchange by volume flux to the dependence of ejection on lost volume, in near saturation conditions ejection will be far greater than near exchange. Noting the values of $p_w/ \Delta p$ in Table 2, and that typically $\Delta V/V$ ~ 0.9, ejection will exceed net exchange even where a dissolved gas is far from saturation. For poorly soluble gases, there is also the requirement to tear material from beyond the waterside mass boundary layer but the argument [7] (p.14) that this only negates the effect of film drops is convincing. Exchange mechanisms deserve more attention but seem less important than ejection mechanisms.

Turning to field measurements of carbon dioxide fluxes, the values in Table 2 should be considered in the context of global evaporation rates (averaging ~3.6 x 10^{-8} m/s or 0.013 cm/h) and latent heat fluxes (order of 100 Wm^{-2}) and the local conditions of the original study [35]. Partial pressure values of 200 μatm and 600 μatm were quite typical for summer and winter conditions respectively, though values nearer equilibrium were also fairly common. Most estimates of enthalpy flux were less than 100 Wm^{-2} and never exceeded 200 Wm^{-2}. None of the inferred values of evaporation rate or latent heat flux for H_{eff} = H are remotely plausible. For a poorly soluble and unreactive gas, comparable ejection and net exchange are only plausible within order of 0.1% of saturation. Ejection is a plausible explanation for the large anomalies in calculated K_w for $H_{eff}/H = 200$ and within 25% of equilibrium, and marginally plausible for either $H_{eff}/H = 100$ or further from equilibrium. However, the plausibility carries the requirement that a large fraction of the evaporation and enthalpy flux is associated with spray.

For soluble gases, a substantial contribution of ejection by spray requires the contribution to flux, $F_7 = \Delta V_s C_w$, to be comparable to the net exchange with a K_a of order of 3000 cm/h (at a wind speed of 10m/s). On one hand, since $K_a/K_w > 100$ a factor ~100 greater ejection is required for a soluble gas. On the other hand, the ejection flux scales with solubility. It is inferred that if $H_{eff}/H > 100$ is necessary for a poorly soluble, then $H_{eff} > 10^4$ is necessary for a soluble gas (H_{eff} = H for a soluble but unreactive gas). The proportionality to solubility implies that the ejection must eventually be dominant at the highest solubilities.

It is tempting to conclude from the analysis of reported anomalies in the transfer velocity of carbon dioxide that spray-mediated ejection must be an important mechanism even at moderate-to high wind speeds for carbon dioxide and by inference also for highly soluble gases. However, that conclusion seems far more doubtful if the best available estimates of the generation of small droplets is considered [37,39]. The mass flux of the true primary marine aerosol (particles that will commonly be suspended for at least several minutes at typical ocean RH of 80%) is insufficient to support a substantial effect except for extremely soluble gases. Values of the production and suspension of rather larger particles can be stretched to give a plausible explanation for a substantial effect, but not with much confidence. The effect has a non-linear response to humidity, since if droplets shrink rapidly to a near-dry size, they may plausibly be suspended long enough to eject all gas, thereby enhancing the ejection effect. It is quite likely that substantial spray-mediated transfer, except for extreme winds speeds or extremely soluble gases, may occur only for relatively low humidities, such as those common where dry continental air reaches coastal seas. However, it cannot be ruled out yet as a more common occurrence and even as a coastal phenomenon it would be globally important. Lakes should also be considered as an important case, where total evaporation of low salinity drops may be typical.

The enhancement of spray-mediated transfer through reactivity requires more investigation. A preliminary assessment suggests that carbon dioxide in aqueous solution occupies a “sweet spot” where the reaction paths are too slow to enhance the direct transfer but are fast enough to enhance the spray-mediated transfer. Direct transfer of carbon dioxide in the context of carbon dioxide in solution was considered by Bolin [9] and his argument stands up with some more recent refinement of the details and rate constants [43]. The reaction scheme of carbon dioxide in an aqueous system involves numerous reactions and both a “water path” and “hydroxide path” between carbon dioxide and bicarbonate (the dominant species in the ocean). At oceanic pH, the hydration path is more important and a rate constant for this path, or better a composite for both paths, can be inverted to a hydration timescale for carbon dioxide, which defines how quickly carbon dioxide concentrations can respond to change though reaction (though in ejection the process is dehydration, the dehydration timescale for carbonic acid is not appropriate for carbon dioxide). The hydration rate is sensitive to temperature and varies from less than 30 seconds in warm seawater to minutes in cold. This time scale needs to be compared to another relevant time scale. For direct transfer, the relevant “other” is the time scale for gas to diffuse across a mass boundary layer and is order of one second. Therefore, the reactivity of carbon dioxide is not considered effective for direct transfer. For spray-mediated transfer, the relevant “other” is the time of suspension, which will typically be several minutes or more for the relevant particles, and therefore long enough for carbon dioxide to be replaced from the bicarbonate and other species (with some doubt for cold water). There will be many drops that fall back to the sea surface within seconds and there will be little chemical enhancement in this case. In general, an enhancement of spray-mediated carbon dioxide transfer by a factor $H_{eff}/H = 200$ seems reasonable for seawater. Other gases need to be considered on an individual basis, but the “sweet spot” is small, therefore carbon dioxide may be an unusual case.

The empirical evidence of an ejection effect for carbon dioxide is more compelling than for other categories and gases, while carbon dioxide is very important in the earth system. However, it is likely that spray-mediated transfer is more broadly significant. Another intriguing observation that motivated this study was that the ocean is a source of urea (an exceptionally soluble gas) though apparently undersaturated in the upper ocean [42], which is qualitatively consistent with ejection on spray drops. On investigation, the observed urea fluxes are much larger than can be explained. However, spray is likely to be important to highly soluble gases and the details should be investigated. The solubility of gases varies over a huge range [44]. For the most soluble gases (including urea), even very small (1 μm radius) particles are significant; firstly, since though their volume flux is very small, a proportionality to concentration in the liquid phase implies an effect growing linearly with solubility; and secondly, the lengthy suspension of these particles ensures full ejection.

The chemistry of gases in aqueous solution is of interest. Evolving drops will rapidly reach an equilibrium temperature and then more slowly evolve as they evaporate, shrink and grow more saline. Therefore, a full description of gas dynamics requires the temperature and salinity dependent solubility of the gases, especially as “salting out” of gases is a common phenomenon. Where all coefficients are available, this enables more precise calculations [8], but each gas must be simulated individually. The simpler equations in the current study are incomplete but can be applied generically. Also, since most gas is ejected if a particle shrinks to half or less of its original size, the scale of the effect is captured without including any additional “salting out”.

5. Conclusions

Direct and bubble-mediated transfer are reasonably well understood and can be framed by considering four categories. Four categories of spray-mediated transfer are also identified, with the two for ejection likely to be more important than those for exchange. Spray-mediated transfer could be an important part of air-sea gas transfer in moderate-to-high wind speeds for two cases:

1. Carbon dioxide;
2. Highly soluble gases

Indirect evidence for strong ejection of carbon dioxide in some circumstances is strong, but it is not clear how general the effect might be, and corroboration by a “bottom up" estimate is highly desirable. That estimate through the simulation of evolving spray is currently plagued by very large uncertainties that will require a major effort to reduce adequately. Uncertainties in the emission and suspension of drops of initial radius 10-300 μm need to be reduced, as previously proposed by Andreas for water vapor [19] (p.492) and only partially resolved since. Since both jet drops and spume drops can dominate within this size range, both types of generation need to be addressed. Simulation of the suspension and evolution of the drops in a turbulent lower atmosphere needs attention. Since the evolution and suspension of the drops is highly sensitivity to humidity and the humidity profile responds the interactions with the spray, measurement and modelling here is also necessary. The reaction of carbon dioxide within the aqueous system of a spray droplet is significant to the resulting exchange and ejection. Substantial effects are also expected for highly soluble gases from a similar size range of drops, while smaller aerosol particles have insufficient volume flux to be important for most gases but may be important for extremely soluble gases. A full description of the physical and chemical dynamics of all gases in brine drops is distant. Progress on the various topics described above are necessary for full understanding of the geophysical implications of spray-mediated gas transfer.

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Abbreviations

The following abbreviations are used in this manuscript:

COARE	Coupled Ocean-Atmosphere Response Experiment
IUPAC	International Union of Pure and Applied Chemistry
SSGF	Sea Spray Generation Function

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