

A Rumsfeldian analysis of uncertainty in air–sea gas exchange

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Abstract. The title of this paper alludes to the oft-repeated statement by ex-U.S. Defense Secretary Donald Rumsfeld, considering ‘known knowns’ (Ks), ‘known unknowns’ (KUs) and ‘unknown unknowns’ (UUs); a qualitative analysis which we apply to classify the degree of knowledge about uncertainties in air-sea gas exchange. We have tried to be comprehensive in our analysis, so this paper is broad in scope rather than deep in detail. We present a table summarizing the uncertainties we can identify and their ‘Rumsfeldian classification’ and go on to explain each source of uncertainty listed. We interpret the classifications as follows: a ‘known known’ uncertainty is one which is relatively well constrained, with some process-based understanding of causes and likely magnitude; a ‘known unknown’ is a source of uncertainty whose magnitude can be estimated at least for typical conditions / gases, but where only limited empirical evidence is available to validate magnitude and underlying processes; an ‘unknown unknown’ is an uncertainty for which we have little or no means to quantify the importance or likely magnitude of a process or phenomenon, with limited theoretical and/or little or no empirical evidence. We hope that this paper will provide a useful ‘checklist’ for researchers quantifying gas exchange and that it will aid in prioritizing future research on air-sea gas fluxes.

Key Words: Gas exchange, ocean-atmosphere flux, transfer velocity, uncertainty analysis

1. Introduction

The air-sea flux of a gas can be considered as a diffusion-limited process driven by a Henry’s law solubility-corrected thermodynamic concentration gradient (ΔC); where the kinetics are controlled by a transfer velocity (K). K represents both physical turbulence and the diffusivity of the gas and can be broken down into k_w and k_a , the water-side and air-side transfer velocity terms respectively see Liss and Slater (1974) [henceforth LS74] and Johnson (2010) [Jo10] for derivations and relationships.

We discuss uncertainty here from the point-of-view of the experimentalist or

modeler taking the ‘K.ΔC’ approach to quantifying air-sea gas fluxes (i.e. applying the product of a parameterized transfer velocity term and a concentration gradient calculated from bulk concentrations and Henry’s law solubility). Uncertainties therefore include i) those introduced by applying a particular parameterization or assumption, ii) those from measurements, iii) those caused by not (or not correctly) accounting for a particular process or phenomenon and iv) those due to the averaging and extrapolations necessary to take any point measurement and interpret it in a wider geographical or temporal context. Many of the uncertainties discussed below are not universal; their magnitude may depend on e.g. environmental conditions, or the chemical properties or biological source/sink of the gas in question. Moreover, it is important to consider that many processes may be asymmetrical in some or all cases i.e. their effects may differ for fluxes in and out of the sea. For these reasons we must put the responsibility on the reader for correctly assessing the potential uncertainty in flux estimates for their gases of interest.

2. Summary of uncertainties and their classification

Table 1 presents an overview of the uncertainties in air-sea gas flux, our qualitative analysis of their likely potential magnitudes and the degree of knowledge we have about each one (the Rumsfeldian classification). These come from extensive literature review and discussion on the part of the authors; where no references are given this is because these potential uncertainties have not, to our knowledge, been previously discussed in the literature. We divide the potential sources of uncertainty into 4 groups, based on points i) to iv) in the previous paragraph. Subsequent sections (3 to 6) of the text of this manuscript discuss these groups of uncertainties in turn.

3. Parameterizations, models and assumptions

3.1 *k-u parameterizations*

Initially, parameterizations of transfer velocity from wind speed (u) were theoretical or based on laboratory experiments (e.g. LS74 and references therein), but they have subsequently been validated to first order by wind tunnel (e.g. Liss and Merlivat 1986) and field studies employing various methods (e.g. Wanninkhof 1992 [W92], McGillis *et al.* 2001 [M01], Nightingale *et al.* 2000 [N00]). Modern k_w - u parameterizations can be divided into two groups: (i) those which represent empirical fits through observationally-derived transfer velocity data by global ^{14}C back-calculation (e.g. W92) or multiple-tracer studies (e.g. N00) and (ii) outputs of physically-based numerical models tuned to e.g. eddy covariance field data (e.g.

Table 1 Summary of uncertainty sources in gas flux estimates and qualitative assessment of their likely magnitude (U_{flux}); with soluble and insoluble gases considered separately. ‘Worst case’ is the maximum likely magnitude (medium, M, large, L or very large, XL) in uncertainty when considered over medium to large time and space scales e.g. regionally, seasonally, globally for typical or average gases. Where key references outlining or quantifying the effects mentioned are available these are cited. Grey shaded lines denote key uncertainties (potentially large magnitude combined with low degree of knowledge), which are referred to in Section 7.

Source of Uncertainty	k or ΔC ?	U_{flux} for soluble gases	U_{flux} for insoluble gases	Worst case	Rumfeldian Classification	Notes / key reference(s) where applicable
Parameterizations, models, assumptions						
k_w -u parameterization	K	small	$\pm 50\%$	XL	KK	Asher (2009)
k_a -u parameterization	K	$\pm 50\%$	small	XL	KU	Johnson (2010)
Gas exchange model	K	small		M	KK	Jähne and Hauffecker (1998), Jähne (2009)
Gas and medium properties	both	small		M	KK	Johnson (2010) estimates worst case: $\pm 30\%$
Drag coefficient	K	$\pm 50\%$	small	L	KU	Johnson (2010)
Whitecap coverage	both	small	?	L	KU	Goddijn-Murphy <i>et al.</i> in press., Woolf (2005)
Assume $K_w = k_w$ or $K_a = k_a$	K	zero/small if correct			KK	Liss and Slater (1974)
Concentration in one phase = 0	ΔC	concn. dependent			KK	Liss and Slater (1974)
Measurement Uncertainty						
Concentration measurement	ΔC	gas dependent		M	KK	Measurement/integration period, precision, accuracy.
Eddy covariance measurements	both	gas dependent		L	KK	Prytherch <i>et al.</i> (2010)
Processes and Phenomena						
Bubbles: kinetic effect	K	assumed small		M	KU	Probably small (Woolf <i>et al.</i> 2007)
injection effect	ΔC	small	*	L	KU	Memery and Merlivat (1985), Keeling (1993), Woolf and Thorpe (1994), Asher <i>et al.</i> , (1996), Woolf (1997), Woolf <i>et al.</i> (2007). *see main text
exchange effect	ΔC	small	*	XL	KU	Vlahos <i>et al.</i> (2011), Vlahos and Monahan (2009)
adsorption effect	ΔC	gas dependent		XL	UU	Frew (1997), Lee and Saylor (2010)
Microlayer kinetic inhibition	K	probably small		XL	KU	μ -layer effects may be large where a significantly chemically different surface layer exists. Turner and Liss (1985), Zhang <i>et al.</i> , (2003).
Microlayer enrichment / depletion	ΔC	probably small		L	UU	Johnson <i>et al.</i> , (submitted).
Microlayer solubility	ΔC	probably small		L	UU	Ho <i>et al.</i> (1997), Zappa <i>et al.</i> (2009).
Chemical enhancement	both	gas dependent		XL	KU	Turk <i>et al.</i> (2010)
Rainfall: direct turbulent effect	K	big if raining!		M	KU	Liss <i>et al.</i> , 1981. UU because effect on k_a unknown
Rainfall: indirect effects	ΔC	gas dependent		L	UU	Phillips (1994, 1997); Doney (1994, 1995).
Heat effects: stratification	K	?	small	L	UU	McGillis & Wanninkhof (2006); Takahashi <i>et al.</i> (2009)
Cool skin / warm skin solubility	K	?	small	M	KU	Gladyshev (1997)
Irreversible thermodynamics	ΔC	?	?	L	UU	Upstill-Goddard <i>et al.</i> (2003). *Gas dependent
Biological turbulence	K	zero	small	M	UU	Effect of reduced light on community structure and therefore gas production / consumption
Biological enhancement	both	zero	*	L	UU	
ΔC due to biological response to mixed layer deepening	ΔC	condition and gas dependent		L	UU	
Averaging, interpolation, extrapolation						
Concentration averaging / interpolation / extrapolation	ΔC	variable		XL	KU	Depends on nature of data, conditions observed and geographical range and timescale of study. e.g. Lana <i>et al.</i> (2011)
Wind speed averaging	K	variable		M	KK	Wanninkhof <i>et al.</i> (2009), Naegler <i>et al.</i> (2006)
Temp and salinity averaging	both	small		S*	KK	Wanninkhof <i>et al.</i> (2009). *T and S well constrained.
Steady-state assumptions	ΔC	timescale-dependent		L	UU	e.g. flux changes concentration or mixing causes concentration change with increasing winds.

M01).

There is a wide spread in k_w - u parameterizations, which is colloquially referred to as a ‘factor of 2’ uncertainty [Jo10] (the approximate range of predicted k_w at an ‘average’ wind speed of ~ 7 m/s). Uncertainty is greater at low winds (due to data paucity) and at high winds (where linear, quadratic and cubic parameterizations diverge greatly). Asher (2009) has demonstrated that around 50% of the spread in k_w - u parameterizations is due to experimental uncertainty. It follows that the remainder must stem either from unaccounted-for physical forcings or phenomena that varied between the different studies or from incorrectly parameterized components of gas exchange models. Many of the uncertainties discussed here are components of this uncharacterized uncertainty in k_w - u relationships.

To our knowledge there are no field-based parameterizations of gas phase transfer velocity (k_a) for gases over the ocean, or even lake surfaces. The only empirical parameterization of k_a for gases applicable to natural surfaces is a reliable wind tunnel study extrapolated to open ocean micrometeorological conditions for a range of trace gases (Mackay and Yeun 1983 [MY83]). This demonstrates the magnitude of the Schmidt number dependence and provides empirical first-order validation for the various physically-based models of k_a (e.g. Duce *et al.* 1991, Jeffrey *et al.* 2010 [Je10]), which apply micrometeorological theory originally developed specifically for water vapour transfer. Je10 provide an improved physically-based model, which is in reasonable agreement with MY83. However, k_a is rather sensitive to the air-water drag coefficient (C_D), which relates the wind speed to the friction velocity, u_* . Application of different parameterizations of the C_D - u relationship (to any of the above k_a parameterizations) leads to a maxima in the range of predicted transfer velocities of more than a factor of 3 at around 6 m/s (Johnson 2010).

3.2 Gas exchange model (Schmidt number exponent)

A series of physical models (e.g. rigid boundary, thin film, surface renewal) have been used to describe the molecular and turbulent transfer through the viscous and mass boundary layers, each predicting a different Schmidt number exponent (n) in the transfer velocity equation ($k \propto Sc^{-n}$). It is normally assumed that $n = 1/2$ in most conditions for k_w , but at lower wind speeds (under smooth surface conditions) it could be $2/3$ (Liss and Merlivat 1986, Jähne and Haußecker 1998) although constraining the value of n by experiment presents difficulties (Asher 2009). However, most k_w - u parameterizations are implicitly tuned to $n = 1/2$. For k_a , n is typically of the order of $2/3$. Compared to uncertainty in flux due to the physical forcings to the transfer velocity terms, uncertainty due to n is likely to be relatively small.

3.3 Estimation of physico-chemical gas and medium properties

The Henry's law solubility of a gas is important in determining the magnitude of ΔC and in the relative contribution of k_a and k_w to total transfer (LS74). Solubility is highly sensitive to temperature and somewhat to salinity. Diffusion coefficients (used to calculate Schmidt numbers in air and water) can be calculated from simple molecular data but these are only accurate to within about $\pm 20\%$ (Poling *et al.* 2001). For both solubility and diffusivity, accurate directly measured values in seawater are the ideal. The densities and viscosities of air and water are also required for calculating Schmidt numbers; these are relatively well constrained in their relationships with temperature and salinity. For a gas where solubility data in pure water is available, Jo10 estimates the maximum uncertainty in flux calculation from estimating T and S dependent solubilities and Schmidt numbers to be $\sim \pm 30\%$. For gases where extensive study of physico-chemical properties has been undertaken, uncertainty should be substantially less.

3.4 Common assumptions

Two assumptions are commonly applied to gas exchange calculations, which may be appropriate in some cases or for some gases, but are not universal. Firstly, following the findings of [LS74] that the exchange of the majority of gases they considered was limited by k_w , it is commonly assumed that $K_w \approx k_w$ (i.e. that the entirety of resistance to transfer is in the liquid phase). This assumption is often made for DMS, although the air-side can contribute significantly to the resistance, under some conditions leading to up to 20% estimates of the transfer velocity if it is not considered (McGillis *et al.* 2000), whilst diiodomethane and methylnitrate can both experience 50% contribution to transfer from each side of the interface under typical conditions (Johnson *et al.* submitted). If the same assumption is applied to a gas that is actually air-side controlled, then transfer velocity may be overestimated by a factor of 10 to 100 for soluble gases such as methanol. These uncertainties can be avoided by using the full flux equation with both k_a and k_w e.g. according to Jo10.

Secondly it may be reasonable in some cases to assume that the concentration in one of the phases is zero (i.e. that ΔC is dominated by the other phase). This may be reasonable for e.g. gases such as DMS where production in seawater, relatively low solubility and rapid reaction in the atmosphere lead to a water phase driven concentration gradient. Nonetheless, in making this assumption there is some overestimation of the flux, which may be as much as 5% in global estimates (Turner *et al.* 1996; Turner *et al.* in prep). The same assumption has a much greater effect for NH₃, which occurs at similar concentrations in both phases but has much greater solubility; it may lead to $> 30\%$ overestimation of global marine emissions (based on data in Johnson 2004 and Bouwman *et al.* 1997); and locally

may be much more significant.

4. Measurement uncertainty

4.1 Concentration measurements (for delta-C calculation)

With the appropriate expertise, most gas concentrations can be measured with an analytical precision of a few percent or less. However uncertainties are introduced in e.g. sample collection and storage issues, pressure, humidity and salinity effects, etc. Nonetheless it is reasonable to assume that most bulk concentration measurements should be within $\pm 20\%$ (and much better for high quality measurements of well studied gases such as CO_2). Measuring the concentration at some distance from the interface does not account for sharp concentration gradients approaching the surface due to biological heterogeneity or photochemical production / loss near the surface. Furthermore, in the gas phase, strong humidity gradients might potentially affect partitioning for some species between gas and aerosol phases (e.g. Johnson 2004). Thus there is significant uncertainty in the applicability of measured concentrations in either phase, which we assume here, for simplicity, is part of the related uncertainties associated with enrichment in the sea-surface microlayer (Section 5. 1) and averaging / extrapolation of discrete measurements over time and space (Section 6).

4.2 Eddy covariance measurements

There is a large uncertainty associated with eddy covariance (EC) measurements at sea, particularly due to the correction for the ships motion at very high measurement frequency; plus drift and error corrections and (in some cases) low precision from optical techniques. Precision depends on the gas in question; e.g. CO_2 EC fluxes are imprecise relative to DMS fluxes (Wannikhof *et al.* 2009), due to the greater signal-to-noise ratio in DMS flux measurements as DMS is relatively far from equilibrium between atmosphere and ocean. Also, concurrent seawater concentration measurements are typically from 5m depth, subject to some delay between sampling and analysis and often at lower frequency than gas phase measurements (e.g. Jacobs *et al.* 2002). These uncertainties all contribute to the overall uncertainty in k_w -u parameterizations (Asher 2009). Recent developments appear to have improved the precision of CO_2 eddy covariance measurements significantly (Prytherch *et al.* 2010).

5. Processes and phenomena

5.1 Microlayer effects

The sea-surface microlayer is (to a variable extent), physically, chemically and

biologically different from bulk surface seawater. It accumulates insoluble organics produced in the surface ocean and can be a visible ‘oily’ film under some conditions. It is subject to the maximum light intensity in the water column and can be populated by very different microbial communities to those immediately below in the bulk water, and in much higher (or lower) population densities (Cunliffe *et al.* 2009). It can inhibit the kinetics of gas exchange by changing turbulent properties at the surface, both as a ‘barrier’ to mass transport and by inhibiting micro-turbulence in the bulk surface (Frew 1997). Recent experimental work has suggested that this may be an important effect (Lee and Saylor 2010). When the microlayer is sufficiently thick and dissimilar to bulk water, the two-phase model of gas exchange may be incorrect and a three-phase model may be more applicable (Martinelli 1979).

Enrichment or depletion of volatile compounds in the surface microlayer may occur for 2 reasons: relatively insoluble gases may accumulate in the less polar matrix of a microlayer rich in insoluble non-volatile organics; or there may be in-situ production or destruction of a gas by photolytic or biological processes which are enhanced in or unique to the microlayer environment. Enrichments of up to and above an order of magnitude have been found for various chemical species (e.g. Zhang *et al.* 2003), although for dissolved gases generally substantially less e.g. Turner and Liss (1985). The collection and analysis of the microlayer is extremely difficult, especially for volatile gases and so the potential uncertainty introduced by measuring bulk seawater rather than microlayer surface concentrations is largely unknown, although likely to be at a minimum in the open ocean, where primary production and organic pollution are normally smaller than in coastal environments, and where enrichment factors are likely to be relatively small (Turner and Liss 1985; Yang and Tsunogai 2005).

In a microlayer that is physically and chemically different to bulk seawater, the solubility of a gas may be altered. This will affect ΔC , but may also enhance or inhibit transfer between the surface microlayer and the bulk water phase due to differing solubilities. Neither of these effects has been quantified for any gas, to our knowledge, and may vary greatly depending on the exact chemical composition of the microlayer and the gas in question.

5.2 Bubbles

Bubbles become increasingly important in near-surface turbulence and water-side controlled gas exchange processes with increasing wind, fetch and whitecapping. There are at least four potential bubble effects, which are discussed below. Wind tunnel and laboratory studies have indicated that there is a strong solubility dependence of the importance of bubbles (backed up by theory e.g. Memery and Merliva 1985; Keeling 1993; Asher *et al.* 1996; Woolf 1997; Woolf

et al. 2007). However the field data to support this in the ocean is rather limited, particularly for far-from-equilibrium trace gases. The effect of bubbles in general, and especially on gases of intermediate solubility is poorly understood, but of potentially large significance to k_w . Whether it increases the uncertainty beyond that in the range of common k_w parameterizations is unclear, even for gases of different solubility to those used in the parameterizations. It is important to note that whitecapping, bubble concentration and related parameters are not solely a function of wind speed, with fetch and other factors such as wave age and wind-wave orientation also being important. Therefore, no bubble effects can be entirely represented by a gas exchange model driven solely by wind speed. As such, bubble effects seem likely candidates for explaining a substantial amount of the $> 50\%$ of the deviation in k_w - u relationships that cannot be explained by experimental / measurement uncertainty (Asher 2009).

Disruption of the surface layer by bubble entrainment leads to a kinetic enhancement of transfer, through increased turbulence and break-up of the stagnant film with increasing bubble forcing; particularly through the return of the turbulent bubble plume to the surface. There are contradictory observations in the literature as to the significance of this bubble effect, however recent tank experiments suggest that it is probably small relative to other bubble effects (Woolf *et al.* 2007). This effect must be implicitly included in empirical k_w - u relationships, and there is no direct gas-specific (solubility / diffusivity related) component. However, there may be secondary gas-specific effects with substantial organic-rich microlayers, where breakup of such may modify microlayer phenomenon (Section 4.1).

Bubbles also inject gases directly into surface water or can provide a secondary pathway (on top of diffusive flux) for bidirectional exchange. Such processes modify the composition of bulk surface seawater and are therefore ΔC effects. There seems to be extensive confusion in the ‘secondary’ literature (review papers, reference books, citing articles) regarding the causes, processes and solubility-dependence of the bubble effect as proposed and developed by Memery and Merlivat (1985), Woolf and Thorpe (1992), Keeling (1993), Asher *et al.* (1996), Woolf (1997) etc. We suggest that much of this may be due to the confusion caused by integrating the bubble fluxes (which are air-sea flux terms in their own rights with their own concentration gradients and transfer velocities) into the transfer velocity term of the diffusive flux. In practice it is difficult to deconvolve the bubble flux and diffusive transfer velocity terms when deriving k_w from measured concentration gradients (e.g. from ^{14}C , multiple tracer, or eddy covariance studies), which is why the integrative approach is taken. Recent work by Stanley *et al.* (2009) has presented a model where the bubble flux is considered separately, which is an important development.

Some gas bubbles will fully dissolve and inject all their constituents directly into surface water. This process is independent of any gas-specific properties and depends only on the air-side concentration of the trace gas (and the bubble volume). This process has been assessed and validated (e.g. Stanley *et al.* 2009) and can lead to relative supersaturations of a few percent (where, at steady-state, the downward injection flux is countered by an upward diffusive flux out of the ocean). This effect is likely to be minor for gases which are far from equilibrium, where a change in the degree of saturation of a few percent will represent a small percentage change in ΔC .

Bubbles which don't completely dissolve will tend to equilibrate (with respect to the gas in question) with the water partially or completely. This 'exchange effect' also favours supersaturation due to overpressure and surface tension effects. It is complicated by the fact that some bubbles will inject gases into the water column on their downward trajectory, but as they return to the surface and their initial pressure they will be undersaturated and tend to re-absorb the gases; and some gases may dissolve at a different rate to the bulk bubble gases (N₂, O₂). The various models describing these bubble processes all predict a solubility-dependence, which is due to the relative capacity of the small volume of air in a bubble to carry molecules of insoluble and soluble gases at equilibrium between water and bubble. It is the *absence* of this solubility-dependent bubble effect, which has been proposed as the cause of apparently linear transfer velocities at high wind speeds calculated from eddy covariance measurements of DMS fluxes (Marandino *et al.* 2009; Huebert *et al.* 2010); and just such a k_w - u relationship was predicted for DMS by Woolf (1997). However, more field data is required to validate the few observations currently available and field experiments to validate the bubble process as the cause.

Vlahos and Monahan (2009) [VM09] propose a novel bubble-related process which may affect any amphiphilic molecules (molecules with polar *and* non-polar ends). They propose that the presence of bubbles would lead to adsorption of such molecules to the bubble-water interface, removing them from exerting a partial pressure at the air-sea interface, but not from being measured in seawater concentration measurements. They interpret this as a change to the transfer velocity, but it is really a ΔC effect, leading to similar confusion as for the previous two bubble effects. Their proposed model can be used to explain the apparent flattening of k_w for DMS at high winds observed in recent Southern Ocean data (Vlahos *et al.* 2011).

To date, there is limited empirical evidence that any bubble effects are strongly gas-specific in the open ocean; at least not to the point where any uncertainty introduced is greater than the range of standard k_w - u parameterizations. Important questions yet to be answered are i) what is the threshold gas solubility at which the

bubble effect stops being important for a particular set of conditions? and ii) how robust are the ‘average’ wind-speed whitecapping relationships? e. g. Woolf (2005), Goddijn-Murphy *et al.* (in press).

5.3 Chemical Enhancement

The enhancement of gas transfer by chemical reaction changing the concentration gradient through the rate limiting surface layer has been assessed and observed for a small number of gases (O_3 , CO_2 , SO_2). The degree of possible enhancement depends on the reaction rate relative to the rate of transport through the mass boundary layer and is thus strongly dependent on the reactivity of the gas of interest, wind speed and temperature. Because this effect occurs within the mass boundary layer (s), it has characteristics of both a k and ΔC effect. It modifies the apparent solubility and therefore the effective concentration gradient, but due to the ‘bending’ effect on the concentration gradient (e.g. Wanninkhof and Knox, 1992) it also changes the apparent depth of the rate-limiting layer. However, the only practical way to consider the enhancement mathematically is as a multiplication factor (α) to k_a or k_w because the enhancement is specific to reactions in one phase so the chemical enhancements must be applied to that specific phase.

The chemical enhancement by hydration reactions of CO_2 (e.g. Hoover and Berkshire 1969 [HB69], Wanninkhof and Knox 1996, Keller 1994), SO_2 (Liss 1971) and O_3 (Fairall *et al.* 2007) have been studied previously. Hydration of CO_2 to carbonic acid is a reversible reaction. Forward and reverse reactions rates differ, thus the enhancement to flux is asymmetrical. Although this is a minor effect for CO_2 hydration it may be important in other reactions. The effect of this enhancement on estimates of global CO_2 flux is unresolved, with estimates ranging from 0 to 20% (Keller 1994). It is worth noting that this effect is implicitly accounted for in bomb ^{14}C -derived k_w - u relationships e.g. Wanninkhof 1992, Naegler *et al.* 2006 etc. In contrast to CO_2 , SO_2 is so reactive in water that (at seawater pH) it almost instantaneously hydrates, such that the flux of SO_2 is always downwards. Liss and Slater (1974) demonstrate by adapting the HB69 model, that the enhancement to k_w for SO_2 is such that the resistance is entirely on the air-side, as it would be for a much more soluble gas. Care must be taken when considering the enhancement due to hydration for other gases. For extremely fast hydration reactions, such as that of formaldehyde, it is impossible to measure the Henry’s law constant in isolation from this effect and so measured solubility implicitly includes the hydration term (Johnson *et al.* submitted).

Other reversible reactions such as acid-base and redox reactions may also lead to chemical enhancement, if they are sufficiently rapid. Protonation reactions tend to be extremely fast, for example. In the case of ammonia it can be demonstrated

that significant chemical enhancement can occur at $\text{pH} < \sim 8.5$ (Johnson *et al.* submitted) due to protonation to ammonium..

Irreversible reactions may also modify the flux, with one major difference to the above: without a reservoir of reacted species to buffer the addition or removal of gas from the surface layer through air-sea flux, a reaction can either enhance or *inhibit* the flux depending on its direction. For example, if a compound is rapidly photolysed at the surface this will enhance a flux into the ocean, but inhibit a flux out. It is not uncommon for photolysis reaction rate constants in water to be of the order of 10^{-3} s^{-1} e.g. Martino *et al.* (2005), which is sufficiently fast to modify the flux under low-to-moderate wind conditions (Johnson *et al.* submitted).

Solving the HB69 equation for the rate of reaction required for a given enhancement reveals that many candidate reactions might be rapid enough to cause a significant enhancement at moderate windspeeds for a range of gases (Johnson *et al.* submitted), so this uncertainty, which is not implicitly included in empirical parameterizations of gas transfer, must be considered on a case-by-case basis. The generalized version of the HB69 equation can equally be applied to the air-side of the interface and such analysis demonstrates that much higher rate constants are required for substantial enhancement. Gas phase reactions do tend to be faster than those in seawater but we are yet to identify any that would significantly enhance or inhibit the flux of gases of biogeochemical interest.

5.4 Heat and water fluxes

There are various ways in which the transfer of heat and water between ocean and atmosphere might affect the flux of gases. In a laboratory study Ho *et al.* (1997) found a ‘significant and systematic’ enhancement of the exchange of SF₆ by simulated rainfall, due to the kinetic effect of increased turbulence. Furthermore, it is possible that diluting the surface of the ocean may change the concentration gradient across the air-sea interface and alter the solubility (through the temperature, salinity or polarity of the medium), and may also change the viscosity of the surface layer, leading to an alteration of the transfer velocity. Turk *et al.* (2010) demonstrate that rainfall can also indirectly affect ΔC for CO₂ substantially, by altering carbonate chemistry. Rainfall is also likely to substantially deplete soluble gases in the boundary layer atmosphere, further affecting ΔC .

Micro-scale stratification or instability due to temperature differences between the atmosphere and ocean might be expected to affect the transfer velocity, at least at low wind speeds when wind stress is small. However, there is limited evidence to support this (Nightingale and Liss 2004). For example Liss *et al.* (1981) found no significant evidence of enhancement to transfer by evaporative conditions in their wind tunnel study, although under condensing conditions they did observe a

significant decrease in transfer velocity due to increased stability. Such stability effects may be stronger and more significant on the air side of the interface, and so of greater significance for soluble trace gases; this is uninvestigated to date, however.

A 'cool skin' effect, due to surface evaporation, causes modification of the solubility and therefore concentration gradient of the gas of interest across the rate-limiting boundary layer (e.g. Robertson and Watson 1992). A warm skin due to solar heating might have the opposite effect. However, McGillis and Wanninkhof (2006) suggest that these effects are probably minor due to the difference in length scales of the temperature and mass boundary layers and this is borne out in the field data of Ward *et al.* (2004). Furthermore, in situations where an evaporative cool skin may exist there is likely to be an enhancement to salinity at the surface, which will approximately cancel out the temperature effect, at least for CO₂ (Takahashi *et al.* 2009).

A further phenomenon arises from the effects of the interactions between heat and gas fluxes. Such 'irreversible thermodynamic' effects, due to the inherent coupling of heat and mass fluxes may be significant under certain conditions (Phillips 1994, 1997), although this has been challenged by Doney (1994, 1995) for the case of insoluble gases under water-phase control. This matter is unresolved, although it is invariably assumed that under environmental conditions where the temperature difference across the interface tends to be small, the effect is insignificant (Nightingale and Liss, 2004). It is important to note that the possible effect on soluble gases has not previously been studied (to our knowledge) and any potential effect is entirely unknown.

5.5 Biological effects

Biological activity can potentially directly or indirectly affect air-sea flux in a number of ways, most of which remain largely unstudied, and none are included in models of air-sea gas exchange, in part due to the difficulty in parameterizing such irregular effects. They may be included implicitly in the empirical k_w - u parameterizations, however, at least for the gases on which the parameterizations are based, and the conditions under which the measurements were made.

Just as chemical reactions might enhance or inhibit transfer by modifying the concentration gradient in the mass boundary layers, biological activity might achieve the same, at least on the water side, by production or consumption. There is some empirical evidence that this may be the case for methane (Upstill-Goddard *et al.* 2003), and O₂ / CO₂ (Garabetian, 1991; Matthews, 1999) and the rates required are not inconceivable (Johnson *et al.* submitted). Furthermore, Calleja *et al.* (2005) found that planktonic metabolism in the top few cm of the ocean can control the magnitude and direction of air-sea CO₂ flux.

It is also interesting to consider the effect of changes in mixed layer depth in response to wind speed during transient events and how this might affect concentrations through biological responses. A deepening mixed layer may tend to transiently reduce primary production (as phytoplankton are exposed to lower average light intensities) or increase it (if nutrient limitation is relieved by entrained nutrients from below the thermocline). Changes in UV stress on the bacterial population associated with being mixed away from the surface may also have significant effects on particular gas concentrations e.g. DMS consumption by bacteria is thought to be UV limited. Deepening or shoaling of the mixed layer could be considered as a form of intermediate disturbance and as such is likely to lead to changes in ecosystem structure on relatively short timescales (days to weeks). As many trace gas concentrations are the net result of a complex web of production and loss terms, strongly dependent on ecosystem composition and function, such changes are likely to be of significance to air-sea fluxes. However, where fluxes are calculated from *in-situ* measured concentrations, and not extrapolated in space or time, such biological effects are implicitly accounted for.

The effect of biologically-induced turbulence at or immediately below the surface layer will enhance k . Whilst the turbulence caused by large organisms (fish, seagulls, whales and the like) may be very significant in extremely localized terms (i.e. scales of metres and minutes), we assume they are unlikely to be significant at the larger scale (kilometres and days). However, it has been suggested that the action of flagella of motile microorganisms may contribute significantly to turbulence and gas transfer in the surface layer of the ocean (Paul Twitchell, ONR Boston, pers. comm.; Gladyshev 1997). It is unclear (due to lack of evidence) how significant this effect might be, but it is probably small.

6. Averaging and interpolation / extrapolation

To quantify the local, regional or global air-sea flux of a trace gas, it is necessary to interpolate between spatial measurements and/or extrapolate from near-instantaneous measurements in time. Furthermore, averaging of measured data is necessary to generate pre-interpolation fields for 2D estimates from discrete measurements (e. g. Lana *et al.* 2011). All of these processes introduce uncertainties, some of which are well quantified, others less so.

6.1 What is a representative average concentration?

Biological production and consumption and physical mixing can lead to short term / small scale variability in concentrations which means that all but the highest resolution concentration measurements are rather difficult to average. For highly bio-reactive compounds this is particularly problematic. For instance, the standing

stock of ammonia in surface waters can be turned over on timescales of a few hours to a day in highly productive waters and de-coupling of production and loss processes can lead to transient spikes in ammonium concentration of as much as an order of magnitude above the ambient (Johnson *et al.* 2007). Other gases which are rapidly turned-over by biological or chemical processes e.g. CH_2I_2 photolysis (Martino *et al.* 2005) may be subject to similar transient peaks due to other decouplings. In evidence of this, the frequency distributions of many observations of trace gas concentrations in seawater are positively skewed, with a long ‘tail’ of high values. Combined with spatial heterogeneity due to local-scale physical processes, this means that low resolution measurements in seawater can yield unrepresentative concentrations over e.g. a day on a research cruise. Gas phase concentrations are more likely to be measured continuously, although possibly integrating over long periods (which introduces uncertainties in itself); however if low-temporal-resolution instantaneous concentrations are measured e.g. by flask sampling, changes in concentration due to e.g. air-mass source may be overlooked.

Extrapolating to the regional or global scale introduces even greater uncertainty. For instance, the recently published update to the global seawater DMS database (Lana *et al.* 2011) contains approximately 5×10^4 discrete measurements, making it the second most measured trace gas in the ocean, after CO_2 . Nonetheless, the uncertainty introduced by interpolation and extrapolation (as estimated by Lana *et al.* 2011), when applied over biogeochemical provinces to give a regionally-resolved estimate of the net global DMS flux from the ocean, is approximately the same as the difference between applying Liss and Merlivat (1986) and Wanninkhof (1992) to calculate the flux from the concentration and wind fields. This suggests that for less well studied gases, extrapolating global flux estimates from concentration alone (without attempting to understand and model underlying biogeochemical production and loss processes) is insufficient to attempt anything other than single-point global average flux estimates (e.g. Turner *et al.* in prep).

6.2 Environmental forcing parameters

In order to calculate fluxes from extrapolated concentrations it is necessary to apply interpolated or averaged temperature, salinity and windspeeds. We assume that temperature and salinity are relatively well constrained, with the average error on e.g. satellite retrieval of temperature being less than 1°C (Wanninkhof *et al.* 2009) and much less from direct measurements; and salinity being relatively well constrained in the field and in climatological data. In field studies quoting near-instantaneous fluxes from concentration measurements it is common to use e.g. 7 day averaged winds to give a representative flux over a meaningful period of time (e.g. Hughes *et al.* 2009), or where there is a long atmospheric integration time

over a spatial range, to apply mean windspeed over that time period (e.g. Johnson *et al.* 2008). Either of these is a valid approach but they may yield substantially different results. Nonetheless the *in situ* windspeed measurements used are likely to be rather precise and at high temporal resolution so the uncertainty is likely to be relatively minor. When extrapolating over wider spatial and temporal scales longer term averaged and/or time-varying wind data e.g. NCEP reanalysis data or satellite-retrieved winds are used. Reanalysis and satellite data can differ significantly due to the lack of resolution of short time and spatial scale details in the former, which leads to a 1.3 m/s difference in the global annual average wind speed between NCEP and QuickSCAT (Naegler *et al.* 2006), and variability in spatial wind distributions (Wanninkhof *et al.* 2009). Further error can be introduced by incorrectly applying long-term averaged winds, due to the inequality between e.g. the square of the mean wind speed and the mean of the wind speed squared (Wanninkhof *et al.* 2009).

6.3 Steady-state assumption

Flux estimates are generally based on a steady-state assumption, i.e. that over the integration / extrapolation period of a flux calculation, processes controlling the concentration gradient are constant. One can envisage this assumption falling down in a number of cases e.g. i) where the flux of the gas is rapid relative to its

Table 2 Key uncertainties

Source of uncertainty	Worst case U_{max}	Rumstic Classification	Gas types and/or conditions under which uncertainty is maximized
k_a -u parameterization	XL	KU	Highly soluble gases; water-side highly chemically-enhanced e.g. SO ₂ ; k_a windspeed relationship poorly known. Use of e.g. Jo10 may cause over or underestimation
Bubble exchange effect	XL	KU	Gases of intermediate solubility where k_w dominates transfer, but where bubble effect is much smaller than for the insoluble gases used in k_a -u parameterizations e.g. DMS, alkyl nitrates, most halocarbons. Use of standard k_a -u parameterizations will lead to overestimation of fluxes.
Bubble adsorption effect	XL	UU	Amphiphilic compounds; high winds. Overestimation of seawater partial pressure will lead to overestimation of sea-air fluxes.
Microlayer kinetic inhibition	XL	KU	Low to moderate winds; productive or polluted waters.
Microlayer solubility	L	UU	Low to moderate winds; particularly (water) soluble or insoluble gases
Chemical enhancement	XL	KU	Compounds undergoing rapid reaction in surface ocean or atmosphere; low winds. May enhance or inhibit, and be very weakly or very strongly asymmetrical.
Stratification / instability	L	UU	Large temperature difference between ocean and atmosphere. Effect for k_a -controlled gases particularly poorly known.
Irreversible thermodynamics	L	UU	largely unknown
Biological enhancement	L	UU	k_w -controlled compounds rapidly produced or consumed by plankton community.
ΔC due to biological response to mixed layer deepening	L	UU	Compounds whose production / consumption would be affected by community response to mixing to depth. May result in change in flux magnitude or direction. Significant when average concentrations extrapolated over changing windspeeds.
Concentration averaging / interpolation / extrapolation	XL	KU	All gases. Averaging / extrapolations over large ranges of space and/or time, particularly when data is sparse and locally / regionally / seasonally biased.
Steady state assumptions	L	UU	Long timescale / high wind / highly variable wind conditions.

concentration (or production / consumption rate) in one or both phases; ii) where concentration changes occur coupled to changes in variables which drive transfer velocity (e.g. wind speed, temperature). Both of the above almost certainly occur under some conditions. For instance i) the typical amount of e.g. methanol or ammonia in the atmosphere is small relative to the flux at high wind speeds leading to a relatively rapid decrease in ΔC as winds become strong and ii) an increase in wind strength may increase or decrease the concentration gradient between atmosphere and ocean by mixing surface waters with deeper ones, depending on the nature of any existing concentration gradient with depth in the bulk ocean. Such a mixing-driven dilution might lead to a reduction in the significance of the higher winds to the net flux of a gas which was supersaturated in seawater (or an increase for one which was undersaturated); or even potentially a reversal in net flux direction. Coupling between fluxes of different gases which interact in atmosphere and/or water will also tend to break the steady-state assumption. For instance, Johnson and Bell (2008) invoke the potential for DMS-driven 'co-emission' of NH_3 to explain the constancy in aerosol ammonium to non-seasalt sulfate reactions; and the flux predicted from NH_3 concentrations alone is different to that with DMS emissions driving the ammonia flux in their model.

7. Conclusions

We have presented a wide range of potential uncertainties involved in quantifying air-sea gas exchange, from the well-known to the obscure. Based on their Rumsfeldian classification and their potential 'worst case' magnitude (Table 1), we can identify the key uncertainties which need improvement to better constrain air-sea gas exchange. These are summarized in Table 2, along with information on the types of gases affected and the conditions under which the uncertainty is likely to be at a maximum. Note that other uncertainties may be extremely important as well, particularly in atypical cases e.g. studies where heavy rain dominated meteorological conditions, or polluted estuarine situations where microlayer effects may be much more important than normal.

It is unrealistic to expect that all future studies will be able to investigate all possible uncertainties for their gases of interest to produce robust uncertainty estimates. Unfortunately no all-encompassing rules of thumb can be applied, particularly in the case of biological effects or chemical enhancement. However, in terms of the K_Ks and K_Us associated with water-side transfer it is useful to observe that application of the commonly-used N00 parameterization with error bars of $\pm 50\%$ covers more than 75% of the range of k_w parameterizations at wind speeds between approximately 4 and 13 m/s. As such, this might be considered a reasonable uncertainty range, representative of the true magnitude of the

uncertainties in estimates of fluxes of insoluble gases under typical conditions. A similar $\pm 50\%$ applied to k_a might also be reasonable.

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