Gas Transfer and Aerosol Transfer Parameteriations

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1. Background

1.1 Air-Sea Transfer of Trace Gases

The kinetics of air-sea gas exchange is poorly understood, and this lack of knowledge impedes our ability to accurately portray the local and regional flux of trace gases between the atmosphere and ocean. Gas transfer is a nonlinear process with complex processes in both the ocean an atmosphere. For gases with strong ocean molecular sublayer resistance (such as CO2), the exchange is significantly increased with the high wind speed production of bubbles and enhanced underwater turbulent processes (Terray *et al.*, 1996). Although air-sea gas transfer is recognized to have a strong correlation with wind speed, other processes are also of importance. For example, at low winds, surfactants, rain, micro-scale wave breaking, and biological productivity may significantly affect gas transfer. Low wind speeds predominate in the tropical regions, where biological productivity is relatively high due to the upwelling of nutrients (as in the equatorial Atlantic and Pacific) and to the abundant flux of solar energy. Climate change and rising sea surface temperatures and changing mixed layer depths will affect regional biological productivity, and the changes in the global distribution of clouds and winds will also affect the air-sea gas flux. Again, it is of critical importance that the physical and biological processes that are important to gas exchange be incorporated into climate models.

In recognition of these problems, NOAA and NSF jointly sponsored the first air-sea gas exchange (GasEx) cruise in the North Atlantic in the spring of 1998. A wide variety of wind speeds and stabilities were encountered during GasEx-1998, and for the first time, high quality direct eddy covariance fluxes of CO_2 were measured over the open ocean along with coincident observations of many of the important physical processes. The result of this study (McGillis *et al.*, 2001a) was that significant progress was made toward understanding air-sea gas transfer and toward the development of realistic gas transfer parameterizations (Fairall *et al.*, 2000). After the success of GasEx-1998, a second study was conducted in the equatorial Pacific in early 2001. Many of the results from GasEx-2001 are still under investigation, but it is clear that there are some important differences between the two data sets. For example, significant biological activity was present during GasEx-1998, while relatively low levels of new production were observed during GasEx-2001 (Hare et al., 2004).

1.2 Parameterization of Air-Sea Gas Transfer

Using scientific knowledge gained by these field deployments, Fairall *et al.* (2000) took a micrometeorological approach to develop a gas transfer model which incorporates more of the physics of air-sea gas transfer than any published parameterization to date. In essence, the model describes the turbulent and molecular processes on both sides of

the two-fluid interface; it incorporates the surface renewal concepts of Soloviev and Schlussel (1994) and the empirical bubble enhancement model of Woolf (1997). Furthermore, this parameterization describes the flux on the scale (sub-hour) of the physical processes which drive the gas transfer. The model has recently been extended to include gases such as ozone that are destroyed by chemical reactions after deposition to the ocean surface.

The expression of the air-sea flux, F, of a gas can be written in terms of the solubility (α) and air-sea partial pressure (fugacity, f_x) difference as:

$$F = k \, \alpha \, (f_{xw} - f_{xa})$$

where the subscripts indicate 'water' and 'air' and k is the modeled gas transfer velocity. There are many hidden details within this expression (see section 3). For CO2 the most uncertain parameter within this expression is that of the transfer velocity. In the past, simple wind speed dependent models for k were presented, such as that of Liss and Merlivat (1986) and Wanninkhof (1992), and these expressions are linear and quadratic with wind speed, respectively. Accurate estimation of the mean air-sea flux of carbon dioxide over any region of the ocean requires determination of the transfer velocity as well as the air-sea fugacity gradient on the time scale of the forcing mechanisms. That is, it is not sufficient to determine monthly averages of these quantities, due to the cross-correlation between them at smaller time scales. By directly measuring the flux and the air-sea fugacity gradient, one can compute 'observed' gas transfer velocities. The chemical/biological data from GasEx-2001 showed that water column biological/chemical budget calculations can be used to calculate a gas transfer velocity that agrees well with direct flux measurements (Strutton *et al.*, 2004). However, it was demonstrated in Hare *et al.* (2004) that deviations exist in the flux data set which cannot be explained by the current generation of the NOAA/COARE gas transfer parameterization. Possible explanations for these discrepancies include inadequate representation of underwater physics or biological influences.

Ozone deposition into the oceans represents a significant loss from the atmosphere. An accepted model for the description of dry deposition relies on the resistance approach (Wesely and Hicks, 2000). For gases which are destroyed by chemical reaction after deposition, the flux equation reduces to the form (see section 3) $F=-V_{dx} f_{xa}$, where the deposition velocity depends on different resistance terms, with $V_{dx} = (R_{at} + R_{am} + R_{cw})^{-1}$. R_{at} is the turbulent/aerodynamic resistance reflecting the turbulent transport to the ocean surface, which is a function of sea surface roughness, wind speed and atmospheric stability. R_{am} is the quasi-laminar boundary layer resistance which describes transport through a thin layer of air in contact with the surface and which is, in addition to the above listed parameters that control R_{am}, also a function of the diffusivity of the trace gas of interest. Finally, R_{cw} is the surface resistance that reflects the surface uptake efficiency; this is controlled by physical, chemical, and biological processes. Field measurements show that ozone deposition tends to be controlled by the R_{cw} term, thus oceanic chemical processes must be accounted for to accurately characterize ozone uptake.

2.   The COARE Air-Sea Gas Transfer Parameterization

The COARE bulk flux algorithm was developed as a state-of-the-art physically-based program to estimate air-sea fluxes of momentum, heat, and moisture (Fairall et al,

1996a). It has been tested against thousands of ship-based direct flux measurements and updated to include surface wave effects (Fairall et al., 2003). The algorithm contains internal models to account for the oceanic warm layer and cool skin effects on relating bulk ocean water temperature to SST (Fairall et al., 1996b). The physics contained in the cool skin model have been adapted to describe the air-sea exchange of trace gases in terms of turbulent and molecular diffusive processes in both fluids (Fairall et al., 2000). Using the notation from Fairall et al. (2000), the budget equation for the mass concentration of some chemical, X, in either fluid is

$$\partial X / \partial t + \vec{U} \cdot \nabla X = -\frac{\partial[-(D_x + K)\partial X / \partial z]}{\partial z}$$

where z is the vertical coordinate, D_x is the molecular diffusivity of X (in water or air), and K the turbulent eddy diffusivity. This equation is used to relate the flux of X to the bulk concentration at some reference height, z_r, in both air (X_{ra}) and water (X_{rw})

$$F_x = \frac{[X_{rw} - \alpha X_{ra}]}{[V_{tw}^{-1} + \alpha V_{ta}^{-1}]} = \frac{[X_{rw} - \alpha X_{ra}]}{[R_{tm} + R_{wt} + \alpha R_{am} + \alpha R_{at}]} = \frac{\alpha u_{*a}[X_{rw} / \alpha - X_{ra}]}{\sqrt{\frac{\rho_w}{\rho_a}}[R_{tm} + R_{wt}] + \alpha[R_{am} + R_{at}]}$$

where α is the dimensionless solubility of the gas in seawater, V_t the transfer velocity of the gas in each fluid, which is represented as the sum of molecular (subscript m) and turbulent (subscript t) layer resistances, R,. Here u_{*a} is the atmospheric friction velocity and ρ the density of the fluid. The COARE cool skin formulation is obtained by setting $X = \rho c_p T$. The fugacity (discussed in the Introduction) is computed from mass concentration through the ideal gas law.

The COARE parameterization uses surface renewal theory to represent the molecular resistance terms (one set for air and one for water)

$$R_m = \Lambda R_r^{1/4} S_c^{1/2} / \Phi$$

R_r is the roughness Reynolds number, S_c the Schmidt number of the gas, Φ a buoyant turbulence energy production factor, and Λ a constant coefficient. For CO2 an addition term is added in the ocean transfer velocity to account for enhanced transport by whitecap induced bubble processes. The coefficients have been tuned to the GASEX field measurements (Hare et al., 2004). Fig. 1 shows the model and the average GASEX data as a function of wind speed.

A recent extension of the NOAA/COARE gas transfer model includes the case of an atmospheric gas (such as ozone) that reacts strongly in the ocean. The budget equation for the concentration is now given by

$$\partial X / \partial t + \vec{U} \cdot \nabla X = -\frac{\partial[-(D_x + K)\partial X / \partial z]}{\partial z} - aX$$

where the last term is the loss rate of *X* due to reactions with some chemical *Y*. Thus, *a=Cxy Y*, where *Y* is the concentration of the reacting chemical and *Cxy* the reaction rate constant. In the limit that the reaction is so strong that the concentration of *X* become negligible within the molecular sublayer, the *K* term can be neglected to give (Garland et al., 1980):

$$D_x \frac{\partial^2 X}{\partial z^2} - aX = 0$$

Assuming that the concentration of *Y* is much larger than *X* so that is remains effectively constant, we can show that the flux is given by

$$F_x = -V_{dx} X_{ra}$$

$$V_{dx} = [V_{ta}^{-1} + R_{cw}]^{-1} = [R_{am} + R_{at} + R_{cw}]^{-1}$$

where V_{dx} is the classical deposition velocity, V_{ta} the atmospheric transfer velocity for *X*, and

$$R_{cw} = [\alpha \sqrt{C_{xy} Y D_{xw}}]^{-1}$$

For highly reactive situations *Y Cxy* is large and V_{dx} approaches V_{ta}. Clearly, the deposition velocity depends on the balance of solubility and diffusivity of *X* combined with the concentration and reactivity with *Y*. Fig. 2 illustrates the expected ozone deposition velocity computed with this model as a function of wind speed and for different values of R_{cw}. The case where R_{cw} is set to 0 is for extreme reactivity right at the air-water interface. These simulations yield ozone deposition velocities comparable to typical experimental values (on the order of 0.05 cm s^{-1}) for R_{cw}.=1000 s/m   The implication is that R_{cw} is not zero and that chemical aspects in the ocean are at least as important as atmospheric processes. Garland et al. (1980) and Chang et al. (2004) discuss various constituents of seawater, there reactions with ozone, and the large experimental difficulty in determining deposition velocity for ozone. Conclusively, these considerations underline the need to more carefully study the fluxes of ozone and their dependency on ocean water properties and conditions.

3.   Aerosol Deposition

The basic aerosol conservation equation is

$$\frac{Dn}{Dt} = -\frac{\partial}{\partial z}\left[\overline{w'n'} - D_p \frac{\partial n}{\partial z} - V_g n + \overline{w_s'n'} + S_n\right]$$

where

z=height above surface
n=size dependent droplet number concentration
w'=vertical air motion fluctuation
D_p=size dependent molecular diffusion coeff
V_g=mean gravitational settling velocity, function of particle radius
w_s'= air-particle slip velocity
S_n=size/height dependent source function in flux form

We can then write a conserved flux variable that includes the source terms:

$$F_z = \left[\overline{w'n'} - D_p \frac{\partial n}{\partial z} - V_g n + \overline{w_s'n'} + S_n \right]$$

We begin with a flux measured at some reference height z above the surface and assume that there are no intervening surface sources; thus, we set S_n to zero. We consider two height zones: layer I dominated by turbulent and mean fall velocity transport and layer II where turbulence is negligible but molecular diffusion and particle inertial impaction are important. Inertial impaction is handled through the particle slip covariance term.
    In layer I we have

$$F_z = \left[\overline{w'n'} - V_g n_z \right] = -\kappa z u_* \frac{\partial n}{\partial z} - V_g n$$

where we have represented the turbulent flux with a standard diffusion-gradient form (here κ=0.4 is von Karman's constant). This provides a differential equation for *n(z)*

$$\kappa z u_* \frac{\partial n}{\partial z} + V_g n + F_z = 0$$

Transforming the variable to *n'=n+F_z/V_g* yields the standard solution relating the concentration at z to the concentration at the bottom of the turbulent layer

$$n'_z / n'_h = (z/h)^{-\frac{V_g}{\kappa u_*}}$$

With a bit of algebra we write this as

$$n_h = n_z f_{zh}^{-1} + \frac{F}{V_g}(f_{zh}^{-1} - 1) \tag{1}$$

Where

$$f_{zh} = \exp[-\frac{V_g}{\kappa u_*}\log(z/\delta_u)]$$

Note we have set h= δ_u , the velocity turbulence microscale length. Below that height turbulence is rapidly eliminated through viscous dissipation.

Layer II yields a similar form the region h>z>0:

$$\frac{\kappa z u_*}{1 + \delta_u / z}\frac{\partial n}{\partial z} + V_g n + C u_* + F_z = 0$$

Here we have added the factor in the denominator of the first term to account for the dissipation of small-scale turbulence near the interface and the Cu* term as a simple parameterization of inertial impaction. C is a factor that depends on the Stokes parameter (see Slinn and Slinn, 1980) and is zero for particles with a viscous stopping distance that is less than δ_u. The solution is the same as above, except we set the surface concentration to 0 and write it in terms of the flux

$$F_z = -\frac{(V_g + Cu_*)}{1 - f_{ho}} n_h \tag{2}$$

where

$$f_{ho} = \exp[-\frac{(V_g + Cu_*)}{\kappa u_*}(\log(\delta_u / \delta_r) + H_r)]$$

This result is an approximation to the analytic expression obtained by Fairall et al. (2000) for the case of Schmidt number >>1. Following the same approach used in the gas transfer section

$$\delta_u = \lambda v / u_*$$
$$\delta_u / \delta_r = \Lambda / 1.5\, S_c^{1/2}$$
$$H_r = \Lambda\, S_c^{1/2}$$

where v is the kinematic viscosity of air and $S_c = v/D_p$. The inertial term is usually parameterized by the Stokes dimensionless number (as per Slinn and Slinn, 1980)

$$C = C(S_t) = \frac{C_{dn}^{1/2}}{\kappa} 10^{-3/s_t} \quad ; \quad S_t = V_g u_*^2 /(g v)$$

We now use the concentration relationship from (1) in the flux equation (2) to eliminate n_h:

$$F_z = -V_d n_z$$

$$V_d^{-1} = \frac{f_{zh}(1 - f_{ho})}{V_g + Cu_*} + \frac{(1 - f_{zh})}{V_g}$$

(3)

It turns out that, to a good accuracy,

$$\frac{a}{1 - \exp(-ab)} = a + 1/b$$

If we use this to expand the two terms in (3) we can recover the Slinn and Slinn (1980) formulation, although the terms are defined slightly differently. Slinn and Slinn partitioned the turbulent vs molecular layers in an ad hoc manner, whereas in this approach the partition follows from the analytic solution. Figure 3 shows a sample of deposition given by this model for a 10 m/s wind speed over the ocean.

4.   References

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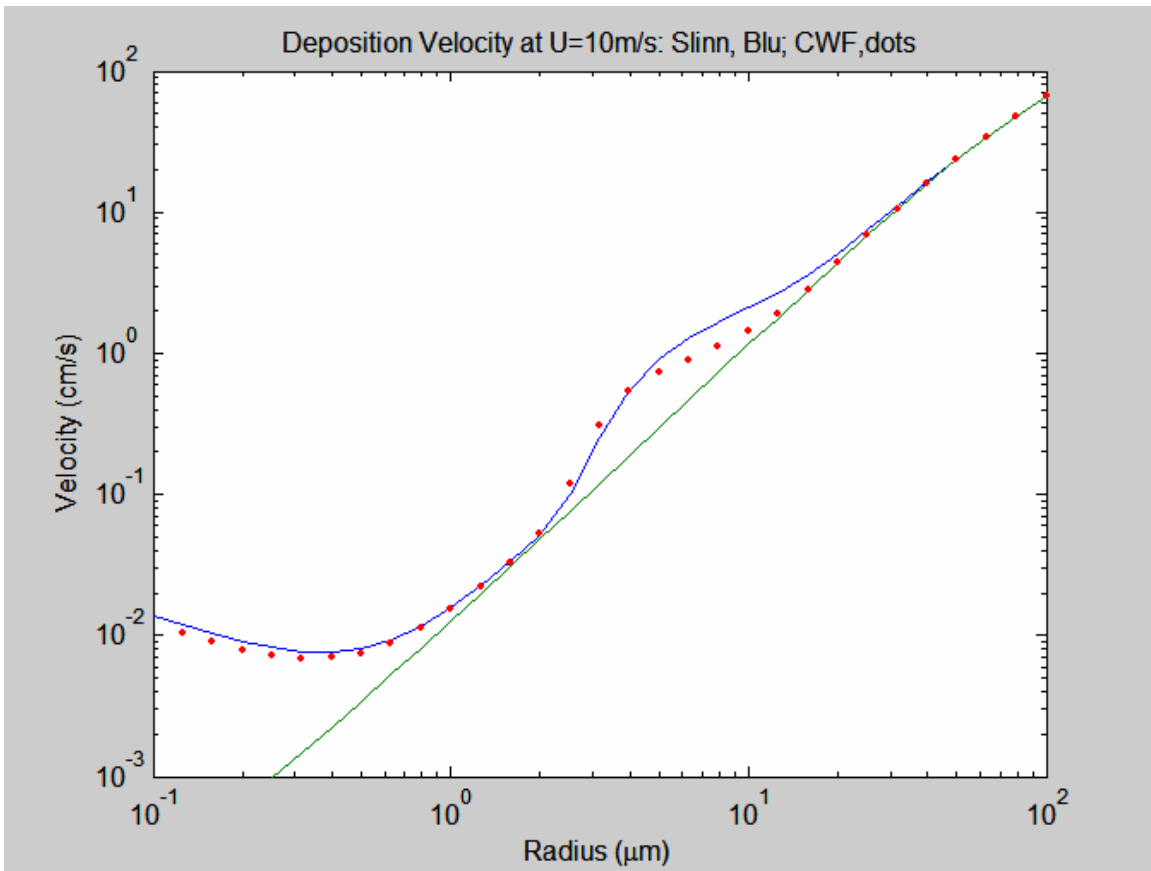
5. Figures
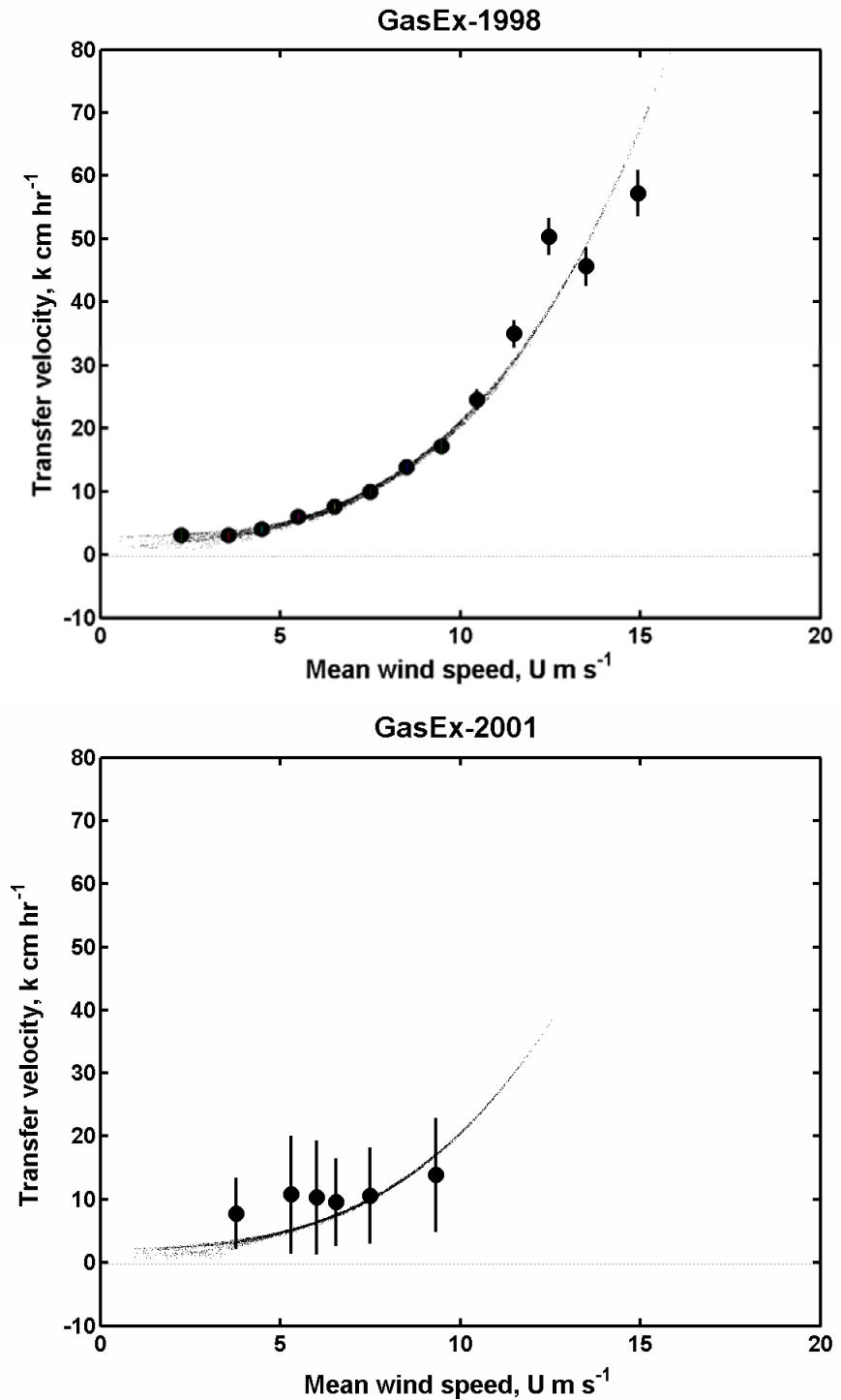
Figure 1. CO2 transfer velocity as a function of observed 10-m wind speed. The filled circles are the mean measurements determined from direct eddy covariance CO2 flux and the line is the COARE bulk flux algorithm for CO2. The upper panel is GASEX-98 and the lower panel is GASEX-01. One adjustable constant was tuned to fit the GASEX-98 data.
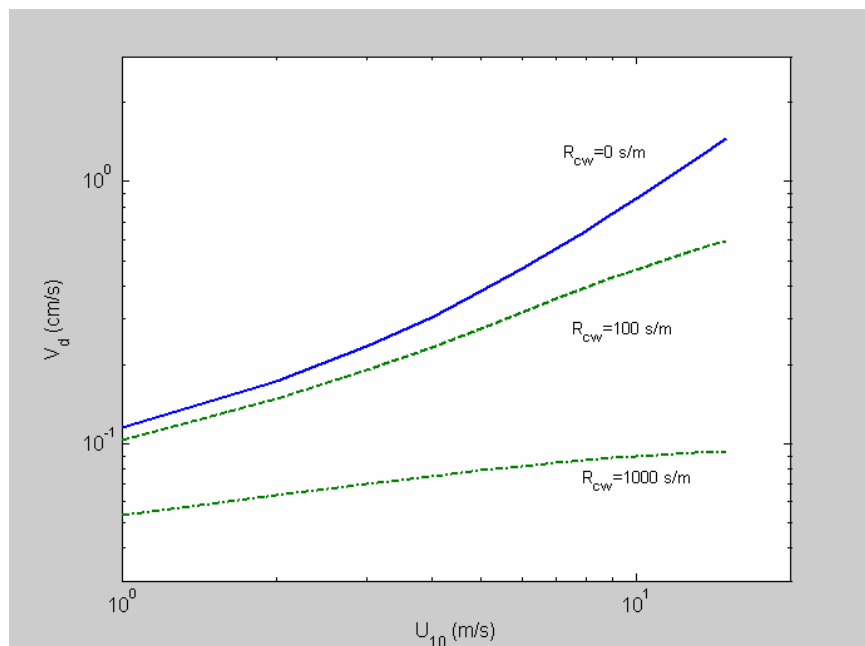
Figure 2. Ozone deposition velocity as a function of 10-m wind speed using the COARE bulk algorithm. The different lines are for different specifications of the oceanic resistance (see section 3).

Figure 3. Deposition velocity over the ocean for aerosol particles as a function of size for a mean wind speed of 10 m/s.