

C. W. Fairall*

NOAA Earth Systems Research Laboratory, Boulder, CO

J. E. Hare

Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO

Detlev Helmig

Institute of Alpine and Arctic Research (INSTAAR) and Program in Atmospheric and Oceanic Sciences (PAOS),
University of Colorado, Boulder, CO

Laurens Ganzveld

Max-Planck Institute for Chemistry, Mainz 55020, Germany

1. INTRODUCTION

Ozone deposition to 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). Deposition is expressed quantitatively by the deposition velocity (V_d), which depends on different resistance terms, with $V_d = (R_a + R_b + R_c)^{-1}$. R_a is the aerodynamic resistance reflecting the turbulent transport to the ocean surface, which is a function of sea surface roughness, wind speed and atmospheric stability. R_b is the quasi-laminar boundary layer resistance which describes the 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_a , also a function of the diffusivity of the trace gas of interest. Finally, R_c is the surface resistance that reflects the surface uptake efficiency which can be controlled by physical, chemical and biological processes. Over water, this concept has been expanded to include turbulent and molecular sublayers in both fluids (Liss 1973). It is also common to use transfer velocities (i.e., reciprocal of resistances) to characterize the sublayer transfers (Fairall et al. 2000).

Garland et al. (1980) were the first to link the oceanic chemical reactivity of ozone to the oceanic deposition resistance. More recently, Chang et al. (2004) have expanded the scope to combine chemical and physical processes as parallel resistances. Chang et al. (2004) also discuss various oceanic chemicals that are expected to be the reacting agent (Iodide being the strongest candidate). Recent research on ocean – atmosphere gas and energy exchange has resulted in improved models that describe the dependencies of deposition on atmospheric and oceanic processes from a more fundamental perspective (Fairall et al., 2000; Hare et al. 2004). In this paper, we will extend this formalism to include the case of a trace atmospheric gas that reacts chemically in the ocean. We extend the approach of Garland et al. (1980) to the case where not

all of the gas reacts within the molecular sublayer.

2. CONSERVATION EQUATION

Using the notation from the 2000 Fairall et al. paper, the budget equation for the concentration of some chemical, X , is

$$\partial X / \partial t + \vec{U} \cdot \nabla X = - \frac{\partial[-(D_x + K)\partial X / \partial z]}{\partial z} - aX \quad (1)$$

where z is the vertical coordinate (depth for the ocean), D_x is the molecular diffusivity of X in water, K the turbulent eddy diffusivity, and the last term is the loss rate of X due to reactions with some chemical Y . Thus, $a=C_{xy} Y$, where Y is the concentration of the reacting chemical and C_{xy} the reaction rate constant. We can move the reaction (aX) term inside the z -derivative and associate this with a flux variable that, in dynamic equilibrium, is constant:

$$-[D_x + K(z)]\partial X / \partial z + a \int_0^z X(z) dz = F_x \quad (2)$$

Here F_x is a flux variable that is independent of z in the atmosphere and ocean.

3. K-THEORY SOLUTION

Turbulent transport is represented by a simple surface layer eddy-diffusion coefficient $K = \kappa z u_*$ where u_* is the friction velocity in the ocean and κ the von Karman constant. The differential equation becomes

$$\frac{\partial}{\partial z} [(D_x / \kappa u_* + z) \frac{\partial X}{\partial z}] - \frac{a}{\kappa u_*} X = 0 \quad (3)$$

If we transform to $y^2 = (D_x / \kappa u_* + z)$, then the solutions are modified Bessel functions of zero-order (Geernaert et al., 1998)

*Corresponding author address: C. W. Fairall, ESRL/PSD, 325 Broadway, Boulder, CO, 80305; email: chris.fairall@noaa.gov

$$X = AI_0(\xi) + BK_0(\xi)$$

$$\xi^2 = \frac{4a}{\kappa u_*} \left(z + \frac{D_x}{\kappa u_*} \right) \quad (4)$$

To determine the constants A and B , we invoke the boundary conditions. If a is uniformly distributed throughout the ocean, the BC's are

$$X(z) \rightarrow 0; z \rightarrow \infty$$

$$-D_x \frac{\partial X}{\partial z} = F_{xs}; z \rightarrow 0 \quad (5)$$

Because l_0 becomes large as z increases, condition (5a) implies $A=0$. If we assume that $X=B^*K_0(\xi)$, then the transport component of the total flux can be evaluated at the surface (condition 5b)

$$\frac{F_{xt}}{B} = -(D_x + \kappa u_* z) \frac{\partial K_0(\xi)}{\partial z}$$

$$= -\frac{(\kappa u_*)^2}{4a} \xi^2 \frac{\partial K_0(\xi)}{\partial \xi} \frac{2a}{\kappa u_*} \xi^{-1}$$

$$= \frac{\kappa u_*}{2} \xi K_1(\xi) = \frac{F_{xs}}{B}$$

$$B = \frac{2F_{xs} / \kappa u_*}{\xi_0 K_1(\xi_0)}$$

$$\xi_0 = \frac{2}{\kappa u_*} \sqrt{aD_x}$$

Determination of B allows us to explicitly write the equation for the profile of X in the water:

$$X(z) = \frac{2F_{xs} / \kappa u_*}{\xi_0 K_1(\xi_0)} K_0(\xi) \quad (6)$$

Notice that (6) implies that the transport flux, $F_{xt}(z)$, is not constant, but declines as the gas is absorbed as described by (2). A bit of algebra shows that (2) can be written

$$\text{Total Flux} = [\xi K_1(\xi) + \int_{\xi_0}^{\xi} \xi K_0(\xi) d\xi] \frac{F_{xs}}{\xi_0 K_1(\xi_0)} \quad (7)$$

The first term is the transport (turbulent plus molecular diffusion) and the second the loss by chemical reaction. Far into the water, the transfer term becomes 0 and the flux entering the fluid has all been consumed:

$$F_{xs} = a \int_0^{\infty} X(z) dz = \frac{\kappa u_*}{2} B \int_{\xi_0}^{\infty} K_0(\xi) \xi d\xi \quad (8)$$

The water-side transfer velocity is obtained simply from the definition of deposition velocity as interfacial flux divided by concentration using (6)

$$V_{xw} = \frac{\kappa u_* \xi_0 K_1(\xi_0)}{2 K_0(\xi_0)} = \sqrt{aD_x} \frac{K_1(\xi_0)}{K_0(\xi_0)} \quad (9)$$

4. DEPOSITION INTERPRETATION

Equation (9) describes transfer process in the ocean. The total transfer from the atmospheric to oceanic boundary layers is characterized by the total deposition velocity

$$V_d = [R_a + R_b + (\alpha V_{xw})^{-1}]^{-1} \quad (10)$$

Where R_a and R_b are the atmospheric resistances as described in the introduction and

$$R_c = (\alpha V_{xw})^{-1} \quad (11)$$

In the limit that the reactivity is very large, the effect of turbulent transport becomes negligible. Using the limits of Bessel functions, we can show that (9) becomes

$$V_{wx} = F_{xs} / X_{ws} = \sqrt{aD_x} \quad (12)$$

which is the original solution from Garland et al. (1980)

5. DISCUSSION

Observed deposition velocities are reported in the literature with values ranging from $V_d \sim 0.01$ to 0.12 cm s^{-1} for ocean water and $0.01 - 0.1 \text{ cm s}^{-1}$ for fresh water. The literature gives little details on the chemical, biological and physical water properties during the observations. Currently, values on the order of $V_d = 0.013$ to 0.05 cm s^{-1} are used in atmospheric chemistry models (Ganzeveld and Lelieveld, 1995; Shon et al., 2002).

The ocean-side transfer velocity given in (9) depends principally on the forcing (atmospheric friction velocity), the molecular diffusivity (or Schmidt number), and the reactivity. The effective 'pull' on the atmosphere also requires the solubility. A simple example of sensitivity to forcing and reactivity is shown in Fig. 1. Here we plot a family of curves (each curve for a different value of u_a) for the dependence of $\alpha_x V_{xw}$ as a function of reactivity. The curves are bounded on the bottom by the no-turbulence theory of Garland et al. (1980). The family of curves spans wind speeds from about 1.0 to 15 ms^{-1} . It is clear from this figure that ocean turbulence could play a significant role in the variability of ozone deposition. Also, for strong winds the deposition velocity is much more weakly dependent on a . Fig.2 shows wind speed dependencies obtained using (9) in (10) when specifying $a = 10^3 \text{ s}^{-1}$. Note the atmospheric transfer velocity (solid line) is about 10

times larger than the effective oceanic velocity. Thus, even for this value of a , the ocean is the dominant bottleneck to transfer; a would have to be two orders of magnitude larger for the oceanic and atmospheric resistances to be comparable. The windspeed dependence of the no-turbulence theory is very weak because it enters only through the atmospheric component - (12) does not depend on u^* . The model of Chang et al. (2004), which empirically incorporates ocean turbulence in a less rigorous way, gives results fairly similar to (9).

The one-layer parameterization has been coded in Matlab and Fortran90 in a form that is easily paired with the NOAA-COARE flux algorithm (Fairall et al., 2003). In addition to the normal near-surface variables needed for bulk fluxes (i.e., in the COARE algorithm), inputs are required for α_x , a , and S_{cw} . For illustration we have computed transfer velocities from a recent field program on the NOAA Ship *Ronald H. Brown* that was conducted off the coast on New Hampshire in July and August, 2004. Further details on the measurements and the field program are available at <http://www.etl.noaa.gov/programs/2004/neags/flux/>. The bulk meteorological variables measured from the ship are input to the NOAA-COARE flux algorithm and then the meteorological fluxes are used to compute the ozone deposition velocity. Deposition velocities are computed for a 16 day period after specifying $\alpha_x=0.3$, $a=1e3\text{ s}^{-1}$, and $S_{cw}=500$. The no-turbulence model shows little variation except for occasional periods of lighter winds and strong atmospheric stability (warm air over cool water) where hydrostatic stability effects suppress both u^* and the atmospheric transfer.

This work has several implications for interpretation and planning of field observations. Typical deposition values quoted in the literature imply that the atmospheric resistance is small compared to the oceanic resistance. Furthermore, the atmospheric resistance is well-characterized after decades of study of temperature, moisture, and trace gas investigations. Thus, oceanic mechanisms dominate the uncertainty in the parameterization of ozone deposition to the sea. This uncertainty involves not only the normal complexity of oceanic mechanisms such as breaking waves and oceanic bubbles (see Fairall et al., 2000) but the additional uncertainty associated with variability in the near-surface chemical reactions. It is clear that significant progress on ozone deposition in the future will require field observations that combine direct covariance ozone measurements with chemical and physical measurements in the ocean in a variety of locations that span reasonable ranges of variables. Furthermore, accurate global modeling/assessment of ozone fluxes will probably require global characterizations of near-surface chemistry relevant to ozone oceanic transfer.

The algorithms and data used in this example are available at the following ftp site:
<ftp://ftp.etl.noaa.gov/user/cfairall/bulkalg/gasflux/ozone/>.

6. ACKNOWLEDGMENTS

This work is supported by the NOAA Office of Global Programs (Carbon Cycle program element), the NOAA Health of the Atmosphere program, and NSF award CHE-BE #0410048

7. REFERENCES

- Chang, W., B. G. Heikes, and M. Lee, 2004: Ozone deposition to the sea surface: chemical enhancement and wind speed dependence. *Atmos. Environ.*, **38**, 1053-1059.
- Fairall, C.W., J.E. Hare, J.B. Edson, and W. McGillis, 2000: Parameterization and micrometeorological measurements of air-sea gas transfer. *Bound.-Layer Meteorol.*, **96**, 63-105.
- Fairall, C. W., E. F. Bradley, J. E. Hare, A. A. Grachev, and J. B. Edson, 2003: Bulk parameterization of air-sea fluxes: Updates and verification for the COARE algorithm. *J. Clim.*, **16**, 571-591.
- Ganseveld, L. and J. Lelieveld, 1995: Dry deposition parameterization in a chemistry general circulation model and its influence on the distribution of reactive trace gases. *J. Geophys. Res.* **100**, 20999-21,012.
- Garland, J. A., A. W. Etzerman, and S. A. Penkett, 1980: The mechanism for dry deposition of ozone to seawater surfaces. *J. Geophys. Res.*, **85**, 7488-7492.
- Geernaert, L.L.S., G. L. Geernaert, K. Granby, W.A.H. Asman, 1998: Fluxes of soluble gases in the marine atmospheric surface layer. *TellusB*, **50**, 111-127.
- Hare, J., C. Fairall, W. McGillis, J. Edson, B. Ward, and R. Wanninkhof, 2004: Evaluation of the NOAA/ COARE air-sea gas transfer parameterization using GasEx data. *J. Geophys. Res.*, **109** (C8): Art. No. C08S.
- Liss, P., 1973: Processes of gas exchange across an air-water interface. *Deep-Sea Res.*, **20**, 221-228.
- Shon Z.-H. and N. Kim, 2002: A modeling study of halogen chemistry's role in marine boundary layer ozone. *Atmos. Environ.* **36**, 4289-4298.
- Wesely M.L. and Hicks B.B., 2000: A review of the current knowledge on dry deposition. *Atmos. Environ.* **34**, 2261-2282.

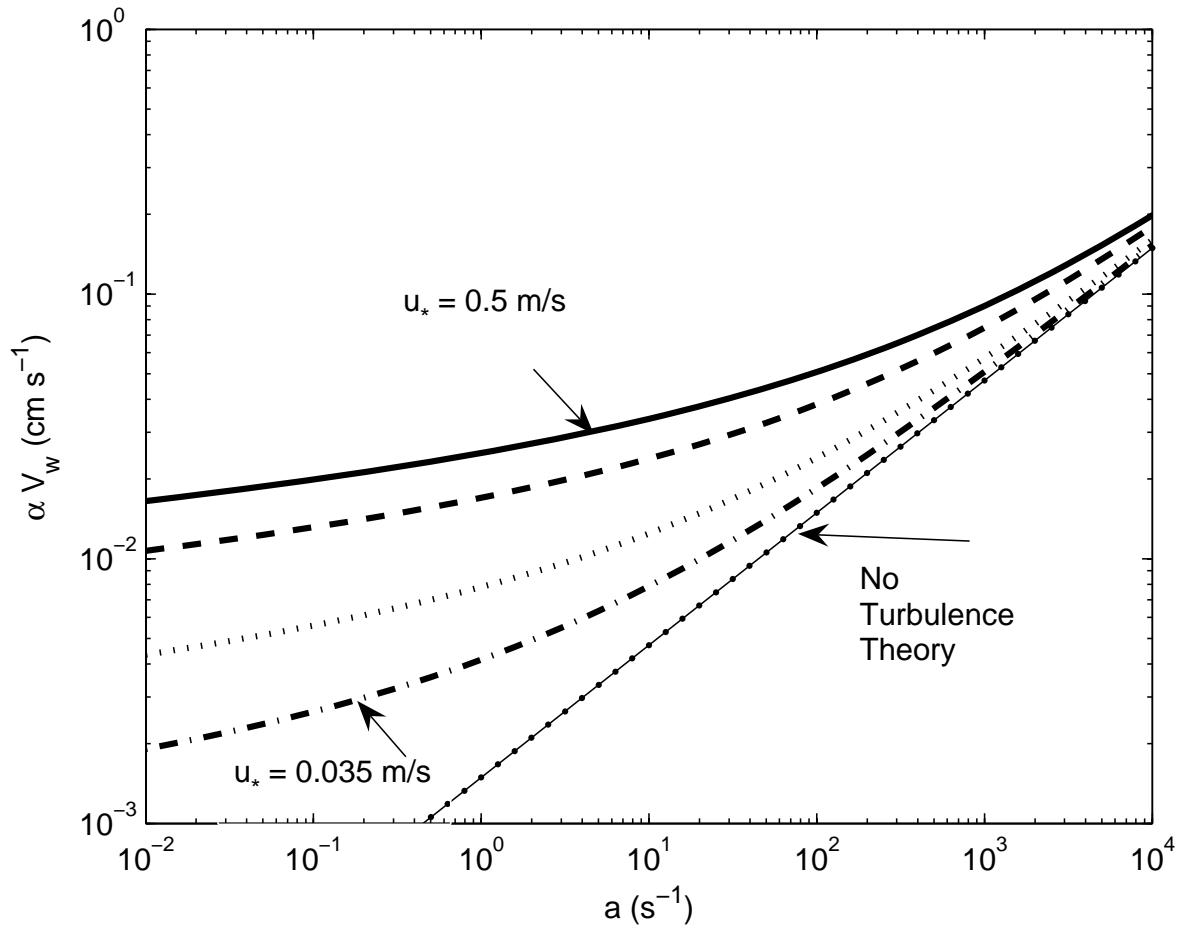


Figure 1. Water-side transfer velocity (multiplied by solubility) for ozone from (9) as a function of reactivity, a . The individual curves are for different values of atmospheric friction velocity: solid – $u_{*a}=0.5 \text{ ms}^{-1}$; dashed – $u_{*a}=0.3 \text{ ms}^{-1}$; dotted – $u_{*a}=0.1 \text{ ms}^{-1}$; dashdot – $u_{*a}=0.035 \text{ ms}^{-1}$. The dots with the thin line are the no-turbulence solution.

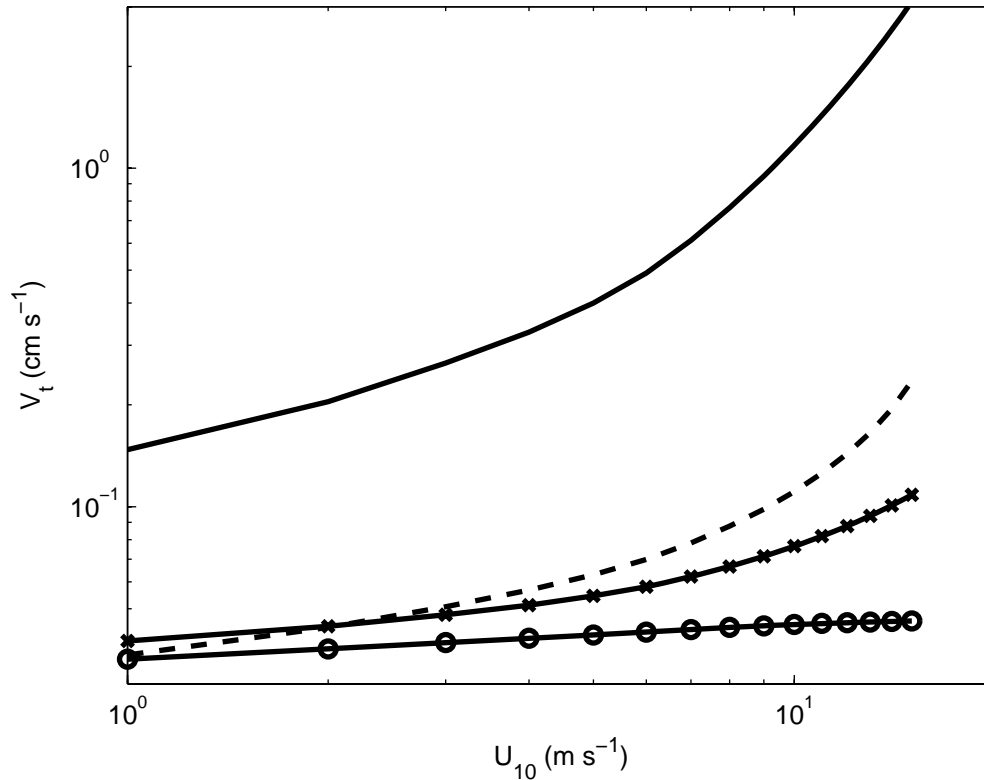


Figure 2. Transfer velocities as a function of wind speed for ozone with $a=1000 \text{ s}^{-1}$. The solid line is the atmospheric component, $(R_a^{-1}+R_b^{-1})^{-1}$ from (10). The dashed line is V_d from (10) using (9) for V_{xw} ; the line with circle symbols is V_d from (10) using (12); the line with x's is V_d from Chang et al. (2004).

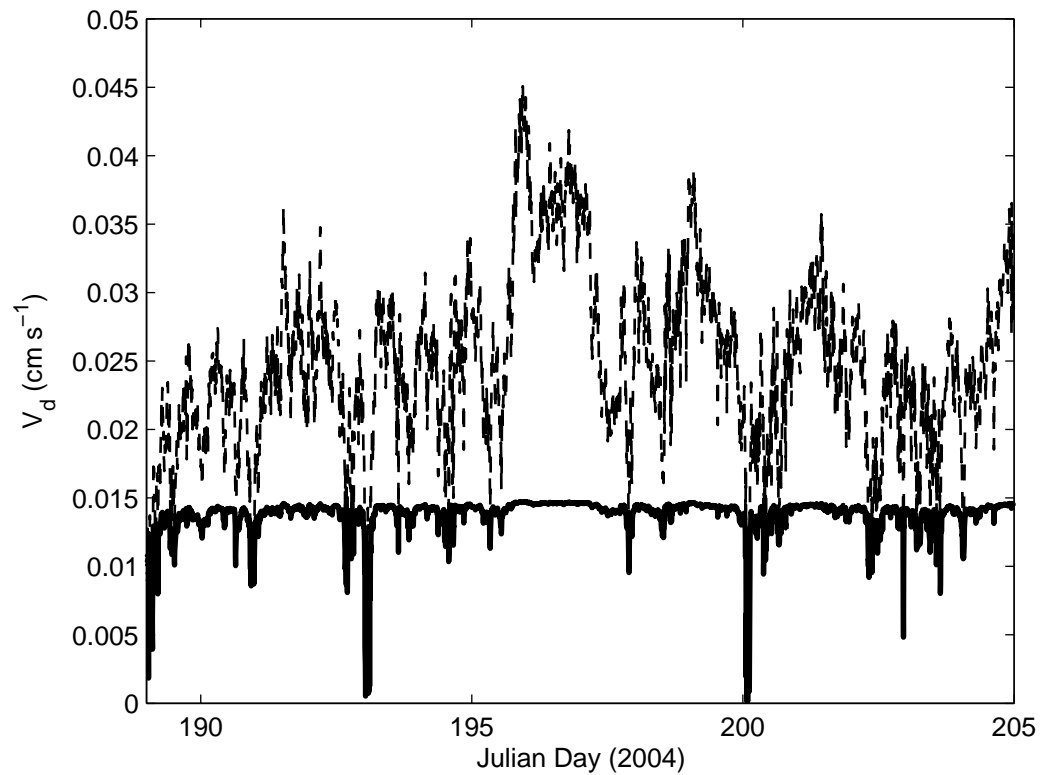


Figure 3. Time series of ozone deposition velocity computed from bulk meteorological measurements from a recent cruise of the NOAA Ship *Ronald H. Brown* off New England in July and August, 2004. The thick line is V_d computed with using (12) in (10), which neglects turbulent transport in the ocean; the thin dashed line is (9) in (10), which includes turbulent transport in the ocean. Ozone variables are specified as $\alpha_x = 0.3$, $a = 1e3 \text{ s}^{-1}$, and $S_{CW} = 500$