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Atmospheric Chemistry and Physics Discussions

Water-side turbulence enhancement of ozone deposition to the ocean

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Abstract

A parameterization for the deposition velocity of an ocean-reactive atmospheric gas (such as ozone) is developed. The parameterization is based on integration of the turbulent-molecular transport equation (with a chemical source term) in the ocean. It extends previous work that only considered reactions within the oceanic molecular sublayer. The sensitivity of the ocean-side transport to reaction rate and wind forcing is examined. A more complicated case with a much more reactive thin surfactant layer is also considered. The full atmosphere-ocean deposition velocity is obtained by matching boundary conditions at the interface. For an assumed ocean reaction rate of 10^3 s^{-1}, the enhancement for ozone deposition by oceanic turbulence is found to be up to a factor of three for meteorological data obtained in a recent cruise off the East Coast of the U.S.

1 Introduction

The transport, formation and depletion of ozone have received significant research attention because of the recognized importance of ozone for the chemical and radiative properties of the atmosphere. Ozone is the most important precursor of the OH radical in the troposphere. Both ozone and OH are fundamental for the oxidizing capacity of the atmosphere and their concentrations determine the removal rates of many atmospheric contaminants. Increased anthropogenic emissions of nitrogen oxides and hydrocarbons, both being precursors of photochemical ozone production in the atmosphere, have led to significant increases in global, surface-level ozone concentrations. It has been estimated that tropospheric ozone has at least doubled since pre-industrial times (Lamarque et al., 2005). Observations from background monitoring sites indicate that ozone continues to rise (Oltmans et al., 1998; Vingarzan et al., 2004; Helmig

et al., 2006[1]). Previous and anticipated future increases in background tropospheric ozone are a concern for several reasons. Ozone is a toxin to humans and animal life on Earth. Furthermore, tropospheric ozone has a significant (~13%) contribution to anthropogenic greenhouse gas forcing (IPCC 2001), which possibly might further increase in the future due to continued increases in ozone and concomitant reductions in the growth rates other important greenhouse gas emissions. These unique roles of ozone in atmospheric chemistry have motivated a plethora of research on improving our understanding of formation, transport and loss processes of atmospheric ozone.

Ozone deposition to the oceans represents a significant loss from the atmosphere; however, atmospheric and oceanic processes that determine the uptake of ozone to surface water are poorly understood. 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 that describes the quasi-laminar 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).

Observed deposition velocities are reported in the literature with values ranging from V_d~0.01 to 0.12 cm s^{-1} for ocean water and 0.01–0.1 cm s^{-1} for fresh water (Ganzeveld

[1]Helmig, D., Oltmans, S. J., Carlson, D., Lamarque, J.-F., Jones, A., Labuschagne, C., Anlauf, K., and Hayden, K.: Surface ozone in the polar regions, Atmos. Environ., submitted, 2006.

et al., 2006[2]). This 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 and Kim, 2002). Because the observations do not yield a consensus on wind speed dependency, the same ozone surface resistance is typically applied to all of the world's oceans and wind conditions.

In general, the deposition of ozone involves both turbulent and molecular diffusive plus chemical processes in air and water. If atmospheric chemical reactions are negligible (see Lenschow, 1982; Geernaert et al., 1998; Sorensen et al., 2005, for counter examples), then the atmospheric part of the problem can be treated with standard similarity theory (Fairall et al., 2000). In the near-surface region, vertical turbulent diffusion in both fluids exhibits near-linear height/depth dependence associated with restriction of eddies by the presence of the boundary. Furthermore, the viscosity of a turbulent fluid causes dissipation of the turbulence that is more intense the smaller the turbulent eddy. This leads to a turbulent microscale $\delta_u \approx 10\nu/u_*$ (ν is the fluid kinematic viscosity and u_* the friction velocity) such that the spectrum of turbulent fluctuations for eddies smaller than δ_u is exponentially attenuated. Because of this suppression of turbulent eddies near the boundary, ozone entering the water from the air is initially transported away from the interface solely by molecular diffusion. This interfacial region dominated by molecular transport is called the *molecular sublayer*. The time scale associated with random molecular transport over a distance δ is $t_D=\delta^2/D_x$ where D_x is the molecular diffusivity of the gas, X, in the fluid. If the time scale of some chemical reaction for X within the fluid can be characterized by $1/a$, then in the absence of turbulent effects, we expect the reaction to be substantially completed within a distance $\delta=[D_x/a]^{1/2}$. Because δ_u is about 10^{-3} m, this simple scale analysis suggests that for ozone turbulent

[2]Ganzeveld, L., Helmig, D., Fairall, C. W., and Pozzer, A.: Biogeochemistry and water-side turbulence dependence of global atmospheric-ocean ozone exchange, Global Biogeochem. Cycles, in preparation, 2006.

transport effects need not be considered when a exceeds about $100\,s^{-1}$.

Garland et al. (1980) used a horizontally homogeneous conservation equation to link the oceanic chemical reactivity of ozone to the oceanic deposition resistance by solving the case where $\delta \ll \delta_u$ (i.e., turbulent diffusion was neglected). Schwartz (1992) discussed the more general problem of the balance of solubility and aqueous reaction kinetics from the point of view of chemical enhancement of solubility for reversible reactions for a variety of gases. Chemical enhancement refers to an apparent increase of the solubility of the gas by reactions in the water. The context for that discussion was the *stagnant film* model, which is equivalent to neglecting turbulent transport in the aqueous phase. In the irreversible limit, Schwartz's results for ozone reduce to the Garland result. More recently, Chang et al. (2004) expanded the scope to combine molecular diffusive - chemical and turbulent diffusive - chemical processes as parallel resistances. In this approach, the oceanside stagnant film resistance of Garland et al. (1980), R_g, acts independently and in parallel with a Schmidt-number dependent oceanic resistance, R_w, taken from Wanninkhof (1992) but which includes a chemical enhancement factor: $R_c=(1/R_w+1/R_g)^{-1}$. 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 apply this formalism to 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. Whereas Chang et al. (2004) postulate that the deposition velocity is a combination of independent parallel resistances, we derive the deposition velocity analytically from the fundamental conservation equations (albeit in simplified form). Their approach includes a characteristic reaction constant, a, plus the chemical enhancement factor, β; in our approach, the "enhancement" effect is a natural consequence of the solutions to the budget equa-

tion.

2 Conservation equation

Using the notation from the 2000 Fairall et al. paper, the budget equation for the mass concentration of some chemical, X_w, in water is

$$\partial X_w/\partial t + \boldsymbol{U}\cdot\nabla X_w = -\frac{\partial\left[\overline{w'x'_w} - D_{xw}\partial X_w/\partial z\right]}{\partial z} - aX_w \tag{1}$$

where z is the vertical coordinate (distance from the interface, i.e., *depth* for the ocean), U the mean horizontal flow, $\overline{w'x'_w}$ the turbulent flux (positive downward), D_{xw} the molecular diffusivity of X in water, and the last term is the loss rate of X_w due to reactions with some chemical Y_w. We represent the turbulent flux in terms of an eddy diffusion coefficient, $\overline{w'x'_w}=-K\frac{\partial X_w}{\partial z}$, where $K(z)$ is the turbulent eddy diffusivity,

$$\partial X_w/\partial t + \boldsymbol{U}\cdot\nabla X_w = -\frac{\partial\left[-(D_{xw} + K(z))\partial X_w/\partial z\right]}{\partial z} - aX_w \tag{2}$$

The reactivity $a=C_{xy}Y_w$, where Y_w is the concentration of the reacting chemical and C_{xy} the reaction rate constant. Assuming Y_w is constant with depth, we can move the reaction ($a*X_w$) term inside the z-derivative and associate this with a flux, F_{xw}, variable which, in dynamic equilibrium, is constant:

$$-\left[D_{xw} + K(z)\right]\partial X_w/\partial z + a\int_0^z X_w(z)dz = F_{xw}. \tag{3}$$

This flux variable is the sum of transport (mixing) fluxes by molecular diffusion, F_{xD}, and turbulent diffusion, F_{xT}, plus an apparent flux associated with the decreasing concentration of ozone as it enters and penetrates the ocean and is destroyed by reaction with Y.

To apply Eqs. (2) and (3) to the case of an inert or weakly reacting gas, we let a=0. This simplifies the analysis because we can directly write an equation for the concentration difference:

$$\frac{\partial X_w}{\partial z} = \frac{F_{xw}}{D_{xw} + K(z)} \tag{4a}$$

$$X_{ws} - X_w(z_r) = F_{xw} \int_0^{z_r} \frac{dz}{D_{xw} + K(z)} = F_{xw} \left\{ \int_0^{\delta_u} \frac{dz}{D_{xw} + K(z)} + \int_{\delta_u}^{z_r} \frac{dz}{D_{xw} + K(z)} \right\} \tag{4b}$$

From Eq. (4b) the resistance law analogy becomes apparent where the total resistance R_{xw} (which is the inverse of the transfer velocity, V_{xw}) is the sum of the molecular diffusion sublayer resistance, R_{xwm}, and the turbulent layer, R_{xwt},

$$X_{ws} - X_w = F_{xw}R_{xw} = F_{xw}(R_{xwm} + R_{xwt}) = F_{xw}/V_{xw} \tag{5}$$

Here R_{xwm} is the integral over the velocity diffusion sublayer and R_{xwt} the integral from the top of the turbulent layer to the reference depth.

We can write a similar equation for the transport of X in the atmosphere (Fairall et al., 2000). Conventionally, the atmospheric equation is defined with the vertical ordinate as height above the interface and transport fluxes are defined positive *upward* so that the flux in the atmosphere associated with deposition to the surface is given by

$$F_{xa} = -V_{dx}X_a = -F_{xws} \tag{6}$$

where X_a is the mass concentration at some reference height in the atmosphere and F_{xws} is the flux into the water at the air-water interface. In equilibrium, the oceanic total flux (remember, this flux is the sum of local transport and accumulated loss of X via chemical reaction) is independent of depth, so F_{xws}=F_{xw}. As in Eq. (5) the atmospheric

flux can be characterized by an atmospheric-side transfer velocity and the difference in the concentration at the interface and the reference height

$$F_{xa} = V_{xa}(X_{as} - X_a) = \frac{(X_{as} - X_a)}{(R_{xam} + R_{xat})} \tag{7}$$

In the absence of atmospheric chemical reactions, the R_a=R_{xam} and R_b=R_{xat} terms would follow from integrating Eq. (4b) with the normal similarity relations (Fairall et al., 2000). A similar relationship applies for the ocean side

$$F_{xa} = -F_{xws} = -V_{xw}(X_{ws} - X_w) \tag{8}$$

Using the solubility relationship X_{ws}=$X_{as} * \alpha_x$, where α_x is the dimensionless solubility of X, we can eliminate the surface concentrations and derive a general flux relationship in terms of the atmospheric and oceanic gas concentrations

$$F_{xa} = \frac{(X_w/\alpha_x - X_a)}{(R_a + R_b) + (\alpha_x V_{xw})^{-1}} \tag{9}$$

Note that Eq. (9) can be applied even if there is a chemical reaction in the ocean, but the interpretation of the atmospheric resistance as a sum of molecular and turbulent diffusion sublayer components only follows directly from the budget equation for a non-reactive atmosphere. For the deposition problem where ozone is destroyed by chemical reaction in the ocean, X_w=0, it follows that

$$R_c^{-1} = \alpha_x V_{xw} = \alpha_x F_{xws}/X_{ws} \tag{10a}$$

$$V_{dx} = (R_a + R_b + R_c)^{-1} \tag{10b}$$

3 Oceanic transfer velocity from the budget equation

In this section we will solve the basic conservation equation for ozone entering the ocean from the atmosphere. To simplify the notation, we will drop the w subscripts in this section because it deals only with oceanic processes.

3.1 Negligible turbulence solution

In the limit that the reaction is so strong that the profile of X_w becomes negligible within the oceanic molecular sublayer (besides ozone, other obvious examples include HNO_3 and SO_2; the paradox that ozone is both strongly reacting in the ocean and is ocean-transfer limited is caused by its weak solubility), we can neglect the K term and write

$$D_x \frac{\partial^2 X}{\partial z^2} - aX = 0 \tag{11}$$

Assuming that the concentration of Y is much larger than X so that it remains effectively constant, the solution is (Garland et al., 1980)

$$X = X_s \exp\left[-\sqrt{\frac{a}{D_x}}z\right] \tag{12}$$

where X_s is the concentration of X at the water surface. The diffusive flux at any depth in the fluid is

$$F_{xD}(z) = -D_x \frac{\partial X}{\partial z} = -D_x \frac{\partial}{\partial z}\left\{X_s \exp\left[-\sqrt{\frac{a}{D_x}}z\right]\right\} = X_s\sqrt{aD_x}\exp\left[-\sqrt{\frac{a}{D_x}}z\right] \tag{13}$$

The diffusive flux is a function of depth but at the interface (z=0)

$$F_{xD}(0) = F_{xs} = X_s\sqrt{aD_x} \tag{14}$$

From Eq. (10) it immediately follows that

$$V_{xw} = F_{xs}/X_s = \sqrt{aD_x} \tag{15}$$

3.2 Non-negligible turbulence solution

To consider the turbulent transport case, we first specify a simple form for the turbulent eddy diffusivity that is obtained from surface-layer similarity scaling (Fairall et al., 2000) $K(z)=\kappa u_* z$. Here we have neglected buoyancy (stability effects), $\kappa=0.4$ is the von Karman constant, and u_* is the friction velocity in the *ocean* surface layer. If we do not neglect turbulent transport, then Eq. (2) becomes

$$\frac{\partial}{\partial z}\left[(D_x/\kappa u_* + z)\frac{\partial X}{\partial z}\right] - \frac{a}{ku_*}X = 0 \tag{16}$$

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)

$$X = AI_0(\xi) + BK_0(\xi)$$
$$\xi^2 = \frac{4a}{\kappa u_*}\left(z + \frac{D_x}{\kappa u_*}\right) \tag{17}$$

Details on modified Bessel functions of order n, I_n and K_n, can be found in Abramowitz and Stegun (1964). To determine A and B, we invoke the boundary conditions. If a is uniformly distributed throughout the ocean, the boundary conditions are defined at the interface (z=0) and infinitely deep in the ocean ($z \to \infty$)

$$\text{Deep Ocean:} \quad X(z) \to 0\ ;\ z \to \infty \tag{18a}$$

$$\text{Surface:} \quad -[D_x + K(z)]\frac{\partial X}{\partial z} = F_{xs}\ ;\ z \to 0 \tag{18b}$$

Because I_0 becomes large as z increases, condition Eq. (18a) implies A=0. If we assume that $X=B^*K_0(\xi)$. In terms of K_0, the total mixing component of the flux is

$$F_{xM} = F_{xD} + F_{xT} = -(D_x + \kappa u_* z)\frac{\partial X}{\partial z} = -B(D_x + \kappa u_* z)\frac{\partial K_0(\xi)}{\partial z} \tag{19}$$

Writing this in terms of the variable ξ, we use the property of K_0 so that $-\xi\frac{\partial K_0}{\partial \xi}=K_1$ to describe the mixing component as a function of depth

$$\frac{F_{xM}}{B} = -\frac{(\kappa u_*)^2}{4a}\xi^2\frac{\partial K_0(\xi)}{\partial \xi}\frac{\partial \xi}{\partial z} = -\frac{(\kappa u_*)^2}{4a}\xi^2\frac{\partial K_0(\xi)}{\partial \xi}\frac{2a}{\kappa u_*}\xi^{-1} = \frac{\kappa u_*}{2}\xi K_1(\xi) \tag{20}$$

We then determine the constant B by evaluating Eq. (20) at the surface (condition 18b)

$$B = \frac{2F_{xs}/\kappa u_*}{\xi_0 K_1(\xi_0)} \tag{21}$$

where

$$\xi_0 = \frac{2}{ku_*}\sqrt{aD_x} \tag{22}$$

Determination of B allows us to explicitly write the equation for the profile of X in the water. We substitute Eq. (21) in Eq. (17a) with A=0:

$$X(z) = \frac{2F_{xs}/\kappa u_*}{\xi_0 K_1(\xi_0)}K_0(\xi) \tag{23}$$

And the profile of the mixing component of the flux

$$F_{xM}(z) = F_{xs}\frac{\xi K_1(\xi)}{\xi_0 K_1(\xi_0)} \tag{24}$$

Notice that Eq. (24) describes how $F_{xM}(z)$ declines as the gas is absorbed; the decline of the mixing flux is balanced by destruction of$X$ by chemical reaction. A bit of algebra shows that Eq. (3) can be written

$$\text{Total Flux} = \left[\xi K_1(\xi) + \int_{\xi_0}^{\xi}\xi K_0(\xi)d\xi\right]\frac{F_{xs}}{\xi_0 K_1(\xi_0)} \tag{25}$$

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

$$F_{xs} = a\int_0^\infty X(z)dz = \frac{\kappa u_*}{2}B\int_{\xi_0}^\infty K_0(\xi)\xi d\xi \tag{26}$$

Through the properties of Bessel functions, $\xi K_0(\xi) = -\frac{\partial(\xi K_1(\xi))}{\partial\xi}$, Eq. (26) provides an alternate method to relate B to the surface flux.

The water-side transfer velocity is obtained simply from using Eq. (23) in Eq. (15)

$$V_{xw} = \frac{\kappa u_*}{2}\frac{\xi_0 K_1(\xi_0)}{K_0(\xi_0)} = \sqrt{aD_x}\frac{K_1(\xi_0)}{K_0(\xi_0)} \tag{27}$$

The limiting values of Bessel functions are well known, so we can examine Eq. (27) in the limit where a is large; in this case, ξ_0 is large and the ratio $K_1/K_0=1$. Thus, we recover the Garland et al. (1980) solution given in Eq. (15). The profile of $X(z)$ in the diffusion sublayer is given by Eq. (4) and the concentration of X approaches 0 for $z>D_x/\kappa u_*$.

For small values of a, we find that

$$V_{xw} \to -\frac{\kappa u_*}{2}\ln\left(\frac{2}{\kappa u_*}\sqrt{aD_x}\right) \tag{28}$$

In this regime the profile of X is linear in the diffusion sublayer and then logarithmic in z and approaches 0 for $z\approx\kappa u_*/4a=\delta_T$. The transition between strongly and weakly reacting regimes occurs for $\xi_0\approx1$

$$a_{\text{crit}} = \frac{(\kappa u_*)^2}{4D_x} \tag{29}$$

Typical open ocean values in Eq. (29) give the transition around $a_{\text{crit}} \approx 1000\,\text{s}^{-1}$. Ganzeveld et al. (2006)[2] find the value of a for ozone considering the Iodide-DMS-alkene chemistry never exceeds $1000\,\text{s}^{-1}$. Introducing highly-parameterized DOM-O3 chemistry based on the chlorofyll concentrations, it is exceeded for some confined regions close to coasts. If a significantly exceeds a_{crit}, then ozone is consumed within the oceanic diffusion sublayer. The dimensionless parameter ξ_0 defined in Eq. (22) is, in fact, the ratio of the chemo-molecular diffusive scale δ_D defined in the Introduction and the chemo-turbulent diffusive scale δ_T defined above.

3.3 Two-layer reactivity (surfactant) solution

In this section we examine a more complicated vertical distribution of reactivity designed to mimic assumed properties of a highly reactive surfactant. A surfactant may be a hydrophilic material that tends to have much enriched concentration at the surface or a soluble compound that influences some surface property of seawater (e.g., viscosity or surface tension). We do not say what this surfactant is but specify its properties as having reactivity a beginning at the interface and down to a depth δ relative to some background reactivity a_o that is present everywhere. Here we consider a two-layer solution

Layer I: $0 < z < \delta$ where reactivity $= a + a_o$ $\quad X(z) = A_I I_0(\xi) + B_I K_0(\xi)$ (30a)

Layer II: $z > \delta$ where reactivity $= a_o X(z) = B_{II} K_0(\xi)$ (30b)

In layer I the solutions are described by Eq. (17a) but A is not 0; in layer II A=0.

In order to find the values of the three coefficients, we must match three boundary conditions: (1) the flux at the surface, (2) the continuity of concentration at the I-II boundary, and (3) the surface flux must equal the total absorption of X by reaction in the medium. For the general form of $X(z)$, the transport flux is

$$F_{xM}(z) = \frac{\kappa u_*}{2}[-A\xi I_1(\xi) + B\xi K_1(\xi)] \tag{31}$$

The three boundary conditions can be written as follows:

$$-A_I\xi_0 I_1(\xi_0) + B_I\xi_0 K_1(\xi_0) = \frac{2F_{xs}}{\kappa u_*}$$

$$A_I I_0(\xi_\delta) + B_I K_0(\xi_\delta) - B_{II} K_0(\xi_\delta) = 0$$

$$A_I(a + a_0)\int_0^\delta I_0(\xi)dz + B_I(a + a_0)\int_0^\delta I_0(\xi)dz + B_{II}a_0\int_\delta^\infty K_0(\xi)d\xi = F_{xs} \tag{32}$$

Alternatively, a flux continuity condition at the I-II interface can be substituted for any one of these equations. The three relationships from Eq. (32) can be written as the product of a 3X3 matrix times a coefficient vector = flux vector (H*$\mathbf{A}$=$\mathbf{F}$):

$$\begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \end{pmatrix} * \begin{pmatrix} A_I \\ B_I \\ B_{II} \end{pmatrix} = \begin{pmatrix} \frac{2F_{xs}}{\kappa u_*} \\ 0 \\ F_{xs} \end{pmatrix} \tag{33}$$

where the h_{ij} coefficients come from the terms in Eq. (32). The coefficients are found by inverting the H matrix, $\mathbf{A}$=H^{-1}*$\mathbf{F}$. Once the coefficients are obtained, the water-side transfer velocity is given by

$$V_{xw} = \sqrt{(a + a_0)D_x}\frac{[-A_I I_1(\xi_0) + B_I K_1(\xi_0)]}{[A_I I_0(\xi_0) + B_I K_0(\xi_0)]} \tag{34}$$

4 Discussion

The ocean-side transfer velocity given in Eq. (27) 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 atmospheric friction velocity u_{*a}) for the

dependence of $\alpha_x V_{xw}$ as a function of reactivity. The atmospheric friction velocity is roughly proportional to wind speed with a value of 0.35 ms^{-1} at a 10-m wind speed of 10 ms^{-1}. If we assume the atmospheric stress drives an equal turbulent stress in the ocean, then the oceanic friction velocity follows from the ratio of the densities

$$u_{*w} = \sqrt{\frac{\rho_a}{\rho_w}} u_{*a} \approx u_{*a}/30 \approx 0.0012 U_{10} \tag{35}$$

The curves in Fig. 1 are bounded on the bottom by the no-turbulence (stagnant film) theory of Garland et al. (1980). The family of curves spans wind speeds from about 1.0 to 15 ms^{-1}. For strong winds the oceanic transfer velocity is much more weakly dependent on a. Regarding the *total* atmospheric deposition velocity, interpretation of the implications of Fig. 1 requires specification of the atmospheric transfer. We use the NOAA-COARE gas transfer model (Fairall et al., 2000; Hare et al., 2004)

$$R_{xa} = R_a + R_b = \left[C_d^{-1/2} + 13.3 S_{ca}^{1/2} - 5 + \frac{\log(S_{ca})}{2\kappa} \right] / u_{*a} \tag{36}$$

where C_d is the momentum drag coefficient at the reference height and S_{ca} the Schmidt number for ozone in air (about 1). In Eq. (36) the C_d term represents R_a and the remaining terms represent R_b. For an atmospheric reference height of 10 m $C_d^{-1/2} \approx 28$; at a wind speed of 10 ms^{-1} the atmospheric resistance $R_a + R_b \approx 100\ \mathrm{sm}^{-1}$, implying a transfer velocity of about 1.0 cms^{-1}. Typical observed ozone total deposition values are on the order of 0.05 cms^{-1} (total $R = 2000\ \mathrm{sm}^{-1}$), so we know that R_c dominates the total transfer resistance. From Fig. 1 we can see that 0.05 cms^{-1} corresponds to $a \approx 10^3\ \mathrm{s}^{-1}$.

Because V_d for ozone is usually dominated by the oceanic component, it is clear from Fig. 1 that ocean turbulence probably plays a significant role in the variability of ozone deposition. This conclusion follows from the observed wind-speed dependence of V_d because the stagnant film result is independent of wind speed. An alternative explana-

tion is that a systematically increases with wind speed, which contradicts the conventional wisdom that surfactants are more prevalent in light winds. Figure 2 shows wind speed dependencies obtained using Eq. (27) in Eq. (9) when specifying $a=10^3\,\mathrm{s}^{-1}$. Note the atmospheric transfer velocity (solid line) is about 10 times larger than the effective oceanic velocity. Thus, 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 wind-speed dependence of the no-turbulence theory for V_d is very weak because it enters only through the atmospheric component – (15) does not depend on u_*. The model of Chang et al. (2004), which empirically incorporates ocean turbulence in a less rigorous way, gives results that are fairly similar to Eq. (27).

The surfactant case has been examined by specifying a background value $a_0=10^{-4}\,\mathrm{s}^{-1}$ to the result of a thin layer of thickness 10^{-5} m of surfactant as suggested by Schwartz (1992) (i.e. deep layers are not required). Figure 3 shows the dependence of $\alpha_x V_{xw}$ as a function of surfactant reactivity for $u_{*a}=0.035\,\mathrm{ms}^{-1}$. The one-layer (27) solution that assumes the reactant is deeply distributed and the two-layer (34) solution become comparable for a on the order of $100\,\mathrm{s}^{-1}$; for $u_{*a}=0.5\,\mathrm{ms}^{-1}$ (not shown) they become comparable for a on the order of $1000\,\mathrm{s}^{-1}$. This suggests that observed values of ozone deposition velocities could be the result of a thin layer of surfactant (i.e., deep layers are not required) as suggested by Schwartz (1992).

The one-layer ozone deposition velocity parameterization has been coded in Matlab and Fortran90 in a form that is easily paired with the NOAA-COARE bulk 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 of 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/neaqs/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 α_x=0.3, a=10^3 s^{-1}, and S_{cw}=500 (Fig. 4). 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.

5 Conclusion

Starting from the fundamental conservation equation, we have derived relationships for the deposition velocity of ozone to the ocean that accounts for the oceanic chemical destruction. 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. The value of reactivity (a=10^3 s^{-1}) that is consistent with observations of ozone deposition velocity suggest a thin ozone penetration depth in the ocean that could be provided by a surfactant microlayer. However, our results show that even in that case oceanic turbulent mixing will still play a role in deposition (e.g., Fig. 2).

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 (see Ganzeveld et al., 2006[2]).

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/.

List of Symbols

a	Chemical reactivity in the ocean (s^{-1})
a_{crit}	Value of a where molecular and turbulent diffusive mechanisms are comparable
t	Time (s)
u_*	Friction velocity; $u_* = \sqrt{-\overline{w'u'}}$ (ms^{-1})
u_{*a}	Friction velocity for air
u_{*w}	Friction velocity for water
u'	Horizontal velocity turbulent fluctuation
w'	Vertical velocity turbulent fluctuation
x'	Turbulent fluctuation of concentration X
$\overline{w'x'}$	Turbulent covariance (vertical flux) of gas X
$\overline{w'u'}$	Turbulent stress or covariance of vertical and horizontal velocity fluctuations
z	Vertical coordinate, depth in water and height in air (m)
z_r	Reference depth (or height in air) far from the interface where bulk concentration is measured
A	Coefficient the I_0 Bessel function term
A_I	Coefficient the I_0 Bessel function term in layer I (surfactant layer)
A_{II}	Coefficient the I_0 Bessel function term in layer II (bulk layer)
B	Coefficient the K_0 Bessel function term
B_I	Coefficient the K_0 Bessel function term in layer I (surfactant layer)
B_{II}	Coefficient the K_0 Bessel function term in layer II (bulk layer)
C_d	Momentum transfer (drag) coefficient
C_{xy}	Rate coefficient for reaction of X and Y, $a=C_{xy}Y_w$
D_x	Molecular diffusivity for gas X (m^2s^{-1})

D_{xa}	Molecular diffusivity for gas X in air
D_{xw}	Molecular diffusivity for gas X in water
F_x	Mass flux variable for gas X ($kgm^{-2}s^{-1}$)
F_{xs}	Mass flux variable for gas X at the air-water interface
F_{xa}	Mass flux variable for gas X in air
F_{xw}	Mass flux variable for gas X in water
F_{xD}	Mass flux variable for gas X associated with the molecular diffusion term
F_{xT}	Mass flux variable for gas X associated with the turbulent diffusion term
F_{xM}	Mass flux variable for gas X by mixing, $=F_{xD} + F_{xT}$
$K(z)$	Turbulent eddy diffusion coefficient (m^2s^{-1})
R	Transfer resistance (sm^{-1})
R_a	Transfer resistance for the atmospheric turbulent sublayer
R_b	Transfer resistance for the atmospheric molecular sublayer
R_c	Transfer resistance for the ocean
R_g	Transfer resistance for the ocean from ozone reactivity from Garland et al. (1980)
R_w	Transfer resistance for the ocean for mixing from Wanninkhof 1992
R_{xt}	Transfer resistance for the atmospheric turbulent sublayer computed via Eq. (4b) $R_{xta} = R_a$
R_{xm}	Transfer resistance for the atmospheric molecular sublayer computed via Eq. (4b) $R_{xma}=R_b$
S_{cx}	Schmidt number$=\nu/D_x$ for gas X
S_{ca}	Schmidt number$=\nu_a/D_{xa}$ for gas X in air
S_{cw}	Schmidt number$=\nu_w/D_{xw}$ for gas X in water
U	Horizontal fluid velocity, wind speed or current speed (ms^{-1})
U_{10}	Wind speed at a reference height of 10 m
V_d	Deposition velocity
V_{dx}	Deposition velocity for gas X
V_{xa}	Transfer velocity for gas X in air, $=1/R_{xa}$

V_{xw}	Transfer velocity for gas X in water, $=1/R_{xw}$
X_a	Concentration of X in air (kgm^{-3})
X_w	Concentration of X in water (kgm^{-3})
X_{as}	Concentration of X in air at the air-water interface (kgm^{-3})
X_{ws}	Concentration of X in water at the air-water interface (kgm^{-3})
Y_w	Concentration of the chemical Y that reacts with X in the water (kgm^{-3})
α_x	Dimensionless solubility for gas X in the ocean, $=X_{ws}/X_{as}$
β	Chemical enhancement factor where solubility is replaced by $\beta\alpha_x$
δ	Transport sublayer thickness (m)
δ_u	Turbulent microscale or velocity sublayer thickness
δ_D	Chemo-diffusive sublayer thickness for molecular diffusion
δ_T	Chemo-diffusive sublayer thickness for turbulent diffusion
ν	Kinematic viscosity of a fluid (m^{2}s^{-1})

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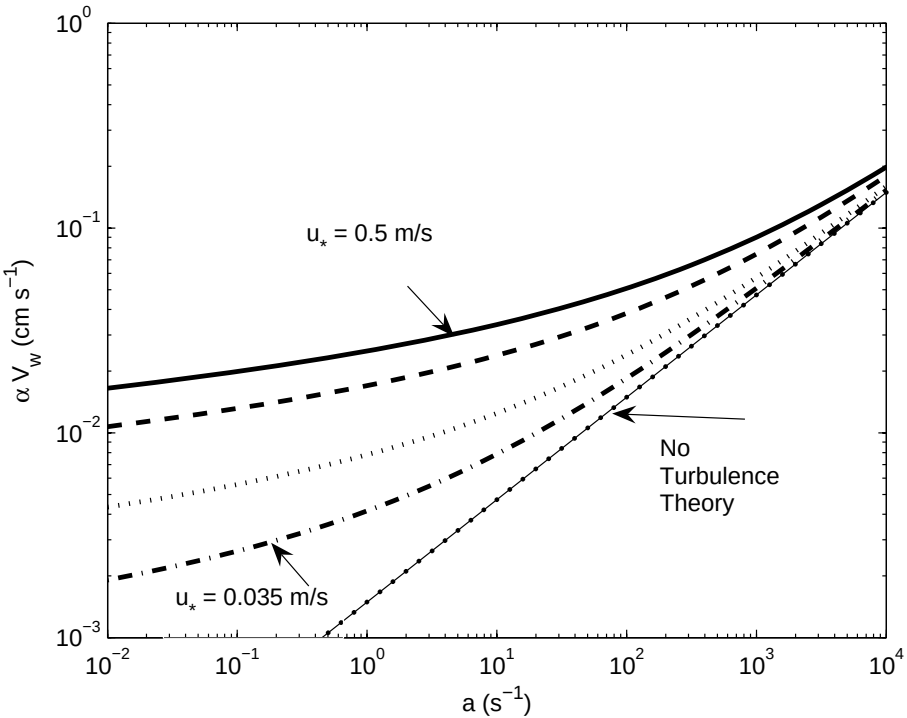

Fig. 1. Water-side transfer velocity (multiplied by solubility) for ozone from Eq. (27) as a function of reactivity, *a*. The individual curves are for different values of friction velocity: solid – u_{*a}=0.5 ms^{-1}; dashed – u_{*a}=0.3 ms^{-1}; dotted – u_{*a}=0.1 ms^{-1}; dashdot – u_{*a}=0.035 ms^{-1}. The dots with the thin line are the no-turbulence solution.

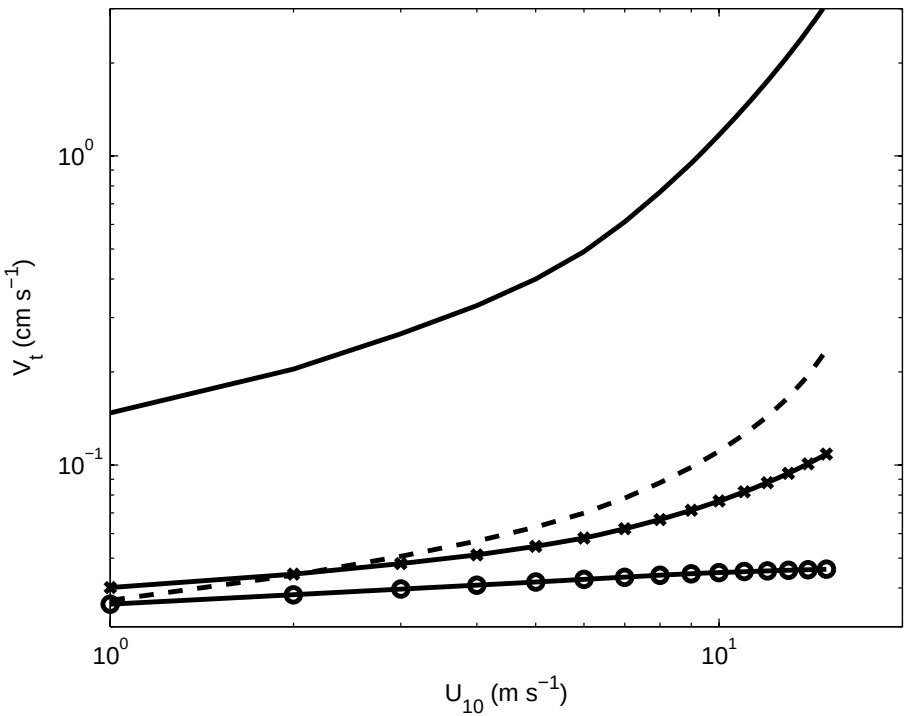

Fig. 2. Total deposition velocity as a function of wind speed for ozone using Eq. (10) with a=1000 s^{-1}. The solid line is the atmospheric component, R_{xa}, from Eq. (36). The dashed line is V_d combining Eq. (36) with Eq. (27) for V_{xw}; the line with circle symbols is V_d combining Eq. (36) with stagnant film result (15); the line with x's is V_d from Chang et al. (2004).

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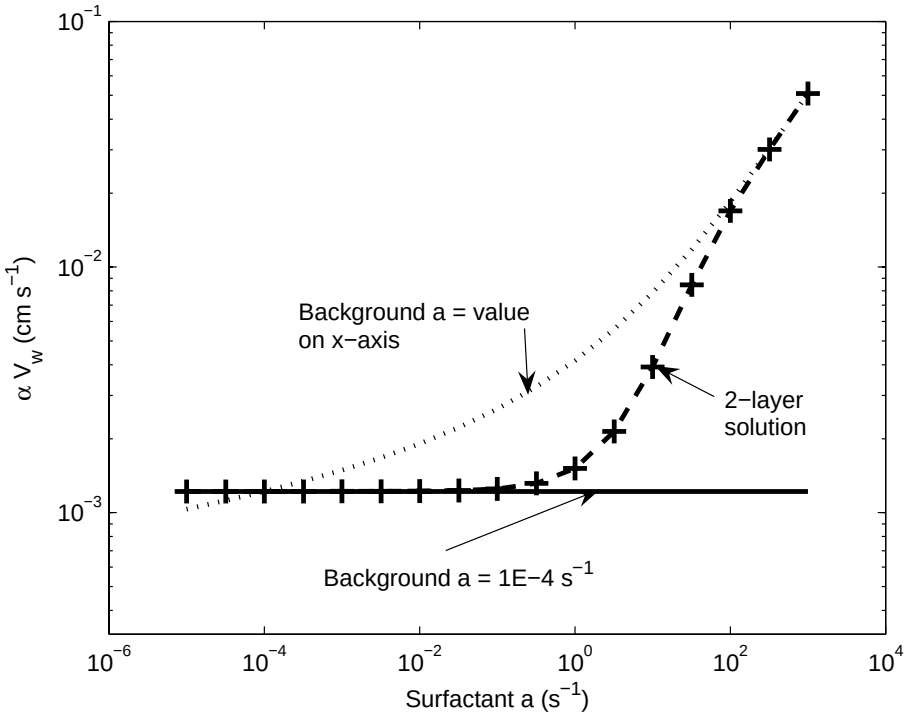

Fig. 3. Water-side transfer velocity (multiplied by solubility) for ozone as a function of reactivity, a, for u_{*a}=0.035 ms^{-1}. The flat solid line denotes the velocity with a fixed background at a=a_0=10^{-4}; the dotted line denotes the velocity computed with Eq. (27) with a taking the values on the x-axis. The dashed line with plus symbols denotes the velocity computed using Eq. (34) with a surfactant layer 10^{-5} m thick with reactivity on the x-axis which is added to the background value.

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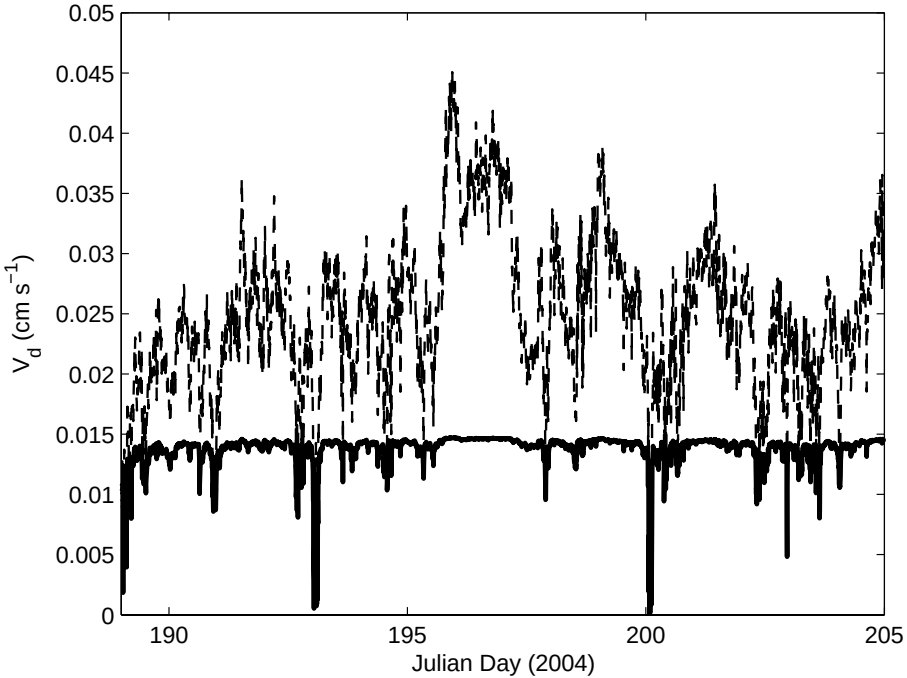

Fig. 4. Time series of ozone deposition velocity computed from bulk meteorological measurements from a recent cruise of the NOAA Ship *Ronald H. Brown* off New England in July and August 2004. The thick line is V_d computed with using Eq. (15) with Eq. (36), which neglects turbulent transport in the ocean; the thin dashed line is Eq. (27) with Eq. (36), which includes turbulent transport in the ocean. Ozone variables are specified as α_x =0.3, a=10^3 s^{-1}, and S_{cw}=500.