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Air-Sea Exchange of Volatile Organic Compounds: A New Model with Microlayer Effects

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Abstract The authors propose a new “three-layer” conceptual model for the air-sea exchange of organic gases, which includes a dynamic surface microlayer with photochemical and biological processes. A parameterization of this three-layer model is presented, which was used to calculate the air-sea fluxes of acetone over the Pacific Ocean. The air-sea fluxes of acetone calculated by the three-layer model are in the same direction but possess half the magnitude of the fluxes calculated by the traditional two-layer model in the absence of photochemical and biological processes. However, photochemical and biological processes impacting acetone in the microlayer can greatly vary the calculated fluxes in the three-layer model, even reversing their direction under favorable conditions. Our model may help explain the discrepancies between measured and calculated acetone fluxes in previous studies. More measurements are needed to validate our conceptual model and provide constraints on the model parameters.

Keywords: air-sea transfer, organic gas, two-layer model, microlayer, surface renewal

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1 Introduction

Volatile organic compounds (VOCs) represent a key class of atmospheric constituents affecting chemistry and climate. A major uncertainty in the current understanding of many atmospheric VOCs is the exchange between the atmosphere and the ocean. One such example is the atmospheric budget of acetone, for which the most important uncertainty is the role of the ocean. Current model and measurement studies differ in their conclusions as to whether the ocean acts as a source or a sink for atmospheric acetone, with estimated air-sea acetone fluxes ranging from +20 to −48 Tg y^{−1} (Singh et al., 2003; de Laat et al., 2001; Jacob et al., 2002; Marandino et al., 2005; Fischer et al., 2012).

The air-sea exchange of a soluble gas is traditionally described by the classic “two-layer” model developed by Liss and Slater (1974). This model considers the interface between the two phases as a system composed of a gas film and a liquid film. The gas transfer within this two-

film system is controlled by molecular transfer, while the bulk of each fluid (outside the films) is well mixed by turbulence. The flux of a soluble gas between air and sea is expressed as

$$F = K_{\text{tot}} \times (HC_w - C_g), \quad (1)$$

where positive flux indicates gas transfer from sea to air. C_g [mol m^{−3}] and C_w [mol m^{−3}] are the concentrations of the soluble gas in the atmosphere and in bulk sea water, respectively. H is the dimensionless Henry’s law constant of the soluble gas, defined as the ratio of the equilibrium concentrations in the air and in the sea. K_{tot} [m s^{−1}] is the total air-sea gas transfer velocity:

$$K_{\text{tot}} = \left(\frac{1}{k_g} + \frac{H}{k_w} \right)^{-1}, \quad (2)$$

where k_g [m s^{−1}] and k_w [m s^{−1}] are the gas transfer velocities in air and in water, respectively; they are determined by the turbulence on either side of the interface and the chemical properties of the transferring gas.

Despite the popularity of the two-layer model, the air-sea fluxes of organic gases thus simulated show important discrepancies when compared with measurements. Marandino et al. (2005) made shipboard measurements of the air-sea fluxes of acetone, as well as the concentrations of acetone in water and in air, over the Pacific Ocean during May–July 2004. Their measurements showed the ocean to be a sink of atmospheric acetone over a wide range of latitudes (equator to 45°N), while the two-layer model predicted the ocean to be a source of atmospheric acetone at lower latitudes.

One shortcoming of the two-layer model is that it does not take into account the presence of a microlayer at the ocean surface and the resulting impacts on the air-sea transfer fluxes. The surface microlayer, typically 1 to 1000 μm in thickness (Donaldson and Vaida, 2006), is a layer of water at the top of the ocean that is often enriched in dissolved organic matter (DOM) and diverse microorganisms by a factor of 10¹–10² relative to bulk sea water (e.g., Carlson, 1983; Frew and Nelson, 1992; Wurl and Obbard, 2004). The surface microlayer periodically exchanges substances with the underlying bulk seawater through wind-driven turbulent mixing (Hatcher and Parker, 1974). Moreover, there may be photochemical and/or biological processes within the microlayer acting as additional sources or sinks for the organic gases. These processes are not well understood, nor are they accounted

for in current atmospheric chemistry models.

In this study, we proposed a new “three-layer” model for the air-sea exchange of organic gases, incorporating the effects of a dynamic microlayer with photochemical and biological processes. We incorporated a parameterization into our three-layer model. We applied our new model to calculate the air-sea fluxes of acetone over the Pacific Ocean and compared the results against those calculated by the traditional two-layer model and shipboard direct flux measurements.

2 Model description

2.1 A conceptual “three-layer” model

Figure 1 illustrates our conceptual “three-layer” model. We assumed the air-sea interface to be a three-layer system: A gas film at the bottom of the atmosphere, a liquid film at the top of the bulk sea water, plus a microlayer on top of the liquid film. Gas concentrations in bulk air (C_g) and in bulk water (C_w) are each well mixed by turbulence. C_{sg} is the concentration at the bottom of the gas film, while C_m is the concentration in the microlayer. The microlayer is sufficiently thin that the gas concentration (C_m) can be considered invariable throughout the microlayer.

Gas transfer within the gas film occurs by molecular transfer, similar to the two-layer model. Gas transfer on the water side takes place not only by molecular transfer within the liquid film but also by surface renewal processes that move substances between the bulk water and the microlayer via turbulence. Within the microlayer, there may be photochemical and biological activities that produce and/or consume the organic gas. C_g and C_w may also be driven by additional external processes, such as photolysis, biological processes, and chemical reactions.

Under strong-wind conditions, the ocean surface is highly turbulent such that the microlayer is broken (e.g., Goldman et al., 1988). We assumed that the air-sea gas

interface is as described by the two-layer model under such conditions.

2.2 Parameterizing the three-layer model

We developed a parameterization scheme for the conceptual “three-layer” model described above for implementation into atmospheric chemistry models. We used an existing parameterization for the two-layer model, AIRSEA, as a springboard for developing our parameterization scheme. The AIRSEA module was developed by Pozzer et al. (2006, 2010, 2011) to calculate air-sea gas transfer in atmospheric chemistry models, with a focus on organic gases. AIRSEA includes parameterizations for the gas transfer velocities of organic gases, with considerations for a number of physical processes, including wind, precipitation, ocean turbulence, and the presence of bubbles and white-caps at the ocean surface. In addition, AIRSEA takes into account the impacts of temperature and salinity on the solubility of organic gases.

We assumed that the microlayer is always present under low-wind conditions (surface wind $U < 10 \text{ m s}^{-1}$) (Frew et al., 2004). In the presence of the microlayer, assuming solubility obeys Henry’s law, the concentrations at the air-sea interface at equilibrium are

$$C_{sg} = H \times C_m. \quad (3)$$

The air-sea flux of organic gas (F_1) in the three-layer model is

$$F_1 = k_g \times (HC_m - C_g). \quad (4)$$

The Henry’s law constant (H) is parameterized in AIRSEA as a function of sea water temperature and inorganic salinity. The gas transfer velocity in air (k_g) is parameterized in AIRSEA as a function of wind speed, friction velocity, and Schmidt number, accounting for the effects of aerodynamic resistance and quasi-laminar boundary layer resistance.

The organic gas concentration in the microlayer (C_m) is

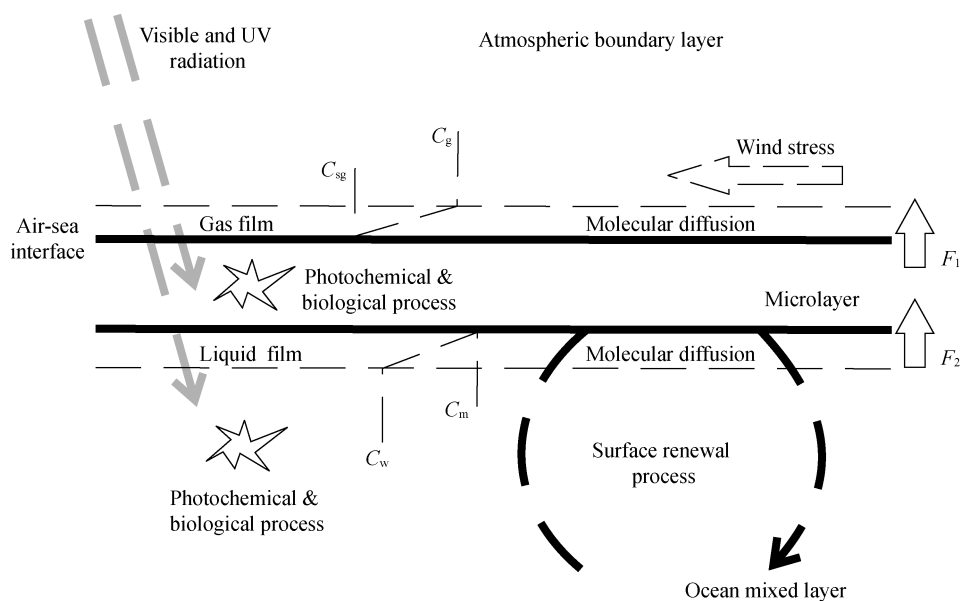


Figure 1 A “three-layer” model for the air-sea exchange of organic gases.

dynamically determined by competing sources and sinks:

$$\frac{dC_m}{dt} = \frac{dC_m}{dt} \Big|_{\text{molecular transfer}} + \frac{dC_m}{dt} \Big|_{\text{surface renewal}} + \frac{dC_m}{dt} \Big|_{\text{photochemical process}} + \frac{dC_m}{dt} \Big|_{\text{microbial effects}} \quad (5)$$

We discuss each of these processes and their parameterizations below.

2.2.1 Molecular transfer between the microlayer and the bulk sea water

Surfactants in the microlayer increase the surface pressure and reduce molecular diffusion at the sea surface (Goldman et al., 1988; Frew et al., 1990). An empirical parameter, R , can be defined to represent the impact on the gas transfer velocity in seawater due to the additional resistance from the microlayer:

$$R = \frac{k'_w}{k_w} \quad (6)$$

where k'_w [m s^{-1}] and k_w [m s^{-1}] are the gas transfer velocities at the sea surface with and without a microlayer, respectively. We adopted R values of 90%, 80%, and 70% for open ocean waters, coastal waters, and estuarine waters, respectively, based on previous studies (Goldman et al., 1988; Frew et al., 1990).

The molecular transfer flux between bulk water and the microlayer, F_2 , is

$$F_2 = k'_w \times (C_w - C_m) \quad (7)$$

The rate of change of C_m due to molecular transfer is:

$$\frac{dC_m}{dt} \Big|_{\text{molecular transfer}} = \frac{F_2 - F_1}{h} \quad (8)$$

where h is the thickness of the microlayer.

2.2.2 Surface renewal process

Due to the thinness of the microlayer, dissolved organic gases in the microlayer may quickly become saturated or depleted due to molecular transfer into or out of the microlayer (Zhou and Mopper, 1997). Turbulent exchange with bulk sea water renews the microlayer, either by bringing materials from the water below to replenish the microlayer or by transporting saturated water downward, thus enhancing the interfacial molecular transfer.

We assumed that surface renewal is driven by Langmuir circulation, which is the dominant turbulent process in the upper ocean over much of the world's ocean surface (Langmuir, 1938; Thorpe, 2004).

The maximum downwelling speed in a Langmuir cell, ω_{\max} [m s^{-1}], can be parameterized as follows (Thorpe et al., 2003):

$$\omega_{\max} = 3.42 \times 10^{-3} \times U_{10} + 2.7 \times 10^{-3} \quad (9)$$

where U_{10} [m s^{-1}] is the 10-m wind speed. Assuming that the Langmuir circulation is harmonic, the downwelling speed $\omega(z)$ at the depth z [m] in a Langmuir cell can be described as (Thorpe et al., 2003)

$$\omega(z) = \omega_{\max} \times \sin\left(\frac{\pi z}{L}\right) \quad (10)$$

where L [m] is the depth of the Langmuir cell, which can also be written as a function of U_{10} (Thorpe et al., 2003):

$$L = 0.235 \times U_{10} + 4.935 \quad (11)$$

The mean downwelling speed of the Langmuir circulation, $\bar{\omega}$, can be calculated from Eq. (10):

$$\bar{\omega} = \frac{\int_0^L \omega(z) dz}{L} = \frac{2}{\pi} \times \omega_{\max} \quad (12)$$

Hence, the characteristic timescale t^* [s] of surface renewal due to Langmuir circulation is

$$t^* = \frac{L}{\bar{\omega}} = \frac{\pi L}{2\omega_{\max}} \quad (13)$$

The parameterizations in Eqs. (9)–(13) are applicable for surface wind speeds of $3 < U_{10} < 22 \text{ m s}^{-1}$. The characteristic timescale calculated from Eq. (13) is typically several minutes, consistent with the 20 minutes reported by Denman and Gargett (1983).

The rate of change of the organic gas concentration in the microlayer due to surface renewal can be described as

$$\frac{dC_m}{dt} \Big|_{\text{surface renewal}} = \frac{1}{t^*} \times (C_w - C_m) \quad (14)$$

2.2.3 Photochemical process

Laboratory and field studies suggest that carbonyls may be produced photochemically in the microlayer (Zhou and Mopper, 1997; Obernosterer et al., 1999; de Bruyn et al., 2011) and that the rate of carbonyl production is proportional to the concentration of UV-absorbing DOM (Kieber et al., 1990). Based on these findings, we parameterized the photochemical production of organic gas in the microlayer as

$$\frac{dC_m}{dt} \Big|_{\text{photochemical production}} = \beta \times J \times (\text{DOM}) \quad (15)$$

J [s^{-1}], the photolysis frequency of ozone to $\text{O}(\text{D})$, is used to represent the UV actinic flux, following Jacob et al. (2002). The concentration of DOM ($[\text{DOM}]$) [mol L^{-1}] can be measured directly. Alternatively, colored dissolved organic matter (CDOM) concentrations observed by satellites can be used as a surrogate for $[\text{DOM}]$. β is the dimensionless photochemical production coefficient, which represents the UV absorption by DOM and the yield of the target organic gas.

If the target organic gas is photo-reactive, it may also undergo photolysis and be removed from the microlayer (e.g., Mopper and Stahovec, 1986; Lin and Carlson, 1991; Chi and Huang, 2004). We parameterized the photochemical loss of the target organic gas in the microlayer as

$$\frac{dC_m}{dt} \Big|_{\text{photochemical loss}} = -\delta \times J \times C_m \quad (16)$$

where δ is the dimensionless photodegradation coefficient, which represents the product of the cross section and quantum yield of the target organic gas in sea water.

The total rate of change of C_m due to photochemical processes in the microlayer is

$$\left. \frac{dC_m}{dt} \right|_{\text{photochemical process}} = -\beta \times J \times [\text{DOM}] - \delta \times J \times C_m, \quad (17)$$

where β and δ can be measured directly in laboratories or obtained empirically by fitting measured flux data.

2.2.4 Microbial effects

The surface microlayer often contains large amounts of microorganisms (Wurl and Obbard, 2004). Previous studies showed that these microorganisms may either consume the target organic species as a nutrient (e.g., Moran and Zepp, 1997; Obernosterer et al., 1999; Sinha et al., 2007) or produce the target organic species as a physiological byproduct (e.g., Kuzma et al., 1995; Nemecek-Marshall et al., 1995).

We used the Monod equation (Monod, 1949) to represent the loss of the target organic gas in the microlayer due to microbial consumption. The Monod equation empirically relates the microbial growth rate in an aqueous environment to the concentration of a limiting nutrient (Levenspiel, 1980). It has been widely used to describe the microbial degradation of substrates in waste water treatment studies. We assumed that the loss rate of the target organic species is proportional to the microbial growth rate; thus,

$$\left. \frac{dC_m}{dt} \right|_{\text{microbial consumption}} = -\frac{k_0 C_m [M]}{Y \times (k_s + C_m)}, \quad (18)$$

where $[M]$ is the mass concentration [mg L^{-1}] of microbes in the microlayer. k_0 [s^{-1}] is the maximum specific growth rate of microbes. k_s [mol L^{-1}] is the Monod constant, which represents the nutrient concentration when the specific growth rate is half of its maximum value. Y [mg mol^{-1}] represents the yield of microbial mass from the consumption of a unit mole nutrient.

Equation (18) can be further simplified for different parts of the ocean. For waters where the concentration of the target organic gas in the surface microlayer is high, such as coastal waters, $C_m \gg k_s$, the right-hand side of Eq. (18) can be simplified to $-\theta_1[M]$, where $\theta_1 = k_0/Y$. For waters where the organic gas concentration in the microlayer is low, such as the remote open ocean, $C_m \ll k_s$, the right-hand side of Eq. (18) can be simplified as $-\theta_2[M]C_m$, where $\theta_2 = k_0/(Yk_s)$.

Microbes may also produce the target organic species as a physiological byproduct while consuming other limiting nutrients. As in Eq. (18) above, we assumed that the production rate of the target organic is proportional to the microbial growth rate described by the Monod equation:

$$\left. \frac{dC_m}{dt} \right|_{\text{microbial production}} = k_m \times \frac{k_0 S [M]}{k_s + S}, \quad (19)$$

where S [mol L^{-1}] is the concentration of the limiting nutrient in the microlayer. k_m (dimensionless) is the ratio of the production rate of the target organic gas and the growth rate of microbes. The right-hand side of Eq. (19) can be simplified as $[M]$, where $\gamma = k_m k_0 S / (k_s + S)$.

In summary, in the presence of the microlayer, the air-sea transfer flux of the target organic gas is showed in Eq. (4). The rate of change of the target organic gas concen-

tration in the dynamic microlayer is

$$\left. \frac{dC_m}{dt} \right|_{\text{dynamic microlayer}} = \frac{F_2 - F_1}{h} + \frac{1}{t^*} (C_w - C_m) + \beta J [\text{DOM}] - \delta J C_m + (\gamma - \theta_1) [M], \quad (20a)$$

for waters where C_m is high, and

$$\left. \frac{dC_m}{dt} \right|_{\text{dynamic microlayer}} = \frac{F_2 - F_1}{h} + \frac{1}{t^*} (C_w - C_m) + \beta J [\text{DOM}] - \delta J C_m + (\gamma - \theta_2 C_m) [M], \quad (20b)$$

for waters where C_m is low, where $\gamma = k_m k_0 S / (k_s + S)$.

2.3 Steady-state assumption in the microlayer

The residence time of the target organic gas in the microlayer can be calculated from Eq. (20) as

$$\tau = 1/a, \quad (21)$$

where

$$a = \frac{k'_w + k_g H}{h} + \frac{1}{t^*} + \delta J, \quad (22a)$$

for waters with high C_m and

$$a = \frac{k'_w + k_g H}{h} + \frac{1}{t^*} + \delta J + \theta_2 [M], \quad (22b)$$

for waters with low C_m .

Under typical surface conditions, the residence time for the target organic gas in the microlayer is 4–20 seconds for waters with both high and low C_m . Molecular transfer is the dominant process affecting C_m .

Environmental variables in Eq. (20), such as the thickness of the microlayer (h), UV-B flux (J), DOM concentration ($[\text{DOM}]$), and microorganism concentration ($[M]$), are stable on timescales of tens of minutes or longer. Thus, a steady-state assumption is valid for the target organic gas in the microlayer.

The steady-state concentration of the target organic gas in the microlayer ($C_{m,ss}$) is

$$C_{m,ss} = b/a, \quad (23)$$

where

$$b = \frac{k'_w C_w + k_g C_g}{h} + \frac{C_w}{t^*} + \beta J [\text{DOM}] + (\gamma - \theta_1) [M], \quad (24a)$$

for waters with high C_m , and

$$b = \frac{k'_w C_w + k_g C_g}{h} + \frac{C_w}{t^*} + \beta J [\text{DOM}] + \gamma [M], \quad (24b)$$

for waters with low C_m .

Inserting $C_{m,ss} = b/a$ into Eq. (4), the air-sea flux in the presence of a microlayer calculated by our new model is (F_{new})

$$F_{\text{new}} = k_g \times \left(\frac{H \times b}{a} - C_g \right). \quad (25)$$

Under strong-wind conditions (surface wind $U > 10 \text{ m s}^{-1}$), the microlayer is broken up, and the air-sea transfer flux reverts to the expression in Eq. (1).

3 Application: The air-sea exchange flux of acetone

We applied our three-layer model to calculate the air-sea fluxes of acetone. Acetone was chosen as a model

species because there have been direct measurements of its air-sea fluxes (Marandino et al., 2005).

We calculated the air-sea fluxes using the three-layer model (F_{new}) as well as the original AIRSEA two-layer model (F_{airsea}). The value of C_w in both models was set to 15 nM, which is the average observed concentration of acetone in global oceans (Fischer et al., 2012). Surface atmospheric acetone concentrations C_g were set to $1.57 \times 10^{-8} \text{ mol m}^{-3}$ for the tropics ($0\text{--}20^\circ\text{N}$) and $3.41 \times 10^{-8} \text{ mol m}^{-3}$ for the northern mid-latitudes ($20\text{--}50^\circ\text{N}$), respectively, based on average values measured by Marandino et al. (2005). Surface air and sea temperatures and 10-m wind speeds were also taken from Marandino et al. (2005). We varied the strengths of the photochemical and biological sources/sinks to assess their impacts on the calculated air-sea flux. The actual magnitudes of these sources/sinks are not currently well known, but a few previous field and laboratory measurements indicate photochemical production rates of $10^{-8}\text{--}10^{-10} \text{ mol m}^{-3} \text{ s}^{-1}$ and biological removal rates of $10^{-9}\text{--}10^{-11} \text{ mol m}^{-3} \text{ s}^{-1}$ over northern low-latitude and mid-latitude oceans (Obenroter et al., 1999; Riemer et al., 2000; Wu et al., 2005; de Bruyn et al., 2011).

Figure 2 shows the ratios of the air-sea acetone fluxes calculated by the two models ($F_{\text{new}}/F_{\text{airsea}}$) at typical locations over the equatorial Pacific (0.4°N , 179.0°E) and

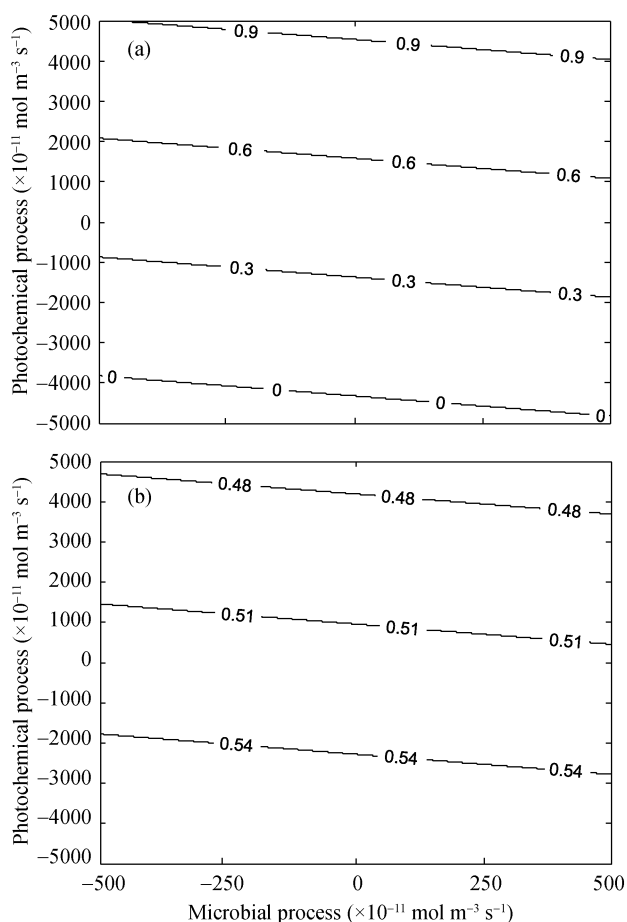


Figure 2 Ratios of the air-sea fluxes of acetone calculated using the three-layer model versus the two-layer model ($F_{\text{new}}/F_{\text{airsea}}$) over the (a) Equatorial Pacific and in the (b) northern mid-latitude Pacific.

over the northern mid-latitude Pacific (44.6°N , 142.1°W). F_{airsea} is the from-sea-to-air flux over the equatorial Pacific and the from-air-to-sea flux over the northern mid-latitude Pacific. Assuming there is no photochemical or biological processes in the microlayer impacting the target organic gas ($\beta=0$, $\delta=0$, $\gamma=0$, $\theta_1=0$, $\theta_2=0$ in Eq. (20)), the acetone fluxes calculated by the three-layer model (F_{new}) are in the same direction but possess half the magnitude of F_{airsea} over both equatorial and mid-latitude waters. This is mainly due to the additional resistance exerted by the microlayer against molecular transfer.

The impacts of photochemical and biological processes in the microlayer differ significantly for equatorial and mid-latitude waters. Over the northern mid-latitude Pacific, the varying strengths of photochemical and biological processes have small effects on the calculated F_{new} . However, F_{new} can vary considerably in magnitude over the equatorial Pacific. F_{new} may even reverse direction when there is strong photochemical degradation and strong biological removal of acetone in the microlayer. The weaker wind speed over the equatorial ocean lengthens the residence time of the gas in the microlayer (Eq. (21)), which in turn amplifies the effects of microlayer processes on the overall flux (Eq. (25)). Additionally, the higher sea surface temperature reduces the solubility of the target organic gas.

Our results provided a viable explanation for the discrepancies between measured and calculated air-sea fluxes of acetone. Direct measurements of acetone fluxes by Marandino et al. (2005) revealed the ocean to be a sink of atmospheric acetone in the Pacific from the equator to 45°N . The two-layer model agrees with the measurements made in the northern mid-latitude Pacific. However, over the equatorial Pacific, the two-layer model predicted a strong sea-to-air acetone flux. Based on the model sensitivity analysis shown in Fig. 2, we speculate that there may be strong photochemical and biological removal of acetone in the microlayer in equatorial waters, resulting in the observed air-to-sea acetone fluxes. Such photochemical and biological processes may also be present in mid-latitude waters but have little impact on the air-sea fluxes.

4 Conclusions

We proposed a new “three-layer” conceptual model for the air-sea exchange of organic gases, including a dynamic microlayer with photochemical and biological processes. We introduced a parameterization into this three-layer model and used it to calculate the air-sea fluxes of acetone over the Pacific Ocean. The air-sea fluxes of acetone calculated by the three-layer model are in the same direction but possess half the magnitude of the fluxes calculated by the traditional two-layer model. However, photochemical and biological processes impacting acetone in the microlayer can cause the calculated fluxes to vary greatly, even reversing the flux direction under favorable conditions. This may explain the discrepancies between measured and calculated acetone air-sea fluxes in previous studies. Our model adds sub-

stantial complexity to our understanding of the air-sea transfer of organic gases. More measurements are needed to validate our conceptual model and provide constraints on the model parameters. Our model may be further expanded to account for other soluble gases, such as CO₂, that are relevant to the climate

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