Atmospheric deposition of methanol over the Atlantic Ocean

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In the troposphere, methanol (CH\textsubscript{3}OH) is present ubiquitously and in second abundance among organic gases after methane. In the surface ocean, methanol represents a supply of energy and carbon for marine microbes. Here we report direct measurements of air–sea methanol transfer along a ~10,000-km north–south transect of the Atlantic. The flux of methanol was consistently from the atmosphere to the ocean. Constrained by the aerodynamic limit and measured rate of air–sea sensible heat exchange, methanol transfer resembles a one-way depositional process, which suggests dissolved methanol concentrations near the water surface that are lower than what were measured at ~5 m depth, for reasons currently unknown. We estimate the global oceanic uptake of methanol and examine the lifetimes of this compound in the lower atmosphere and upper ocean with respect to gas exchange. We also constrain the molecular diffusional resistance above the ocean surface—an important term for improving air–sea gas exchange models.

Background

Atmospheric methanol affects tropospheric oxidative capacity and air pollution by participating in the cycling of ozone and the hydroxyl radical (OH). Methanol is primarily released to air from terrestrial plants (during growth and decay); other identified sources include industrial emissions, biomass and biofuel burning, and atmospheric production (1–5). Methanol reacts with OH in the troposphere with a photochemical lifetime of ~10 d, leading to formaldehyde (6) and carbon monoxide (7), among other products. Observations suggest that methanol can be further removed from air via deposition to land (8) and to the sea surface (9, 10). In the upper ocean, methanol supports the growth of methylotrophic bacteria (11) and has recently been found to be consumed by SAR11 alphaproteobacteria, the most abundant marine heterotrophs (12). The turnover time of seawater methanol is thus quite short, on the order of a few days (13, 14). However, significant oceanic concentrations of methanol have been detected in the range of 50–400 nM (9, 15–17), leading to questions about its source.

To understand the global cycling of methanol, it is imperative to quantify its transport between the ocean and the atmosphere. Heikes et al. (3) modeled a gross air-to-sea depositional loss of ~80 Tg yr\textsuperscript{-1} and also argued for an oceanic source of 30 Tg yr\textsuperscript{-1} to sustain an observed concentration of 0.9 ppb in the marine atmospheric boundary layer (MABL) of the Pacific and Atlantic. Based on aircraft measurements over the Pacific, Singh et al. (18) estimated a loss of ~8 Tg yr\textsuperscript{-1} to the surface ocean with no appreciable oceanic source, which was later modified to ~10 Tg yr\textsuperscript{-1} by Jacob et al. (4). Millet et al. (5) modeled a gross deposition of ~100 Tg yr\textsuperscript{-1} to the ocean—a sink largely offset by an oceanic production of 85 Tg yr\textsuperscript{-1}. From in situ seawater concentration measurement and modeled atmospheric distribution over the Atlantic, Beale et al. (17) recently calculated a net oceanic emission of 12 Tg yr\textsuperscript{-1}, but saw evidence for both oceanic production and uptake. Amid these large discrepancies is the fact that the air–sea methanol flux has never been measured directly (e.g., with eddy covariance)—a void we address with this report.

Here, C\textsubscript{a} and C\textsubscript{s} are the bulk concentrations of the gas in air and atmosphere. H is the dimensionless Henry’s solubility expressed as the ratio of liquid-to-gas concentrations at equilibrium. C\textsubscript{a}/H denotes the concentration on the airside of the interface that would be equilibrated with the waterside. When C\textsubscript{a}/H is less than C\textsubscript{s}, surface water is undersaturated relative to the atmosphere and the flux is from air to sea. K\textsubscript{s} is the total gas transfer velocity from the perspective of atmospheric concentrations. Governed by molecular and turbulent transfer in both phases, K\textsubscript{s} encompasses the kinetic forcing in gas exchange.

Molecular sublayers exist on both sides of the air–sea interface, where turbulent transport diminishes and molecular diffusion dominates. Conceptualizing the system as two resistors in series, K\textsubscript{s} can be partitioned to individual transfer velocities in air and water (k\textsubscript{a} and k\textsubscript{w}, respectively):

\[
K_s = 1/(1/k_a + 1/(Hk_w)).
\]

For sparingly soluble gases (low H), transport through the aqueous molecular sublayer is the rate-limiting step (i.e., K\textsubscript{s} ∼ Hk\textsubscript{w}).

Significance

Transport of gases between the ocean and the atmosphere has profound implications for our environment and the Earth’s climate. An example of this transport is the oceanic uptake of carbon dioxide, which has buffered us from a higher concentration of this greenhouse gas in the atmosphere while also causing ocean acidification. Here we describe the first direct measurements of air–sea methanol transport. Atmospheric methanol, a ubiquitous and abundant organic gas of primarily terrestrial origin, is observed to be transported over thousands of kilometers and deposited over the ocean, where it is likely consumed by marine microbes. We quantify the rate of methanol deposition and examine the governing processes near the air–sea interface.

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Such waterside controlled gases, including carbon dioxide (CO\textsubscript{2}) and sulfur hexafluoride (SF\textsubscript{6}), have been the subjects of decades of research (20). In contrast, transfer of very soluble (high \(H\)) and/or surface reactive gases is limited on the airside (i.e., \(K_{aw} \sim k_{aw}\)). For the highly soluble methanol with \(H \approx 5,000\) at 25 °C (21), the second term in Eq. 2 contributes at most a few percent to \(K_{aw}\).

The airside transfer velocity is dictated by resistances from aerodynamic transport in the turbulent atmosphere \(R_{t}\) and diffusion in the airside molecular sublayer \(R_{m}\):

\[
k_{aw} = 1/(R_{t} + R_{m}).
\]

Our knowledge of \(k_{aw}\) stems mostly from studies of latent heat (water vapor) and sensible heat (conduction due to the air–sea temperature difference). Resistance-based models (22, 23) and, more recently, the Center for Coupled Ocean-Atmosphere Response Experiment (COARE) gas transfer model (24) suggest that at a height well above the sea surface (e.g., 10 m), \(R_{t}\) substantially exceeds \(R_{m}\). The predominance of turbulent transport might be one reason why rates of water vapor transfer measured over the ocean are significantly lower than those observed in laboratories (25, 26), where dynamics are different.

To relate \(k_{aw}\) of water vapor or sensible heat to other gases, \(R_{m}\) is assumed to be proportional to \(S_{C}^{1/2} S_{a}^{2/3}\) where \(S_{C}\) is the airside Schmidt number (ratio of kinematic viscosity to molecular diffusivity in air). However, limited open-ocean observations of airside-controlled trace gases have demonstrated diverging behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained. Eddy covariance measurements of the very soluble acetone resulted in behaviors from water vapor, which are so far unexplained.
Discussion

We first examine the influence of air–sea exchange on the atmospheric and oceanic methanol budgets. The vertical gradient in $C_a$ within the atmospheric surface layer (the lowest $\sim 10\%$ of the MABL) can be approximated from similarity theory as $-\frac{\text{Flux}}{\kappa u-z}$, with $\kappa$ being the von Karmon constant and $z$ the sampling height. In this case, $C_a$ is estimated to increase with height at an average rate of $-0.002 \text{ ppb} \cdot \text{m}^{-1}$. For a 1-km-high MABL with a mean mixing ratio of 1 ppb, deposition to the ocean removes methanol from air with a timescale of $\sim 80\%$ of the total removal of atmospheric methanol.

The atmosphere does not appear to be the sole source of seawater methanol, however. Assuming a 50-m-deep oceanic mixed layer with a dissolved methanol concentration of 29 nM, at a mean flux of $-10 \text{ mol} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$, the replacement time for seawater methanol is 140 d with respect to gas exchange, approximately two orders of magnitude longer than the typical turnover time due to biological consumption (13, 14). Thus, a suggested “missing” source of seawater methanol (3, 5, 13) seems justified for mass balance. Furthermore, we found methanol concentration at $\sim 500 \text{ m}$ depth to be $60\%$ of the $5\text{-m}$ value, proportionally similar to depth profiles observed previously (9, 17). Given the measurable biological consumption of methanol at depth (14), the presence of significant concentration there suggests that its production is not limited to the near surface. A recent work shows that methanol may be produced by the marine proteobacteria Alteromonadales (31).

Now we turn our attention to the process of air–sea methanol transfer. We calculate $K_a$ from measured flux using observed $C_a$ (Fig. 3A) and by setting $C_a$ to zero (Fig. 3B). To account for buoyancy effects, $K_a$ is adjusted to neutral atmospheric stability based on similarity theory (32) and plotted against the measured friction velocity ($u_*$, related to wind stress) as well as the approximate 10-m neutral wind speed. Also shown are parameterizations from Mackay and Yeun (25), Liss (26) adjusted for molecular weight (19), and COARE (24). The aerodynamic limit from COARE (1/R) defines the theoretical rate of atmospheric turbulent transfer. In addition, we show the in situ transfer velocity of sensible heat $k_{heat} = w T_w / \Delta \rho$, where $T_w$ is the air temperature from the sonic anemometer corrected for humidity, and $\Delta \rho$ the air–sea temperature difference.

With the two-layer approach using observed $C_a$ (Fig. 3A), the polynomial fit $11,766 u_* + 13,804 u_*^2$ ($R^2 = 0.87$) describes the nonlinear relationship between $K_a$ and $u_*$. $K_a$ is similar to $k_{heat}$ and the aerodynamic limit at low to moderate winds ($u_* < 0.4 \text{ m} \cdot \text{s}^{-1}$), which confirms the expectation that methanol is airside controlled and has minimal lateral resistance. At $u_* > 0.4 \text{ m} \cdot \text{s}^{-1}$, $K_a$ trends $\sim 15\%$ higher than the aerodynamic limit, and significantly exceeds $k_{heat}$ by $\sim 20\%$ ($\chi^2$ test at 95% confidence), which is inconsistent with physical theory. Uncertainties in $K_a$ amplify in high winds due to the small sample size as well as...
greater measurement errors (Methods). Nevertheless, based on Eq. 3, \( K_a \) for methanol should be \( \sim 10\% \) lower than \( k_{\text{Heat}} \) because of the higher \( Sc_{w} \) for methanol (1.09) (33) relative to heat (\( Sc_{w} = 0.64 \)), which is not reflected in Fig. 3A.

Transfer velocity calculated with \( C_a = 0 \) equates to a one-way deposition velocity (Fig. 3B). By specifying the maximum air-sea concentration difference, the deposition velocity represents the lower limit of \( K_a \). The mean deposition velocity of 2.444 cm\( \cdot \)s\(^{-1} \) converts to 0.68 m\( \cdot \)s\(^{-1} \), which is several times higher than previous estimates based on temporal trends in the atmospheric methanol concentration (10) and vertical profiles from the MABL to the free troposphere (18). We note that our measurements by eddy covariance are the most direct and do not require assumptions about the seawater saturation or atmospheric chemistry of methanol.

With \( C_a = 0 \), \( K_a \) demonstrates a near linear relationship with \( u^* \), and may be fitted by 8.814 \( u^* \) + 6.810 \( u^* \)\(^{-1} \) (\( R^2 = 0.89 \)), which is lower than the aerodynamic limit as well as measured \( k_{\text{Heat}} \), and lies between laboratory results (25, 26) and the resistance-based parameterization (24). Compared with Fig. 3A, as expected, the periods with the highest saturation values had the largest reductions in \( K_a \). We further solve for resistance in the airside molecular diffusion sublayer above the ocean surface by taking the difference between \( R_i \) and 1/\( K_a \), which is illustrated in Fig. 4. The derived \( R_i \) is between the parameterization of 5.0 \( Sc_{w}^{0.67} \) \( u^* \) from Hicks et al. (22) and 13.3 \( Sc_{w}^{0.67} \) \( u^* \) from COARE (24). Because using \( C_a = 0 \) yields the minimum \( K_a \) and so maximum airside resistance, our results suggest that \( R_i \) may be overestimated in the COARE model.

It is surprising that using \( C_a = 0 \) yields a more physically consistent \( K_a \) than using the measured \( C_a \). For \( K_a \) in Fig. 3A to be \( \sim 15\% \) lower (i.e., to approach the aerodynamic limit), \( C_a \) needs to be reduced by \( \sim 50\% \). We examine the possibility of a near surface gradient in \( C_a \). Microorganisms and dissolved organic matter tend to be enriched in the \( \sim 0.1\)-mm-thick aqueous molecular sublayer (34, 35). This microlayer covers both the productive regions and the oligotrophic waters and at wind speeds of up to \( \sim 10\) m\( \cdot \)s\(^{-1} \) (36). Breaking waves temporally disrupt the surface, but a coherent microlayer appears to reform within seconds, in part due to efficient scavenging of surface active organic materials from bulk water by rising bubbles (37). Considering the methanol budget in the microlayer, the air-to-sea transport in our study adds 10 \( \mu \)mol\( \cdot \)m\(^{-2} \)\( \cdot \)d\(^{-1} \). If the concentration in the microlayer were maintained at 50\% lower than in the bulk water, 26 \( \mu \)mol\( \cdot \)m\(^{-2} \)\( \cdot \)d\(^{-1} \) of methanol would be diffusing into the microlayer from below at steady state (with \( k_a = 11\) cm\( \cdot \)h\(^{-1} \) from COARE). The total methanol input into the microlayer (36 \( \mu \)mol\( \cdot \)m\(^{-2} \)\( \cdot \)d\(^{-1} \)) divided over a thickness of 0.1 mm would yield a concentration increase of 4 nM\( \cdot \)s\(^{-1} \). A methanol depletion of the same rate is required for mass balance (without any in situ production), which would be at least three orders of magnitude faster than any observed biological consumption (13, 14).

The mixing time between the sea surface and 5 m depth, dependent on the turbulent diffusivity, is typically on the order of a few minutes (38). Thus, enhanced consumption in the top meters of the ocean with a timescale of a few nM\( \cdot \)per minute could result in a vertical gradient in bulk \( C_a \). Photochemically mediated destruction of methanol by OH radical in water is fast, with a rate constant of \( 1 \times 10^9 \) M\(^{-1} \)\( \cdot \)s\(^{-1} \) (39). However, the OH concentration in the surface ocean is only \( 1 \sim 10 \times 10^{-18} \) M (40) and therefore too low to be a significant sink for dissolved methanol. A pronounced photochemical effect would also imply a greater \( K_a \) during the day than at night, which was not observed during this cruise. In sum, known methanol sinks do not appear to

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**Fig. 3.** (A) Methanol transfer velocity calculated using measured \( C_a \) (8) calculated using \( C_a = 0 \) (n = 73). Measured friction velocity and the approximate wind speed are shown on the abscissa. Using measured \( C_a \), calculated methanol transfer velocity sometimes exceeds the aerodynamic limit, particularly in high winds. In contrast, using \( C_a = 0 \) leads to more reasonable \( K_a \) implying low dissolved methanol concentrations close to the air-water interface. \( K_{\text{Heat}} \) adjusted to neutral stability is shown as averages in \( u^* \)-bins. Error bars on \( K_a \) \( K_{\text{Heat}} \), and \( u^* \) correspond to the respective SEs.

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**Fig. 4.** Resistance in the molecular diffusion sublayer above the ocean surface (\( R_i \), calculated as the difference between aerodynamic resistance (\( R_i \)) and 1/\( K_a \)) of methanol (with \( C_a = 0 \)). \( R_i \) estimated from methanol transfer lies between the parameterizations from Hicks et al. (22) and COARE (24). In all cases, \( R_i \) at a height of 18 m is several times greater than \( R_a \).
be rapid enough to cause a substantially lower dissolved concentration at the interface relative to the bulk seawater. Interestingly, in an earlier measurement of acetone flux (8), a lower dissolved concentration at the surface would also help to reconcile the difference between observed uptake and predicted emission in the tropical Pacific. Along with previously measured SO$_2$ deposition velocities that are lower than expected (28), these results allude to potential processes not well understood in the transfer of airside controlled trace gases.

**Conclusion**

In this study, we report direct measurements of air–sea methanol transfer by eddy covariance. The surface ocean consistently took up methanol from the atmosphere, with enhanced influx in continental outflow regions and during high winds. The low saturation of methanol in the surface seawater implies rapid oceanic destruction of this compound. Methanol transfer resembles a one-way depositional process, suggesting that methanol concentrations at the water surface may be even lower than what were measured at ~5 m depth due to processes currently unknown. Further field measurements along with other airside-controlled compounds (e.g., water vapor, ethanol), as well as laboratory experiments of methanol uptake with and without biology would help to determine whether the deposition model always holds for highly soluble gases.

**Methods**

**Atmospheric Measurements.** During AMT-22, atmospheric and seawater methanol concentrations were alternately quantified by a high-resolution PTR-MS (Ionicon), which was housed in the meteorological laboratory near the foredeck of the ship. Acetone and acetaldehyde were also measured and will be described elsewhere. For ~19 h of a day, the PTR-MS operated under atmospheric mode and continuously measured at ~2.1 Hz. Air was drawn in from an intake on the starboard side of the ship's foremast (~18 m above mean sea level) via ~25 m of 6.4 mm (inner diameter) perfluoroalkoxy tubing by a vacuum pump at a flow rate of ~23 standard liters per minute, as monitored by a digital thermal mass flow meter. A triply deuterated methanol gas standard (2.0 ± 0.1 ppm of methanol-d3; Scientific and Technical Gases Ltd.) was injected continuously into the inlet line at 30±0.3 standard cubic centimeter per minute, as regulated by a digital thermal mass flow controller; this allows $C_m$ to be calculated from the ratio between the ambient and deuterated signals. The use of the isotopic standard minimizes uncertainties due to instrumental drift and variable efficiencies. Background values were taken by directing ambient air through a platinum catalytic converter (350 °C) for 2 min every hour. The detection limit for mean atmospheric concentration (minutely averaged) and the noise level at ~2.1 Hz were 0.048 and 0.21 ppb, respectively. The standard injection system was initially designed and the instrument performance characterized in detail at a coastal site (41).

In eddy covariance (EC), $C_m$ is correlated with concurrent vertical wind velocity ($u$) and averaged over time to yield the vertical flux $(C_m/u)_v$, where primes denote deviations from the respective means and the overbar signals averaging over nominally ~1 h. Wind measurements on a ship are influenced by the ship’s movement, necessitating a motion correction. Mounted ~40 cm from the gas intake, a sonic anemometer (WindMaster; Gill Instruments) and a motion sensor (Motionpak II; Systron Donner) measured 3D wind velocities, linear accelerations, and rotational rates at 10 Hz. Observed winds were corrected for ship’s motion (42), and further sequentially decorrelated with ship velocities and accelerations to yield true winds (24). The EC friction velocity (derived from $u^* = U_{10}^*$, where $u$ is the wind velocity along the mean wind direction) closely agrees with modeled $u^*$ (24) as a function of wind speed, validating the motion correction (Fig. 5).

Methanol flux is computed as the integral of the $C_m$-$u$ cospectrum from 0.002–1 Hz, omitting low-frequency contributions possibly related to horizontal heterogeneity. Only the wind sector from ~50 to 110 degrees is considered for flux, excluding periods of contamination from the ship’s exhaus and distortion of ambient wind fields due to the ship’s superstructure. A total of 484 h of valid methanol flux observations were made, of which 29 h were during high wind conditions ($u^* > 0.4$ m s$^{-1}$). As expected, correlating the methanol-d3 signal with $w$ resulted in “null” fluxes scattered around zero. After dividing by $u^*$, methanol flux also does not correlate with measured sensible heat flux or computed latent heat flux, implying minimal sensitivity in the instrument response to ambient fluctuations in temperature and humidity. However, in heavy swells, $C_m$ exhibited spurious correlations with the vertical platform acceleration and displacement at the frequency of ship’s motion (~0.1 Hz). The former artifact was likely due to motion-induced variability in the water vapor source flow of the PTR-MS, and the latter from heaving of the ship vertically across the $C_m$ gradient. Applying a similar decorrelation algorithm as described above to $C_m$ removes the erroneous spike at ~0.1 Hz and also reduces the magnitude of methanol flux by an average of 24%.

Mean methanol and sensible heat cospectra over 10 h on October 17 are shown in Fig. 6, which are well described by the expected spectral shape for atmospheric turbulent transport (43). Based on an empirical filter function (44) with a response time of 0.5 s and the shape of the theoretical spectrum at frequencies above the Nyquist (~1 Hz), a correction for high-frequency attenuation is applied to the measured methanol flux, which is on average 17% and increases with wind speed, consistent with estimates from an ogive approach (41). Fluxes are processed hourly and averaged to 1° latitude bins. At a nominal ship velocity of 18 km h$^{-1}$, each latitude bin corresponds to ~6 h. Random uncertainty in methanol flux is ~20% for the bin average giving a sampling error of ~50% for hourly measurements (45).

**Seawater Measurements and Computation of $K_m$** Discrete seawater samples (triplicates) were taken primarily from predawn and noontime conductivity, temperature, salinity (CTD) hydrocasts daily. Unfiltered water was transported from the 5-m Niskin bottle via a short piece of Tygon tubing into prime...
opaque glass bottles (~300 mL). Contact with air was avoided by sampling first from the Niskin and overfilling the glass bottles before capping. An additional sample from the deepest Niskin (nominally at 500 m depth) was collected at noon. Several water samples were also obtained from the ship’s nontoxic underway water supply on November 13, when no CTD was com-
menced during a storm, and on November 20, after the completion of CTD work. An intercomparison earlier during the cruise yielded no significant differ-
ence in CTD between the 5-m CTD and the water collected underway.

To minimize any loss due to bacterial consumption, water samples were kept at ambient water temperature and analyzed within 3 h of sampling. Methanol was extracted from seawater across a semipermeable silicon membrane thermostated at 50 °C into a supply of clean nitrogen flowing directly into the PTR-MS, as described in ref. 16. The first of the triplicate samples was used to condition the membrane; reported CMe values represent the average of the latter two samples. The system was calibrated every 2 wk using water standards prepared by serial dilution of reagent-grade metha-
ol. Calibration constants were stable over the entire cruise, varying less than 10%. Estimated as three times the noise of the nitrogen blanks, the detection limit for seawater methanol concentration was ~6 nM.


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For the computation of KMe, latitudinally bin-averaged flux and CMe were linearly interpolated to the times of water collection. Given the transect format of the cruise, uncertainties due to horizontal gradients were random and should not contribute to any bias in KMe. Any proportional error in CMe should also be reflected in the flux and so not affect KMe. Judging from a recent survey (46), uncertainties in H for methanol should be within 10%.

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