Parameterizing the bubble-mediated air-sea flux of a non-ideal gas, DMS

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Bubble Effects

- Enhancement in gas transfer rate
- Equilibrium super-saturation condition [Woolf 1997]

- Physical-Chemical effects
  
  .....What are bubble effects for non-ideal gases such as DMS

  - chemical properties may be useful in predicting bubble effects for non-ideal gases such as methylated sulfur species
  - Couple with air-sea bubble model
Addressing solubility in a bubbly surface ocean

In senescent conditions

\[ C_{i,w} \approx \gamma_{i,w}^{-1} V_i^{-1} \]

At high wind speeds (>12 m/s)

\[ C_{i,mix} \approx \gamma_{i,mix}^{-1} V_i^{-1} \approx (1-x_b)C_{i,w} + (x_b) K H C_{i,w} + K_{b\text{-film}} C_{i,w} \]

\[ \approx [(1-x_b)\gamma_{i,w}^{-1} + (x_b)\gamma_{i,b}^{-1} + \Phi_B \gamma_{i,b\text{-film}}^{-1}] V_i^{-1} \]

Where \( \Phi_B = f(x_b) \) = bubble surface area per m²
\( \gamma_{i,j} \) = activity coefficient of substrate I in phase j
\( V_i \) = molar volume of substrate i in cm³mol⁻¹
\( X_b \) = volume fraction of bubbles in sample volume
Henry’s Law Constant, $K_{iH}$

$$K_{iH} = \text{vapor pressure/solubility}$$

$$= \frac{\rho_i}{C_{i,w}}$$

$$= \gamma_{iw} \rho_{iL} V_w$$

$$K_i = K_{iH}/RT \ (\text{dimensionless})$$

$$K_{i,\text{mix}} = K_i/(1+(C_{\text{mix}}/C_w) \Phi_B)$$

$\uparrow$

$K_{b-\text{film}}$
In terms of flux

\[
\text{Flux} = k_i \Delta C_{AW}
\]

\[
k_i = \left[\frac{1}{k_a K_{i,mix}} + \frac{1}{k_w}\right]^{-1}
\]

where \(K_{i,mix} = \frac{K_i}{1 + \left(\frac{C_{mix}}{C_w}\right) \Phi_B}\)
Predicted influence of wind speed on transfer velocities of surface active gases

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Formula</th>
<th>MWt, g/mol</th>
<th>Solubility, (mol/L)</th>
<th>K, (dimensionless, air/water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSH</td>
<td>CH₃SH</td>
<td>48.11</td>
<td>0.195</td>
<td>0.0115</td>
</tr>
<tr>
<td>DMS</td>
<td>C₂H₆S</td>
<td>62.13</td>
<td>0.355</td>
<td>0.08</td>
</tr>
<tr>
<td>DMSO</td>
<td>C₂H₆SO</td>
<td>74.12</td>
<td>miscible</td>
<td>5.25 x 10⁻⁷</td>
</tr>
<tr>
<td>DMDS</td>
<td>C₂H₆S₂</td>
<td>94.20</td>
<td>0.0363</td>
<td>0.0428</td>
</tr>
</tbody>
</table>

From Vlahos et al (2011), *Gas Transfer at Water Surfaces, 2010*
simulated total bubble number density (number per m$^3$) at $u_{10} = 17.5$ m/s.
Relationship between bubble e-folding depth $z_0$ and wind speed $u_{10}$. (Black dots: observations by Vagle et al. [2010]; Blue circles: bubbly flow solutions assuming waves in equilibrium with local winds.)
This model

- bubbles of sizes **>35 microns** are included
- fraction of different gases change with time
- considers the effect of ambient pressure change on bubble size change
- readily **coupled** to upper ocean dynamic model
- Bubble injection is **constrained** by laboratory and *in situ* observations
**Total Gas Flux**

\[ F = F_{sfc} + F_p + F_c + SP \frac{C_{mix}}{C_w} \int \frac{d\Phi}{dt} dz \]

- \( F_{sfc} \) is the gas flux through the ocean surface
- \( F_p \) is the gas flux through large bubbles that partially dissolve
- \( F_c \) the gas flux through small bubbles that completely dissolve
- the last term is an effective gas flux due to the change of bubble surface area assuming a proportionate fraction of molecules attach
Estimated from Liang Model

\[ F = k_{sfc} (S_{eff} P - C) + k_b [S_{eff} P(1 + \Delta_{overpressure}) - C] + F_c + SP \frac{C_{mix}}{C_w} \int \frac{d\Phi}{dt} dz \]

\[ F = k_{tot} [S_{eff} P(1 + \Delta) - C] \]

\[ \Delta = \frac{k_b}{k_T} \Delta_{overpressure} + \frac{F_c + SP \frac{C_{mix}}{C_w} \int \frac{d\Phi}{dt} dz}{k_T SP \left( 1 + \frac{C_{mix}}{C_w} \Phi \right)} \]
the total injected bubble amount in the model is based on observations, which are limited, and a source of possible uncertainty; $\Phi_B = 0.40 \,(U/10)^3$

(2) the formula for $k_w$ in VM09 is at the lower end of observed values $\Phi_B = 0.090 \,(U/10)^3$
Sensitivity test on injected bubble amount

Enhancement of gas flux

Attenuation due to solubility

Blonquist & Huebert
Southern Ocean 2008
Gas flux profile for organic gases
Temperature effects

![Graph showing temperature effects](image-url)
DMS and derivatives expected to be moderately surface active

At high winds (> 12 m/s) the surface ocean is significantly altered

- the effective activity coefficient and therefore the fugacity of surface active compounds is expected to decrease
- The result is higher relative water-side concentrations in the bubble influenced layer and lower transfer velocities
Air-sea flux of DMS may be overestimated using traditional empirical models.

DMS air-sea flux reaches upper thresholds governed by a piston velocity near 25 cm/h and the corresponding concentration gradient. This sets upper DMS air-sea transfer rates at $120 \mu\text{Mm}^{-2}\text{d}^{-1}$ based on observed field concentrations. (DMS $C_w$’s range from <1 to 20 nM (Lee et al 2010; Zang et al, 2008))
- Sensitivity analysis on nitrogen and oxygen
- Coupling to Lagrangian model
  - Equilibration of fast dissolving gases in partially dissolved bubbles will be explicitly resolved.
  - Bubble size distribution will be better resolved.
  - Add equilibration effect to the model Woolf [1993], Keeling [1993]
- Modeling of other biogenic gases

Next Steps...
That’s all for now...
- DMS C_w’s range from <1 to 20 nM (Lee et al 2010; Zang et al, 2008)

- DMSP p + d, 9.22 (2.85-19.73) and 17.50 (4.33-36.09)nM (Zang et al, 2008)

- Photodegradation rates 0.006 to 0.028 nM/(Wm\(^{-2}\)) (Miles et al., 2009)

- DMS degradation rates 0.04 to 0.66 d\(^{-1}\) (Kieber et al., 1996)

- DMS production rates 0.7 to 0.9 nMd\(^{-1}\) (Bailey et al 2008)
Phytoplankton DMSP lyase

Bacterial DMSP lyase

Sulfate aerosols

Grazing, lysis

DMSO and other products

DMS cycle
DMSP sources

\[
\text{DMSP Lyase} \quad \xrightarrow{\quad} \quad \text{DMS} \quad \xrightarrow{\quad (pK_a=4.4) \quad} \quad \text{Acrylate} \quad \xrightarrow{\quad} \quad \text{DMS} \quad \xrightarrow{\quad} \quad \text{Acrylic Acid}
\]
DMS box model

Sources:
- phytoplankton
- DMSP_d breakdown
- advection

Sinks:
- Air-sea exchange
- Biodegradation
- Photodegradation
- advection
Equatorial Pacific (PMEL)- 15°N to 15°S DMS is relatively constant both seasonally and interannually (2.7 ± 0.7 nM (Bates and Quinn, Geophys. Res. Lett., 24:861-864, 1997).

Observations
Surface ocean DMS

Earth Interactions Volume 8 (2004)
DMS fluxes

Bates et al. [1992]