The Role of the Ocean in the Global Atmospheric Budget of Acetone

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Accessibility
The role of the ocean in the global atmospheric budget of acetone

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[1] Acetone is one of the most abundant carbonyl compounds in the atmosphere and it plays an important role in atmospheric chemistry. The role of the ocean in the global atmospheric acetone budget is highly uncertain, with past studies reaching opposite conclusions as to whether the ocean is a source or sink. Here we use a global 3-D chemical transport model (GEOS-Chem) simulation of atmospheric acetone to evaluate the role of air-sea exchange in the global budget. Inclusion of updated (slower) photolysis loss in the model means that a large net ocean source is not needed to explain observed acetone in marine air. We find that a simulation with a fixed seawater acetone concentration of 15 nM based on observations can reproduce the observed global patterns of atmospheric concentrations and air-sea fluxes. The Northern Hemisphere oceans are a net sink for acetone while the tropical oceans are a net source. On a global scale the ocean is in near-equilibrium with the atmosphere. Prescribing an oceanic acetone budget is highly uncertain, with past studies reaching opposite conclusions as to whether the ocean is a source or sink. Here we use a global 3-D chemical transport model (CTM). Since then, measurements of the quantum yield for acetone photolysis have led to upward revision of the atmospheric lifetime of acetone [Blitz et al., 2004]. In addition, field observations have shown that the ocean can be a either a source or a sink of acetone [Marandino et al., 2005; Sinha et al., 2007; Taddei et al., 2009; Williams et al., 2004]. Here we use GEOS-Chem to integrate these new experimental data into an improved understanding of the role of the ocean in the global budget of atmospheric acetone.

2. Methods

[4] We use the GEOS-Chem global 3-D CTM including detailed ozone-NOx-VOC-aerosol chemistry (version 9.01.01, www.geos-chem.org) to simulate the global atmospheric distribution of acetone. GEOS-Chem is driven by NASA/GEOS-5 assimilated meteorological data with 0.5° × 0.67° horizontal resolution, 47 levels in the vertical, and 3–6 hour temporal resolution. We degrade the horizontal resolution to 2° × 2.5° for input into GEOS-Chem. We use a 1-year simulation for 2006, with a 1-year spin-up to remove the effect of initial conditions.

[5] Sources of acetone include direct emissions from biogenic, anthropogenic, and biomass burning sources, as well as the atmospheric oxidation of organic precursors (Table 1). The ensemble of sources is described by Jacob et al. [2002] and updates are described below. We use the RETRO (Reanalysis of the TROpospheric chemical composition) emission inventory for anthropogenic emissions of acetone and of the isoalkane precursors [van het Bolscher et al., 2008]. The RETRO emission inventory is for 2000, and we scale it to 2006 with activity factors from van Donkelaar et al. [2008]. We use 2006 GFED2 monthly biomass burning emissions for acetone and the isoalkanes [van der Werf et al., 2009]. Terrestrial biogenic emissions of acetone from metabolism and decay are calculated locally using the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.0) [Guenther et al., 2006]. Acetone production from biogenic monoterpenes and 2-methyl-3-buten-2-ol is calculated using MEGAN emissions for these VOCs and fixed yields from Jacob et al. [2002].
Table 1. Global Budget of Atmospheric Acetone

<table>
<thead>
<tr>
<th>Source</th>
<th>This Work</th>
<th>Jacob et al. [2002]</th>
<th>Other Estimates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inventory, Tg a⁻¹</td>
<td>5.6</td>
<td>3.8</td>
<td>3.8–7.2</td>
</tr>
<tr>
<td>Emissions</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthropogenic</td>
<td>0.73ᵇ</td>
<td>1.1 ± 0.5</td>
<td>1.1–2</td>
</tr>
<tr>
<td>Open biomass burning</td>
<td>2.8</td>
<td>4.5 ± 1.6</td>
<td>2.4–9</td>
</tr>
<tr>
<td>Terrestrial Biosphere</td>
<td>32</td>
<td>35 ± 10</td>
<td>20–172</td>
</tr>
<tr>
<td>Atmospheric Production</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation of isoprenes</td>
<td>26ᵇ</td>
<td>21 ± 5</td>
<td>1–28</td>
</tr>
<tr>
<td>(mainly anthropogenic)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation of biogenic VOCs</td>
<td>5</td>
<td>7 ± 3</td>
<td>7</td>
</tr>
<tr>
<td>Sinks, Tg a⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation by OH</td>
<td>33</td>
<td>27</td>
<td>18–27</td>
</tr>
<tr>
<td>Photolysis</td>
<td>19</td>
<td>46</td>
<td>9–22</td>
</tr>
<tr>
<td>Land uptake</td>
<td>12</td>
<td>9</td>
<td>9–19</td>
</tr>
<tr>
<td>Net Ocean exchange, Tg a⁻¹</td>
<td>–2</td>
<td>13 ± 6</td>
<td>–62–2.5</td>
</tr>
<tr>
<td>Gross source</td>
<td>80</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Gross sink</td>
<td>82</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

ᵇIncluding biofuel use.
ᵇIncluding 22 Tg a⁻¹ from propane and 4 Tg a⁻¹ from the higher alkanes.
ᵇPositive values indicate upward fluxes.

[6] Losses for acetone in the model include oxidation by OH, photolysis, and deposition. Exchange with the ocean is discussed below. We use a rate constant \( k = 1.33 \times 10^{-13} + 3.28 \times 10^{-11} \text{ exp}[-2000/T] \text{ cm}^2 \text{ molecule}^{-1} \text{ s}^{-1} \) for the oxidation of acetone by OH [Sander et al., 2011]. Photolysis of acetone is computed using absorption cross sections and pressure-dependent quantum yields from Blitz et al. [2004], and local actinic fluxes from the Fast-JX radiative transfer scheme [Wild et al., 2000] as implemented in GEOS-Chem by Mao et al. [2010]. We assume a dry deposition velocity of 0.1 cm s⁻¹ for ice-free land as in Jacob et al. [2002].

[7] There is evidence that the ocean mixed layer is a large acetone reservoir, containing ~5 times the atmospheric burden [Williams et al., 2004]. We compile in Table 2 literature values for observed surface seawater concentrations and air-sea fluxes. The processes controlling acetone concentrations in seawater are uncertain. Production can take place by photo-degradation of dissolved organic matter [Zhou and Mopper, 1997] and directly by phytoplankton and bacteria [Nemecek-Marshall et al., 1995]. Loss can take place by photo-degradation or biotic consumption [Mopper and Stahovec, 1986; Nemecek-Marshall et al., 1995]. Two recent field campaigns support a biologically mediated acetone source in seawater. Sinha et al. [2007] measured the air-sea flux of acetone while also monitoring phytoplankton abundance. They found systematic upward fluxes in the presence of both strong sunlight and biological activity. Taddei et al. [2009] also observed upward acetone fluxes in phytoplankton bloom areas in the South Atlantic.

Table 2. Measurements of Acetone Concentrations in Surface Seawater and Air-Sea Fluxesa

<table>
<thead>
<tr>
<th>Period</th>
<th>Location</th>
<th>Concentration (nM)</th>
<th>Flux (ng m⁻² s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oct–Nov 2002</td>
<td>Tropical Atlantic</td>
<td>17.6 ± 8.1</td>
<td>–3.8–6.1</td>
<td>Williams et al. [2004]</td>
</tr>
<tr>
<td>May–Jul 2004</td>
<td>W. Pacific (mid-latitude)</td>
<td>13.6 ± 3.0</td>
<td>–10.2ᵇ – 7.4ᵇ</td>
<td>Marandino et al. [2005]</td>
</tr>
<tr>
<td>May–Jul 2004</td>
<td>W. Pacific (equatorial)</td>
<td>13.9 ± 11.7</td>
<td>–2.6ᵇ – 1.1ᵇ</td>
<td>Marandino et al. [2005]</td>
</tr>
<tr>
<td>May–Jun 2005</td>
<td>Norwegian fjord</td>
<td>–</td>
<td>0.21</td>
<td>Sinha et al. [2007]</td>
</tr>
<tr>
<td>Jan–Feb 2007</td>
<td>S. Atlantic (bloom)</td>
<td>–</td>
<td>0.67</td>
<td>Taddei et al. [2009]</td>
</tr>
<tr>
<td>Jan 2007</td>
<td>S. Atlantic (non-bloom)</td>
<td>–</td>
<td>~1.0 – 0.2ᵇ</td>
<td>Taddei et al. [2009]</td>
</tr>
<tr>
<td>Jul–Aug 2008</td>
<td>Northwest Pacific</td>
<td>19.0 ± 4.4</td>
<td>–</td>
<td>Kameyama et al. [2010]</td>
</tr>
</tbody>
</table>

ᵃValues are means ± standard deviation unless otherwise noted.
ᵇFluxes were either directly measured by eddy covariance or mesocosms, or were inferred from the measured saturation ratios. The latter are indicated by asterisks. Positive fluxes are upward.
ᶜRanges of concentrations and inferred fluxes. The authors reported a flux of 15.7 ng m⁻² s⁻¹ based on an acetone concentration of 55 nM in the surface micro-layer. We repeated their flux calculations using their measured bulk seawater concentrations.
ᵈThe authors reported a discrepancy between the fluxes measured by eddy covariance and inferred from saturation ratios. Both are shown here. All measured fluxes were downward, but the range of saturation ratios (0.35–6.5) implied both upward and downward fluxes.
ᵉTaddei et al. [2009] report "near zero, negative or highly variable low acetone fluxes" in non-bloom conditions. They do not report a mean value for non-bloom conditions, thus a range is given here based on DOY 28 – 30 in Figure 4 of Taddei et al. [2009].
3. Global Atmospheric Distribution of Acetone

Figure 1 shows the simulated acetone mixing ratios in three altitude ranges and for two seasons. Mean observations from aircraft missions, ship cruises, and surface sites are overlaid as circles. The observations are generally for years other than 2006 but we expect that interannual variability is small relative to other aspects of variability. Table S1 in the auxiliary material gives details of the observations. Figures S1 and S2 show comparisons with the aircraft vertical profiles. 1

![Graph showing simulated and observed global distribution of atmospheric acetone for two seasons and three altitude bins.](image)

298 K respectively. Observed acetone mixing ratios in the marine boundary layer are typically in that range [Singh et al., 2000], so the ocean can be either a net source or sink for acetone depending on the local atmospheric concentration and surface temperature.

Figure 2 presents the simulated annual mean air-sea acetone fluxes. The ocean parameterization produces a weak net global sink of 2 Tg a
\(^{-1}\), but the net flux varies geographically and seasonally (Figure S3). The ocean is a net sink at northern latitudes but a net source between 20°N and 40°S. At high southern latitudes the atmosphere and ocean are near equilibrium during summer and the ocean is a weak sink during winter. Comparison with observed fluxes is discussed below (see auxiliary material for further details).

[11] The atmospheric simulation shows no systematic bias compared to the observations in Figure 1 and provides in general a good representation of observed latitudinal and seasonal variability as well as land-ocean gradients. The acetone mixing ratios in Figure 1 are overlaid as circles. The observations are generally for years other than 2006 but we expect that interannual variability is small relative to other aspects of variability. Table S1 in the auxiliary material gives details of the observations. Figures S1 and S2 show comparisons with the aircraft vertical profiles. 1

Auxiliary materials are available in the HTML. doi:10.1029/2011GL050086.
free troposphere over the North Pacific [Singh et al., 2003] and data over the Northwest Atlantic showing the ocean to be a sink for acetone in continental outflow [Mao et al., 2006]. Based on acetone / CO ratios from the INDOEX and MINOS field campaigns, de Reus et al. [2003] speculated that the ocean serves a sink for acetone in polluted regions and a source in clean air masses. Our global results are consistent with this view. Marandino et al. [2005] find a stronger ocean sink than the model over the northwest Pacific (Figure 2) but their atmospheric acetone observations are very high (averaging 1.05 ppbv) and anomalous relative to the other data in Figure 1.

[13] The lowest tropospheric concentrations simulated by the model are over the Southern Ocean, reflecting the remoteness from terrestrial sources and the cold ocean temperatures. There the mean concentration is 0.2 ppbv and the ocean is a weak net sink. These results are consistent with cruise data in the Southern Ocean between South Africa and Chile [Taddei et al., 2009].

4. Atmospheric Budget

[14] Table 1 summarizes our global atmospheric budget of acetone and compares it to previous estimates. We separate the ocean source and sink terms since we view them as independent. We find a global source of acetone of 146 Tg a\(^{-1}\) including 80 Tg a\(^{-1}\) from the oceans, 33 Tg a\(^{-1}\) from the terrestrial biosphere, and 26 Tg a\(^{-1}\) from the atmospheric oxidation of isoalkanes. We calculate a mean tropospheric lifetime of 14 days with ocean uptake contributing 56% of the sink; reaction with OH, photolysis, and land uptake contribute 23%, 13%, and 8% respectively.

[15] The updated acetone photolysis rates triple the tropospheric lifetime of acetone against photolysis relative to Jacob et al. [2002] and reverse the relative importance of oxidation versus photolysis. We estimate an atmospheric burden of 5.6 Tg, which is larger than the estimate by Jacob et al. [2002] (3.8 Tg), because our weaker photolysis sink increases the burden in the upper troposphere. This is consistent with observations, as shown in Figure 1. Arnold et al. [2005] previously found with the TOMCAT CTM that the updated (slower) photolysis loss increases the acetone tropospheric burden by 50%. Our results are highly dependent on the Blitz et al. [2004] quantum yields for acetone photolysis, which represent the only direct measurements to date. Arnold et al. [2005] show that the Blitz et al. [2004] quantum yields reduce model bias relative to aircraft profiles from the remote Pacific, but Arnold et al. [2005] assumed a net zero acetone air-sea flux. Given the implications for constraining other budget terms, independent verification of the quantum yields for acetone photolysis would be very useful.

[16] Separation of the ocean source and sink in our budget suggests that the ocean exerts a major control on the abundance of atmospheric acetone. Using a seawater concentration of 15 nM, we find that on a global scale the atmosphere is in near equilibrium with the ocean. The net ocean sink of 2 Tg a\(^{-1}\), is within the uncertainty of the other source and sink terms. However there are coherent regions where the ocean is either a net sink or a net source, depending on the atmospheric acetone concentration and temperature. Marandino et al. [2005] proposed that the ocean is a large global net sink based on extrapolation of their measurements in the North Pacific Ocean, but as pointed out above their measurements were taken under conditions of anomalously high acetone concentrations in surface air. The other flux measurements in Table 2 do not support this extrapolation.

[17] We explored the sensitivity of our findings to seawater acetone concentration through simulations with fixed seawater concentrations of 10 and 20 nM, values near the low and high ends of the data ensemble in Table 2. Both options produce atmospheric acetone distributions inconsistent with observations. With a seawater acetone concentration of 10 nM, the model underestimates acetone mixing ratios by a factor of 2 in the marine boundary layer at northern mid-latitudes. Under this scenario, the ocean is a net sink (13 Tg a\(^{-1}\)) as the tropical oceans shift to a net acetone sink. With the seawater acetone concentration set to 20 nM, the atmosphere remains near equilibrium with the ocean on a global scale, but atmospheric acetone over the remote tropical oceans is overestimated by approximately a factor of 2 compared to observations. Seawater acetone concentrations clearly vary spatially and seasonally, but there is presently insufficient information to constrain this variability in models. Better quantification of the sources and sinks of acetone in the oceans is critical to improve our understanding of the budget of atmospheric acetone.

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