A 20th century atmospheric history of ethane and implications for the methane budget

Kristal R. Verhulst¹, M. Aydin¹, E. S. Saltzman¹, P. Lang², S. A. Montzka², K. Sorg³, D. A. Plotkin³ M. Battle³, Q. Tang¹, and M. J. Prather¹

¹UC Irvine, Department of Earth System Science
²NOAA/ESRL/GMD, Boulder, CO
³Bowdoin College, Department of Physics and Astronomy

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Overview

- Ethane atmospheric histories developed using firn diffusion model
- CTM and box model used to explain changes in atmospheric ethane levels throughout 20th century
- Implications of derived fossil fuel emissions

Ethane budget

Sources:
- Fossil fuels
- Biomass burning
- Biofuel use

Sink:
- OH
  (summer lifetime ~1-2 mo.)

<table>
<thead>
<tr>
<th>Source</th>
<th>Ethane (Tg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuels</td>
<td>4.8 - 8</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>2.4 - 5.6</td>
</tr>
<tr>
<td>Oceans</td>
<td>0.2 - 0.5</td>
</tr>
<tr>
<td>Vegetative/Soils</td>
<td>0.4 - 2.5</td>
</tr>
<tr>
<td>Wetlands</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Rice</td>
<td>&lt; 0.2</td>
</tr>
<tr>
<td>Total</td>
<td>~8-17</td>
</tr>
</tbody>
</table>

(Xiao et al., 2008)
Surface air observations (NOAA/HATS flasks)

- Seasonal drawdown due to OH (winter maxima)
- Summit mean: ~1.4 ppb
- S Pole mean: ~210 ppt
- Summit = high latitude NH levels, S Pole = high latitude SH levels, (based in Simpson et al., 2006)
- UCI measurements show agreement with Blake & Rowland measurements (2004-2007)

(D. Blake, A. Beyersdorf)
Firn diffusion model: tuning and validation

• 1-D firn diffusion model used to simulate gas diffusion in firn columns at S Pole, WAIS-D and Summit.

• Model generates a set of functions describing age distribution of air as a function of depth

• The diffusivity profile is tuned to reproduce the measured CO$_2$ profile (WAIS, S Pole) or CFC-12 and CH$_3$CCl$_3$ (Summit) using known atmospheric histories

• Validation using other gases with well known atmospheric histories (e.g. halocarbons, CH$_4$).

(Etheridge et al., 1996,1998; Dlugokencky, 2009)
Objective minimization algorithm minimizes a cost function based on:
- chi-square term (statistical fit to firn data)
- smoothness parameter

Present day mean atmospheric ethane level ~210 ppt
• S Pole atmospheric histories for ethane better constrained after 1920s

• Ethane levels over Antarctica roughly doubled between 1930-1980, stabilized during 1980’s, and declined to modern mean level
• Atmospheric history for Summit better constrained after 1950s
• Ice core ethane measurements needed to constrain older part of histories at Summit
NH versus SH ethane histories

- Similar trends in both hemispheres:
  - Increasing levels through 1970s
  - Decline since 1980s
- Decline ~12x larger in NH
- Ratio of change Greenland/Antarctica implies variability is driven by changes in NH source

<table>
<thead>
<tr>
<th></th>
<th>Rate</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summit</td>
<td>+10 ppt/yr</td>
<td>+15%</td>
</tr>
<tr>
<td>(1950-1980)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S Pole</td>
<td>+3.3 ppt/yr</td>
<td>+71%</td>
</tr>
<tr>
<td>(1920-1980)</td>
<td></td>
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<table>
<thead>
<tr>
<th></th>
<th>Rate</th>
<th>% change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summit</td>
<td>-23 ppt/yr</td>
<td>-30%</td>
</tr>
<tr>
<td>(1980-2006)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S Pole</td>
<td>-2.4 ppt/yr</td>
<td>-25%</td>
</tr>
<tr>
<td>(1980-2009)</td>
<td></td>
<td></td>
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</tbody>
</table>
Ethane source distribution

- Sources affect S Pole mixing ratios equally (UCI-CTM)
- UCI-CTM underestimates observed mixing ratios at Summit
- Summit mean levels ~50% higher than NH mean (based on HNH levels from Simpson et al., 2006)
- S Pole mean ~70% of the SH mean (based on HSH levels from Simpson et al., 2006)

Ethane 2-box model

- Variable OH (based on CH$_4$ concentrations)
- Developed FF source histories based on statistical fit to ethane atmospheric histories for Summit/S Pole
Ethane box model inversions:

1. BB fixed at 1, 2, 3, and 4 Tg

2. BB vary (solid red line)
   - Fixed biofuel source (EDGARv.1.4) used for all inversions

• Model reproduces rollover in the FF ethane source independent of changes in BB source
Implications: ethane fossil fuel source

- Assuming a constant methane/ethane ratio from fossil fuels:
  - ~40 yr difference in timing of ramp-up
  - Rollover occurs when growth of methane and ethane FF source thought to be most rapid
  - Reduction in FF ethane source is not in agreement with existing emissions inventories

- Alternative hypotheses:
  - Ratio of methane/ethane emitted from fossil fuels may have changed dramatically
  - Sink with Cl atom
    - Rollover in ethane levels may also be reproduced with a small Cl sink, on the order of ~3% of the total methane sink
Conclusions

• Ethane levels increased at polar latitudes until 1970s, decreased since 1980s

• Reduction in hydrocarbon emissions during the production, transport, storage, and/or use of fossil fuels is still a possibility, however this is not in agreement with existing emissions inventories

• Alternative explanations include a changing ratio of methane/ethane emitted from fossil fuels, and/or an increasing in the atmospheric ethane sink
Variable FF + BB simulation:

- Biomass burning trend similar to estimate from Schultz et al (2008)
- Estimate for Biomass burning + Biofuel use is comparable to estimate from Xiao et al (2008) and scaled estimate from Stern and Kaufman (1996)
Ethane 2-box model: OH Lifetime

- OH controlled by CH$_4$
- Methane and ethane lifetimes due to OH getting longer (more CH$_4$ = less OH)
- Modern CH$_4$ lifetime: 9.6 (IPCC TAR)
- Modern ethane lifetime: ~2 months
- Difference in ethane lifetime between hemispheres, getting smaller over time

<table>
<thead>
<tr>
<th>Year</th>
<th>$1/k$ (OH) (yr)</th>
<th>$1/k$ (Total) (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900</td>
<td>7.30</td>
<td>5.94</td>
</tr>
<tr>
<td>1950</td>
<td>8.21</td>
<td>6.04</td>
</tr>
<tr>
<td>2000</td>
<td>9.59</td>
<td>6.23</td>
</tr>
<tr>
<td>IPCC (TAR)</td>
<td>9.6</td>
<td>8.4</td>
</tr>
</tbody>
</table>
Implications for the CH$_4$ budget

- Ethane decline coincides with decrease in atmospheric growth rate of methane, suggesting related change
- Constant methane/ethane ratio from FF:
  - Ramp-up in FF source ~40 yr early
  - Rollover in FF occurs during time when growth thought to be most rapid

- Alternative explanations:
  - Changing ratio of methane/ethane emitted from fossil fuels.
    - Did hydrocarbon fuel use efficiency improve dramatically throughout the last half of the 20th century?
  - Sink with chlorine atom
    - Cl atoms preferentially oxidize ethane relative to methane (~1000x) compared to their respective reaction rates with OH.
Implications for the CH$_4$ budget

- Ethane decline coincides with decrease in atmospheric growth rate of methane, suggesting related change
- Constant methane/ethane ratio from FF:
  - 1900-1960 ramp up in FF methane source earlier than prior analyses
  - Predicted rollover in FF source occurs during time when FF CH$_4$ growth thought to be most rapid

- Alternative explanations:
  - Changing ratio of methane/ethane emitted from fossil fuels.
    - Did hydrocarbon fuel use efficiency improve dramatically throughout the last half of the 20th century?
  - Sink with chlorine atom
    - Cl atoms preferentially oxidize ethane relative to methane ($\sim$1000x) compared to their respective reaction rates with OH.
Ethane 2-box model: Source distribution

- Fraction of source contributing to ethane levels at high latitudes based on:
  - surface air observations (Simpson et al., 2006)
  - literature estimates (Xiao et al., 2008)
  - UCI CTM perturbation experiments
- Summit mean levels ~50% higher than NH mean
- S Pole mean ~70% of the SH mean
- Sources affect S Pole mixing ratios equally (remote location, approx equal time for transport)
- Large NH sources close to Summit, difficult to determine directly
- UCI CTM underestimates observed mixing ratios at Summit

<table>
<thead>
<tr>
<th></th>
<th>FF</th>
<th>BB</th>
<th>Biofuels</th>
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<tbody>
<tr>
<td><strong>NH mean</strong></td>
<td>0.9</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Summit</strong></td>
<td>1.6</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>S Pole</strong></td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
</tbody>
</table>

(Simpson et al., 2006; Xiao et al., 2008)