Long-term measurements of anthropogenic trace gases at the German GAW site Hohenpeißenberg

Christian Plass-Dülmer and Stefan Gilge,
Hohenpeißenberg Meteorological Observatory, DWD
Deutscher Wetterdienst

Meteorology 1781

Hohenpeissenberg Observatory

Bio-VOC 2000

OH radicals 1998

Aerosol 1995

(anthropogenic) reactive tracegases 1995

Cooperative Global Air Sampling Network 2006

Precipitation chemistry 1995

FEHp – 05/2009 C. Plass-Dülmer and S. Gilge
NO₂ distribution – time series

mixing ratio, ppb

95 96 97 98 99 00 01 02 03 04 05 06 07

NO₂_0
NO₂_1
NO₂_5
NO₂_10
NO₂_25
NO₂_50
NO₂_75
NO₂_90
NO₂_95
NO₂_99
NO₂_100
AVGNO₂
4 Parameter Fit for Trend-Analysis of Trace Gases

\[
\text{FIT (t)} = \{A + B \cos \left[(t_{JD} - C) \frac{2\pi}{365}\right]\} \exp \left[ D (t - t_0) / 365 \right]
\]

Least Square Fit after rejecting 10% outlying values
Based on monthly means of (noon-time) data
Sine + trend – fit of CO (ppb)

Uncertainties: 2-σ of multiple fits after arbitrarily rejecting 2 years
Selected anthropogenic hydrocarbons

- Ethane
- Acetylene
- Ethene
- Benzene
- Toluene

Mixing Ratio, pptv

Mean mixing ratios (1998)

- alkanes
- alkynes
- aromatics
- CO
- SO2
- NO, NO2
- alkenes

reaction rate constant OH, cm³/s

mixing ratio, ppt
NO, NO₂, ethene, n-pentane, n-heptane, propyne
Ozone - Trend
Weekly Cycles derived from all data, all seasons
Simulated weekly cycles

<table>
<thead>
<tr>
<th>K(OH)*[OH]</th>
<th>CO, Ethane K= 2E-13</th>
<th>Benzene K= 1E-12</th>
<th>NO, NO2, Ethene K= 1E-11</th>
<th>Propene, Xylenes K=2E-11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Winter [OH]=5E5</td>
<td>1E-7</td>
<td>5E-7</td>
<td>5E-6</td>
<td>1E-5</td>
</tr>
<tr>
<td>Summer [OH]=3E6</td>
<td>6E-7</td>
<td>3E-6</td>
<td>3E-5</td>
<td>6E-5</td>
</tr>
</tbody>
</table>
Calculated for \([\text{OH}]=1\text{E6 /cm}^3\)
Conclusion

• Anthropogenic trace gases are declining at MOHp
• Trends are stronger for shorter lived compounds
• NOx decline (-1.0% / y) weaker than expected – emissions?
• Weekly cycles show reduced emissions by about 60% on Sundays
• Weekly and annual cycles provide powerful tools to constrain emission estimates
These results were achieved due to great technical work by K. Michl, E. Plörer, M. Hofmann, E. Tensing, R. Wilhelm, R. Schafranek, T. Elste, and G. Stange.

Thank you!