Species Measured

- Hydrogen Peroxide, H2O2
- Methylhydroperoxide, CH3OOH
- Formaldehyde, CH2O aka HCHO

Photochemical significance

- VOCs → CH2O → CO → CO2
- CH2O → HOx → O3
- HOx → H2O2 → HOx
- CH4 and some OVOC → CH3OO → CH3OOH
- CH3OO → CH3OOH → CH2O and HOx
Climate Connections

CO2 (+1.6), CH4 (+0.5), O3 (+0.4) and sulfate (-0.4)

• VOCs and OVOCs $\rightarrow$ CH2O $\rightarrow$ CO.
• CH4 $\rightarrow$ CH2O
  – and CH4 $\rightarrow$ CH3OOH.
• Peroxides and formaldehyde are directly relatable to ozone.
• Heterogeneous sulfur dioxide oxidation.
Climate Connections
adapted from Ricky Rood (UMich), “blog” Weather Underground, June 2010

Global radiative forcing due to emissions of aerosols and precursors changes from 1750-2005

Black Carbon ---- Positive Radiative Forcing
Sulfate and Organic Carbon ---- Negative Radiative Forcing
Cloud Albedo Effect -- Negative Radiative Forcing

[IPCC, WG1 4th Assessment Report, 2007]
Formaldehyde Method - I

- Gas-to-aqueous collection
- Enzyme catalyzed derivatization
- Fluorescence product detection
- ~80% collection efficiency in CalNex
- Gas and aqueous stds.
- LN2 used for carrier gas and blanks
Formaldehyde Status

- Temporal resolution 2 minutes.
- Significant lag, ~ 25 minutes.
- LOD, 0.05 to 0.10 ppb.

- C-tainer temp effects and peroxide “cross-talk”.
  - Need to remove data under conditions of “rapid” change.
  - Need to remove data from periods of peroxide repair.

- Near final data reduction; ~ 1 month to go.
Peroxiode Method - I

- Gas-to-aqueous collection.
- HPLC separation of hydroperoxides.
- Enzyme catalyzed derivatization.
- Fluorescence detection.

- 100 / 70% collection of H2O2 / CH3OOH.
- Gas and aqueous stds.
- LN2 used for carrier gas and blanks.
Peroxide Method - Status

- Nearly every component failed at some point in the deployment.
- 30-sec sample every 4 minutes.
- Precision
  - H2O2, 0.01 to 0.05 ppb
  - CH3OOH 0.03 to 0.1 ppb
- Hand analysis of chromatograms - time consuming.
  - Four more months to an archival product.
Example Data: 5/18-19/2010

Los Angeles Region

MHP:HP

\( \text{H}_2\text{O}_2 \) and \( \text{CH}_3\text{OOH} \), ppb

\( \text{CH}_2\text{O} \), ppb
Example Data June 1-2, 2010

Monterey to San Francisco Bays
Summary

- Formaldehyde data in ~1 month.
- Peroxide data in ~4 months.
- Dynamic photochemical interplay between peroxides and between peroxides and formaldehyde.
- Will examine BL height, cloud and ocean surface and hydrogen peroxide.
It’s a small world at times; sometimes even even smaller.