Gas, Cloudwater, and Rain Hydrogen Peroxide and Methylhydroperoxide Measurements in RICO

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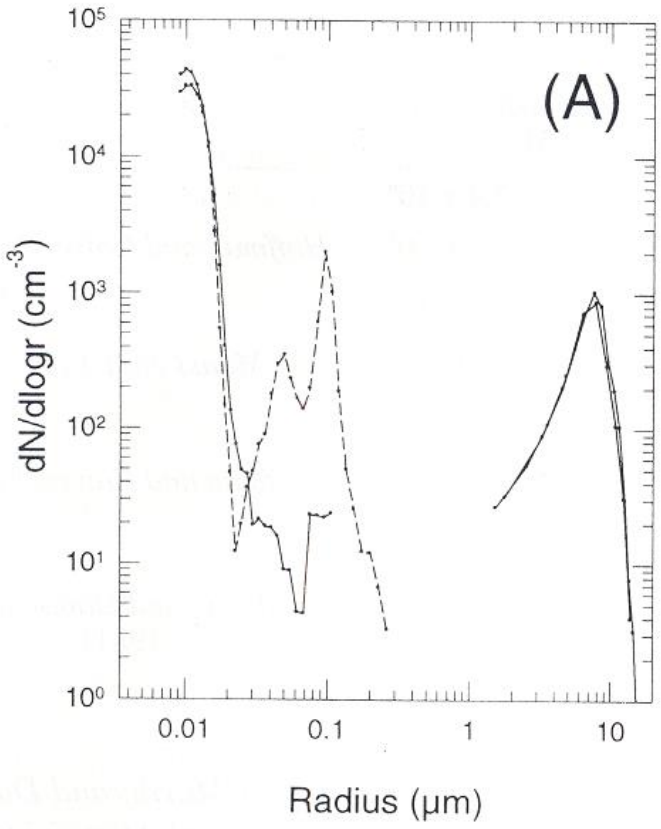
RICO Peroxide Component

- Goals of our proposal
- Role of the peroxides
  - Aqueous phase oxidation of SO_2
  - Using peroxide measurements to constrain gas phase oxidation of SO_2
  - Using the peroxides to help constrain cloud age and/or entrainment
- Measurement techniques
- Hypotheses we hope to evaluate

Goals of the RICO Peroxide Component

- to understand the impact of H_2O_2 and CH_3OOH on aqueous SO_2 oxidation in wet haze, and cloud, and the evolution of aerosol sulfate,
- to evaluate the H_2O_2 and CH_3OOH ratio as a diagnostic of precipitation or in-cloud chemistry,
- to help constrain estimates of SO_2 oxidation in cloud free air by constraining other photochemical oxidants like hydroxyl radical, HO, and to understand H_2O_2 and CH_3OOH distributions in clear and cloudy air in the marine boundary layer and lower free troposphere,
- place H_2O_2 and CH_3OOH chemical constraints on cloud parcel age,
- place H_2O_2 and CH_3OOH chemical constraints on FT-MBL entrainment and cloud entrainment.

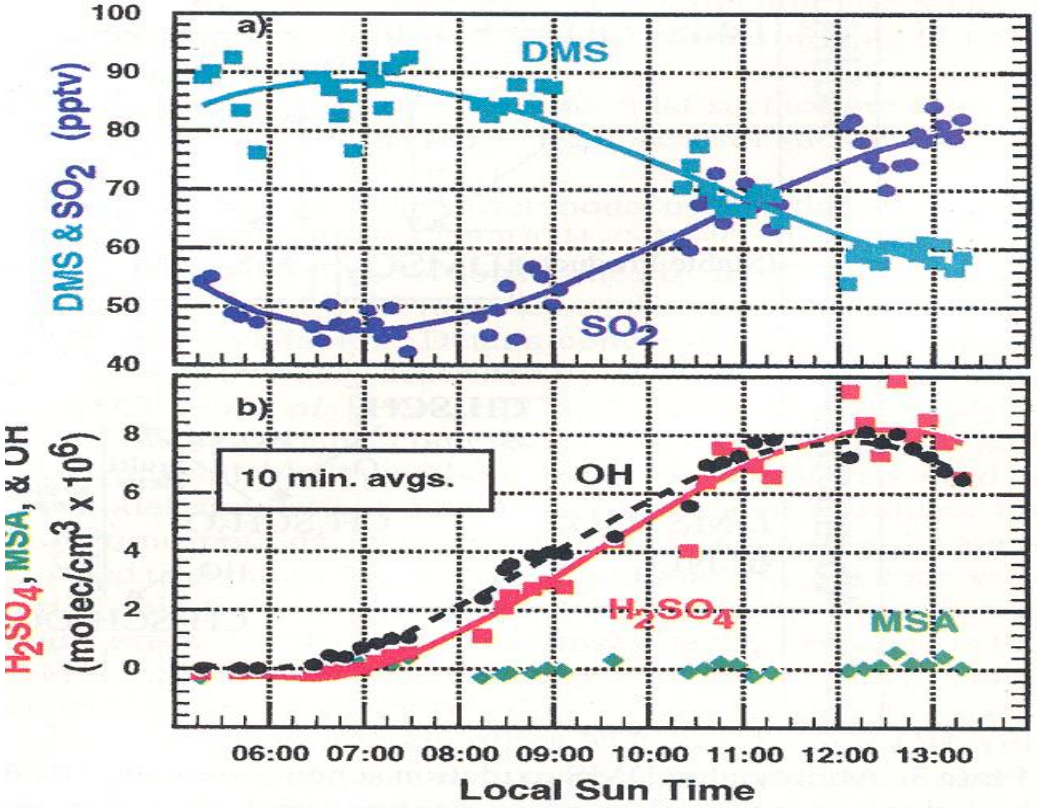
Aqueous phase oxidation of SO_2 by H_2O_2



- H_2O_2 is the principle oxidant for aqueous SO_2 at pH < 5, forming non seasalt sulfate (NSS).
- The original aerosol CCN is altered by the NSS.
  - Increasing the number of particles
  - Increasing the water content of a particular aerosol
- Cloud chamber studies have demonstrated aerosol growth by in cloud reactions of SO_2 and H_2O_2 and O_3, Caffrey et al. (2001).

Marine Boundary Layer gas phase oxidation of DMS and SO_2.

- Use peroxide measurements to constrain levels of hydroxyl radicals, HO and HO_2.
  - Methylhydroperoxide is produce via hydroxyl radical oxidation of methane.
  - Hydrogen peroxide is produced by HO_2 bi-reaction, and its subsequent photolysis generates hydroxyl radical.
- Gas phase oxidation of DMS and SO_2 by hydroxyl radical leads to the formation of non-seasalt aerosol sulfate.



Link between DMS oxidation, formation of SO_2 and sulfuric acid in the marine boundary layer near Christmas Island in the Equatorial Pacific as HO radical increases with the sun rise, Davis et al. (1999).

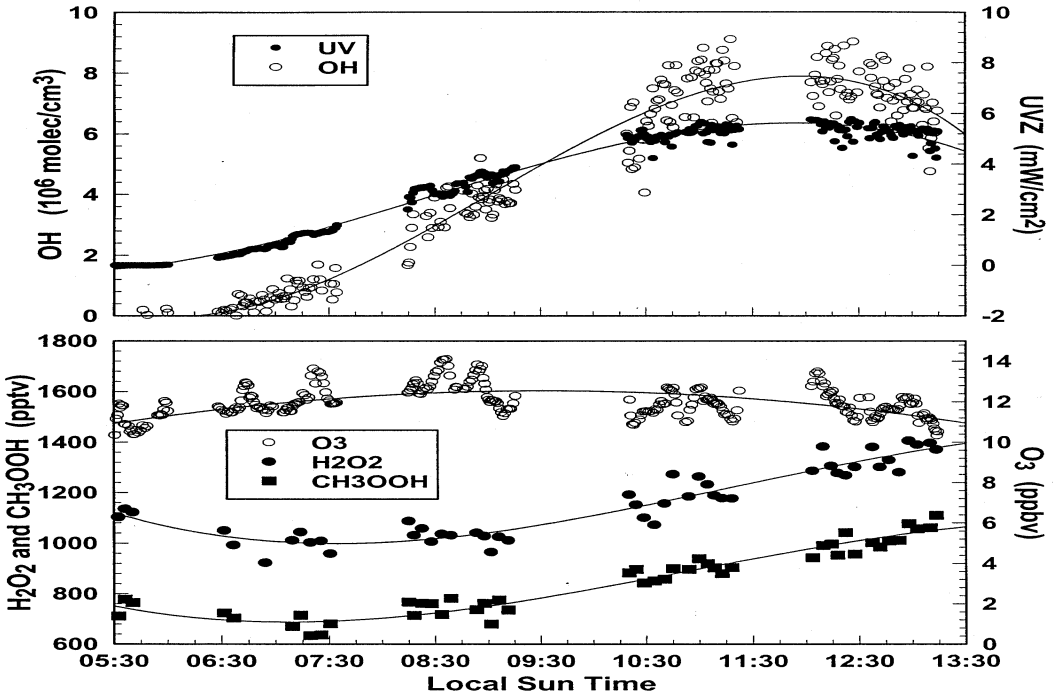
Symbols are in situ measurements, and the lines are the photochemical model output.

Peroxide Measurements

- Gas phase measurements
  - Air is sub-sampled with a forward facing diffuser style inlet. The gas phase peroxides are partitioned in to an aqueous collection solution in a concurrent-flow collection coil.
  - Peroxides are separated via HPLC and quantified by post column derivatization to form a fluorescent dimmer.
  - H_2O_2 and CH_3OOH are separated in about 2 minutes
    - Detection Limit for H_2O_2 is 15 pptv.
    - Detection Limit for CH_3OOH is 25 pptv.
- Counter-flow Virtual Impactor samples will also be analyzed for the peroxides.
  - Determine peroxide content of cloudwater and precipitation.
  - Examine the gas-aqueous phase partitioning of the peroxides.

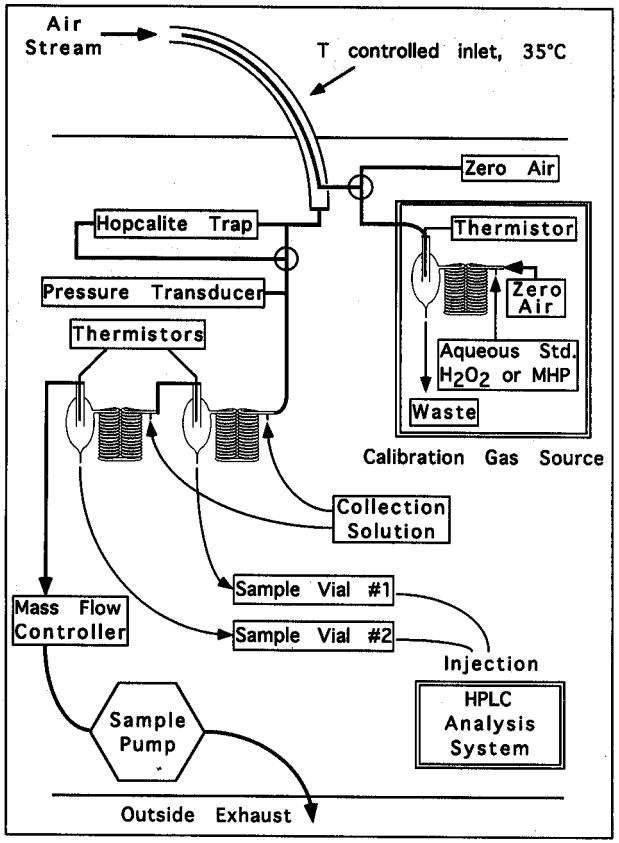
Hypotheses to be tested

- *H1: "The aqueous phase gas-to-particle conversion is rapid enough in some clouds to substantially increase the amount of soluble material in cloud droplets, thus enhancing the activity of CCN upon evaporation."*
- *H2:"Cloud age, **tau**$_c$, is constrained by chemical observations."*
- *H3: "Free-troposphere marine-boundary-layer entrainment velocity, we, and cloud entrainment, **epsilon**$_c$, are constrained by chemical observations."*
- *H4: "The occurrence of recent precipitation in an air parcel's history is detectable from observations of H_2O_2 and CH_3OOH ."*



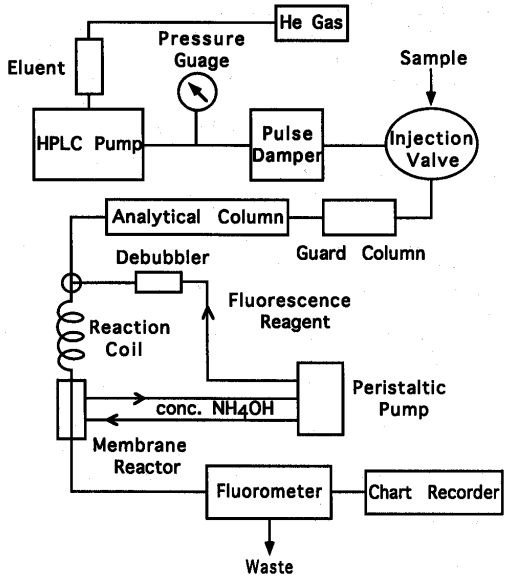
- Relationship between the peroxides and HO radical in the marine boundary layer near Christmas Island in the Equatorial Pacific, Chen et al. (2001).
- Symbols are in situ measurements and the smooth lines are the photochemical model output.
- Predicted H_2O_2 and CH_3OOH depend on the predicted HO and HO_2 levels, allowing the observed peroxide levels to constrain the HO and HO_2 radical levels.

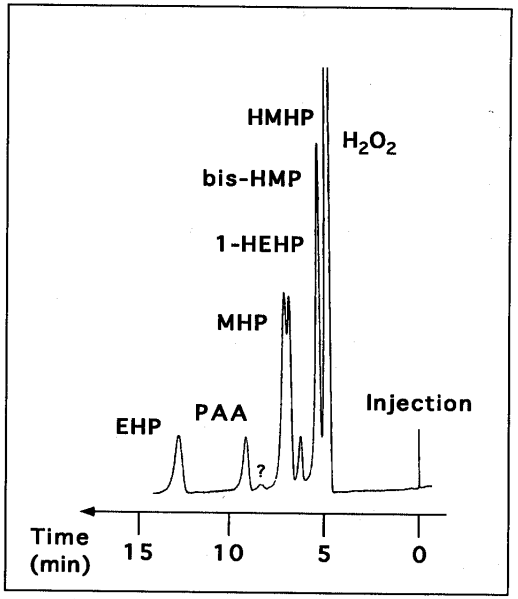
Gas phase Peroxide Measurements



- Gas phase peroxides will be collected from a forward facing diffuser style inlet.
- Peroxides are continuously partitioned in to an aqueous collection solution base on Henry's Law.
- The collection solution is sampled and injected in to an HPLC for peroxide separation and quantification.
- Collect a 30 second sample every 2 minutes minutes when operating two HPLC systems.

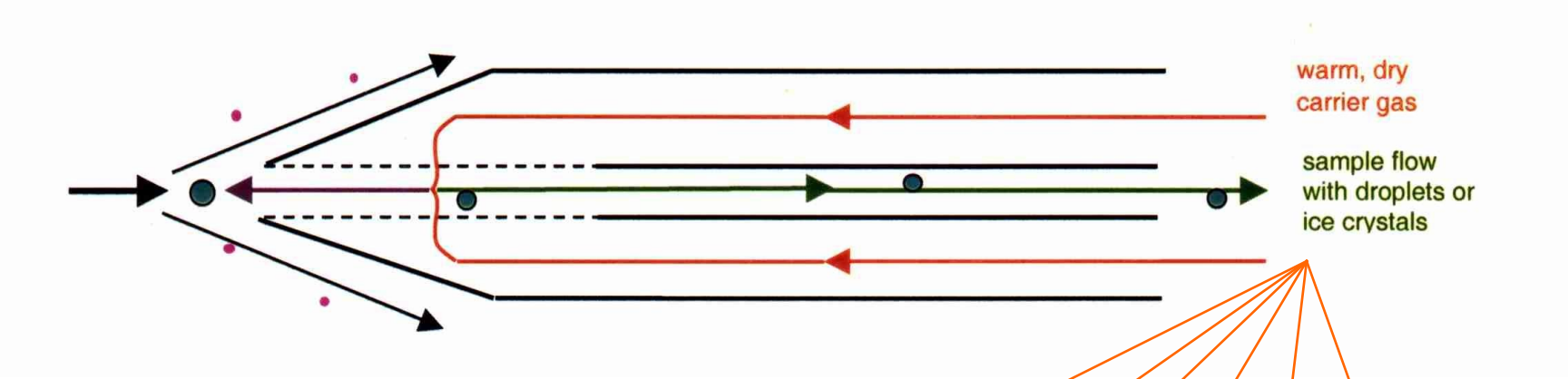
Peroxide Analytical System



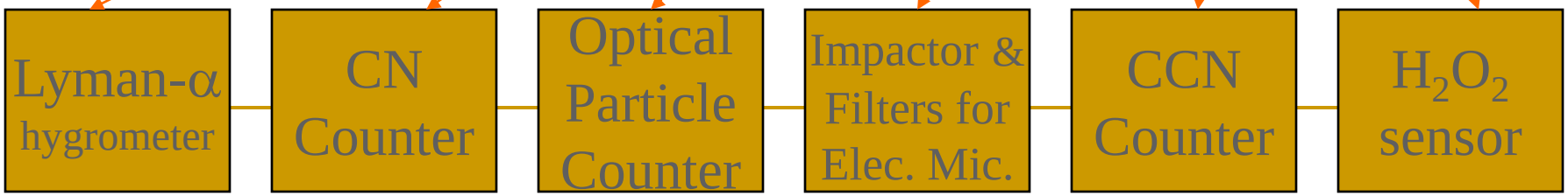


- Peroxides are separated on a C-18 column, and undergo a post column derivatization with p-hydroxyphenyl acetic acid to form a fluorescent dimmer.
- H_2O_2 and CH_3OOH are separated in about 2 minutes
  - Detection Limit for H_2O_2 is 15 pptv.
  - Detection Limit for CH_3OOH is 25 pptv.
- Samples from the CVI inlet will also be analyzed for the peroxides.

Counterflow Virtual Impactor (CVI)



- Cloud droplets (8-50 μm) are impacted into dry nitrogen gas and evaporated. Interstitial particles and gases excluded.
- Volatile gases and non-volatile residual particles are measured.



HO_2 radical production

Ozone Photolysis

$$O_3 + h\nu\ (\lambda < 310\ nm) \rightarrow O(^1D) + O_2$$
$$O(^1D) + H_2O \rightarrow OH + OH$$
$$OH + CO\ (+O_2) \rightarrow CO_2 + HO_2$$

Formaldehyde Photolysis

$$CH_2O + h\nu\ (\lambda < 370\ nm)(+O_2) \rightarrow 2HO_2 + CO$$

Peroxide Sources

Hydrogen Peroxide

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Alkyl Organic Peroxides

$CH_4 + OH\ (+O_2) \rightarrow CH_3O_2 + H_2O$

$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2$

Hydroxyalkyl hydroperoxide

$CH_2{=}CH_2 + O_3 \rightarrow CH_2OOOCH_2 \rightarrow CH_2OO + CH_2O$

$CH_2OO + H_2O \rightarrow CH_2(OH)OOH$

Peroxide Sinks

Homogeneous Loss

Photolysis

$H_2O_2 + h\nu\ (\lambda \leq 360\ nm) \rightarrow 2\ OH$

$CH_3OOH + h\nu\ (\lambda \leq 360\ nm)\ (+O_2) \rightarrow CH_2O + OH + HO_2$

Reaction with hydroxyl radical

$H_2O_2 + OH \rightarrow H_2O + HO_2$

$CH_3OOH + OH \rightarrow CH_3O_2 + H_2O$

Heterogeneous Loss

Seasurface

Aerosols

The NO Card

High NO concentrations

$$NO + HO_2 \rightarrow NO_2 + OH$$

$$NO + CH_3O_2 \rightarrow NO_2 + CH_2O + HO_2$$

Ozone Formation

$$NO_2 + h\nu (\,295 < \lambda < 430\ nm) \rightarrow O + NO$$

$$O + O_2\ (+M) \rightarrow O_3 + M$$