



Multi-Phase Atmospheric Chemistry Present and Future

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Objectives

- u Determine fundamental physical and chemical properties of key atmospheric trace species.
- u Design and improve measurement techniques.
- u Conduct field programs to characterize spatial and temporal distributions of key trace species.
- u Interpret field data to gain mechanistic understanding of factors governing their atmospheric transformation, transport, and deposition

Laboratory Investigation

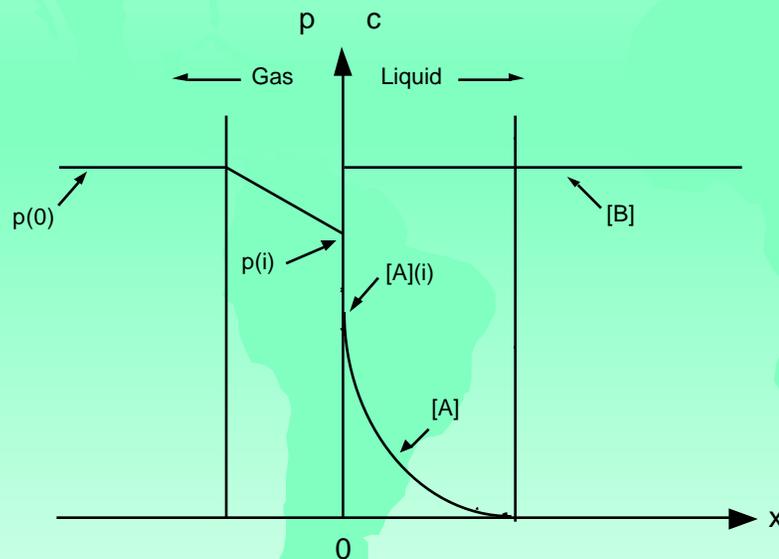
u Kinetics of fast aqueous-phase O_3 reactions

Kinetics and mechanism data are needed to quantitate:

- Rate of O_3 deposition to vegetation, surface water, and human respiratory system.
- Extent of cloud processing affecting O_3 and O_3 precursors.
- Effectiveness of disinfection of drinking water by ozonation.

Absorption of gas in the moderately fast reaction regime

- Concentration gradient across a gas-liquid interface showing that reaction takes place mainly in the film

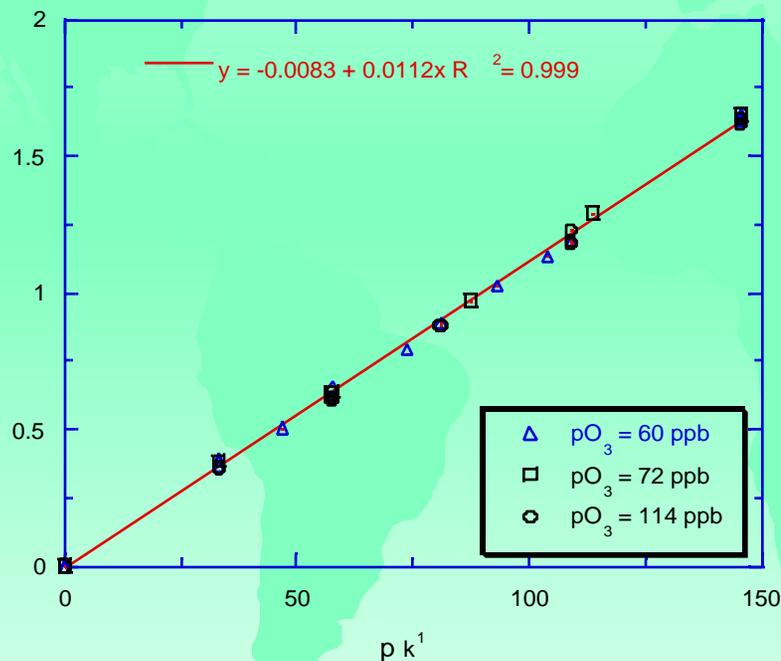


- The absorption of a gas A into agitated liquid accompanying moderately fast reaction with a solute B is given by

$$R_{\text{abs}} = N_A a = a (k^{(2)} D_A [B])^{1/2} [A]_i$$

Calibration using the known Na_2SO_3 reaction kinetics

u O_3 depletion as a function of $k^{(1)}$



The behavior of ozone reaction in a gas-liquid reactor obeys the equation derived from the film model:

$$\ln(p\text{O}_3^0/p\text{O}_3^t) = C k^{(1)}$$

u A calibration curve using Na_2SO_3 as reference compound ($k^{(2)} = 1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Conditions: $F_g = 2.0 \text{ L/min}$, $V_1 = 50 \text{ mL}$, $T = 22.0 \text{ }^\circ\text{C}$, $[\text{phosphate}] = 10 \text{ mM}$ @ pH 6.80.

Summary of O₃ reaction kinetics

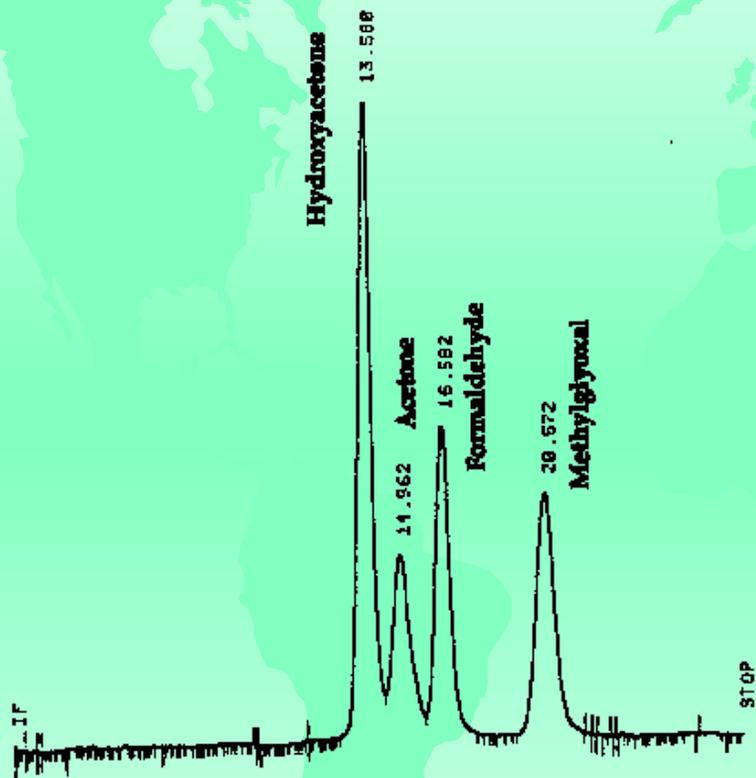
(all in units of 10⁹ M⁻¹ s⁻¹, 22.0 °C, except where specified)

<u>Compound</u>	<u>pH = 6.80 (phosphate)</u>	<u>9.08 (borate)</u>	<u>9.32(borate)</u>
KI	2.34 ± 0.07	2.55 ± 0.07	2.59 ± 0.08
NaNO ₂ x10 ⁵ M ⁻¹ s ⁻¹	6.41 ± 0.34		6.39 ± 0.10
Na ₂ S + NaHS		2.94 ± 0.11	
Humic Acid x10 ⁵ (g/L) ⁻¹ s ⁻¹		2.98 ± 0.19	3.53 ± 0.13
Resorcinol		0.57 ± 0.014	1.08 ± 0.04
Guaiacol		0.64 ± 0.04	1.31 ± 0.09
Ascorbic acid	1.64 ± 0.22	1.75 ± 0.22	
Phenol	1.11 ± 0.07	1.80 ± 0.15	
	(pH = 10.2)	(pH = 10.8)	
Glutathione		1.26 ± 0.12	
Cysteine	0.10 ± 0.02	2.0 ± 0.3	

Method Development

u Hydroxyacetone (HA)

- We have recently developed a technique for HA, a downstream product of isoprene. The method is based on sulfur (IV) complexation of dissolved carbonyls followed by ion chromatographic (IC) separation and post-column fluorescence detection of re-released S(IV) using *o*-phthaldehyde in the presence of NH_4^+ . A chromatogram showing the separation of several atmospheric carbonyls is shown below. The limit of detection is estimated to be 0.3 ppbv (3 min integration).



Ion chromatogram showing the detection of hydroxyacetone (HA, 10 μM) along with several other carbonyl compounds (10 μM of acetone, and 2 μM of FA and MG). Pre-column derivatization with 10 mM S(IV) at pH 9.0 and post column derivatization with NH_3 and *o*-phthaldehyde at pH 9.7 followed by fluorescence detection ($\lambda_{\text{ex}} = 330 \text{ nm}$ and $\lambda_{\text{em}} = 380 \text{ nm}$). IC separation achieved with a 3 cm anion separation column (Vydac, 300IC405) under isocratic condition at flow rate = 0.6 mL min^{-1} . Mobile phase is a 1.5 mM hydrogen phthalate buffer maintained at pH 2.5 using formic acid.

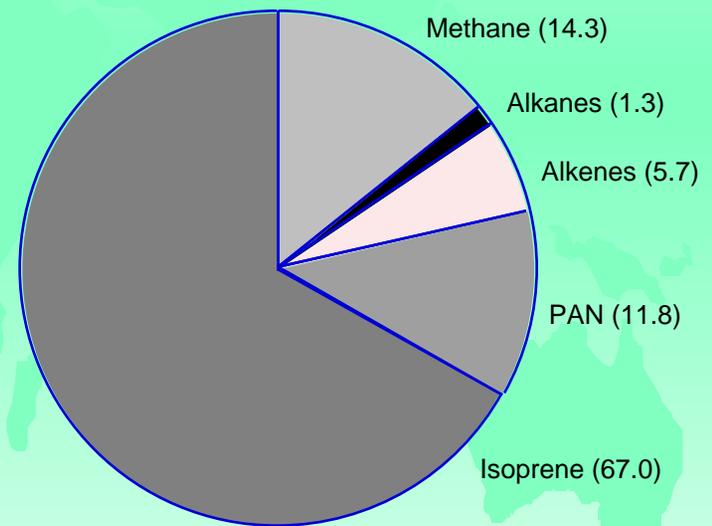
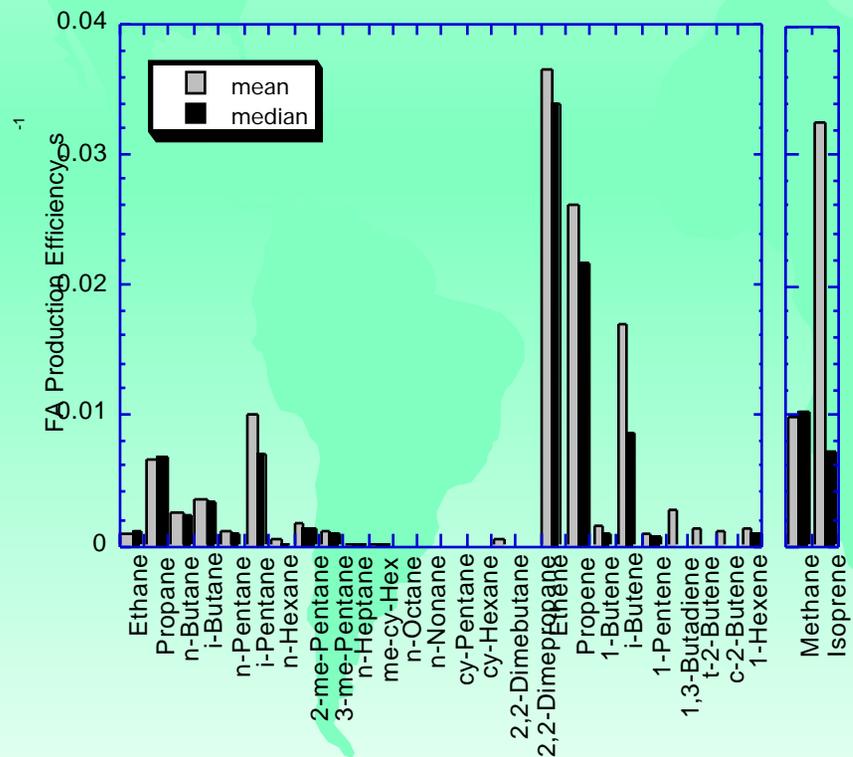
Field Measurement Campaigns

- u 1995 Nashville/Middle Tennessee Ozone Study
- u 1996 NARE -Spring Expedition
- u 1996 NARSTO-NE/New York Metropolitan Area
- u 1997 NARE -Fall Expedition

1995 Nashville O₃ study

Formaldehyde production efficiency of VOC's measured on the G1

Relative contribution to formaldehyde production using $[OH] = 1 \times 10^7 \text{ cm}^{-3}$



$d[FA]/dt = 2.56 \text{ ppbv hr}^{-1}$

1995 Nashville O₃ study

u Major findings:

- Isoprene is the dominant source of formaldehyde and glyoxal, methylglyoxal, and glycolaldehyde.
- Formaldehyde plays a central role in radical chemistry:
 - a key OH sink, comparable to isoprene and CO
 - a key source of HO₂, accounting for ~1/3 of total radical production.
- Having a major source in isoprene, formaldehyde can serve as a proxy for isoprene to test the various versions of isoprene emission inventory.

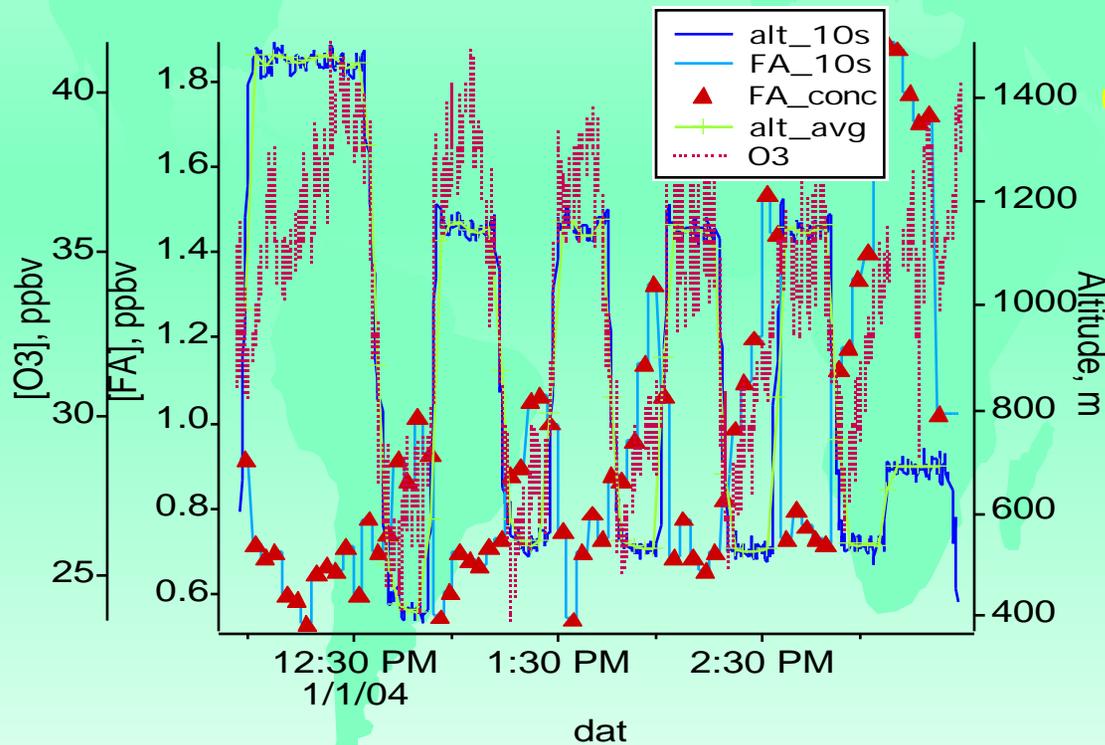
1995 Nashville O₃ study

u Publication:

Y.-N. Lee, X. Zhou, L. I. Kleinman, L. J. Nunnermacker, S. R. Springston, P. H. Daum, L. Newman, W. G. Keigley, M. W. Holdren, C. W. Spicer, D. D. Parrish, J. Holloway, J. Williams, J. M. Roberts, T. B. Ryerson, F. C. Fehsenfeld, V. Young and B. Fu. **Atmospheric chemistry and distribution of formaldehyde and several multi-oxygenated carbonyl compounds during the 1995 Nashville/Middle Tennessee Ozone Study**, J. Geophys. Res., 1998. Submitted.

1996 NARSTO-NE

u Morning flight of 7/11/96 over the Harvard Forest



u Break-up of nocturnal inversion and development of mixing layer is clearly seen in the observed formaldehyde concentration build-up.

Instrument Design and Improvement

- u Formaldehyde measurement intercomparison
 - BNL coil-DNPH-HPLC technique
 - NCAR tunable diode laser absorption spectrometry
 - TTU diffusion scrubber-Hantzsch reaction
 - URI coil-NADH enzyme fluorescence

All on-line continuous capable of 5 min time resolution.

u Results

The BNL technique was found to agree with the NCAR TDLAS technique to within -12% for a fairly wide concentration range, 0.8 ppbv ~ 5 ppbv.

Formaldehyde intercomparison-continued

u Publications:

Gilpin, T., Apel, E., Fried, A., Sewell, S., Wert, B., Calvert, J., Zhang, G., Dasgupta, P., Harder, J. W., Heikes, B., Hopkins, B., Westberg, H., Kleindienst, T., Lee, Y. -N., Zhou, X. and Lonneman, W. J. Intercomparison of six ambient [CH₂O] measurement techniques. *J. Geophys. Res.*, *102*, 21161-21188, 1997.

Li, S. -M., Macdonald, A. M., Strapp, J. W., Lee, Y. -N., and Zhou, X. Chemical and physical characterizations of atmospheric aerosols over southern California. *J. Geophys. Res.*, *102*, 21341-21353, 1997.

Future Research

- u Effort will continue in the following areas:
 - Fundamental Laboratory Study
 - Instrumentation Development
 - Field Measurement Programs

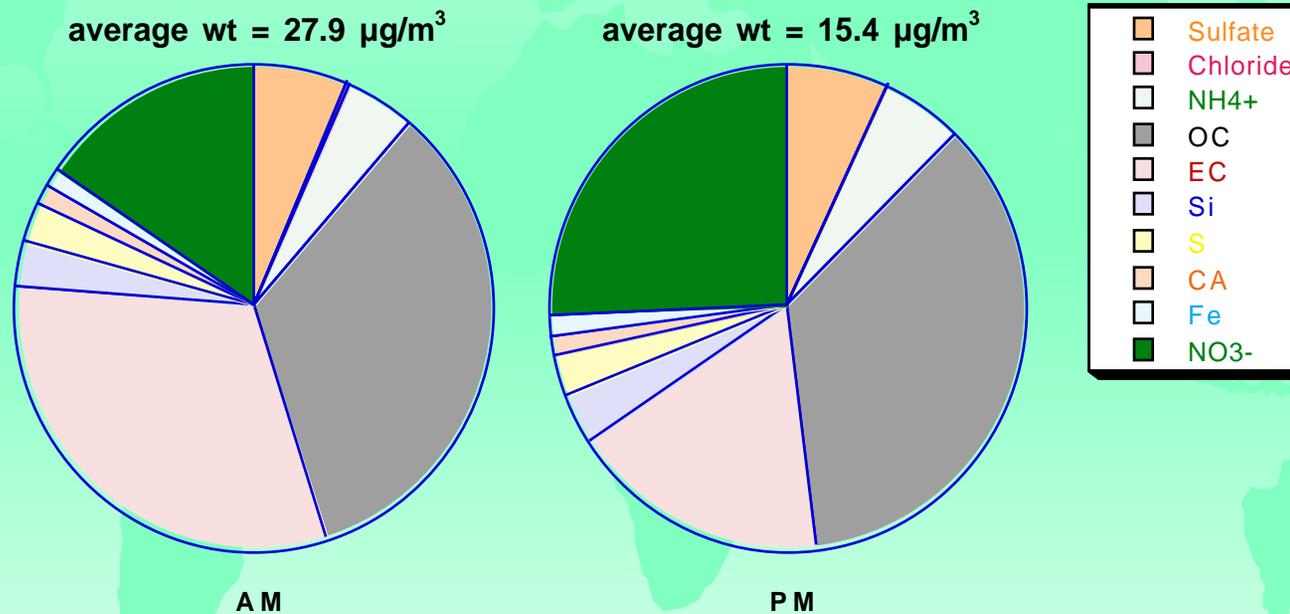
- u Focus will expand to include characterization of ambient aerosol particles
 - number and size distribution
 - size dependent chemical composition
 - F inorganic ions
 - F minerals
 - F carbonaceous materials

An Improved Aircraft Formaldehyde technique

- u An on-line continuous capability will be integrated into the current BNL formaldehyde technique by incorporating on-board real time HPLC analysis. The advantages include:
 - near real time data collection (time delay 10 min).
 - eliminate the labor intensive preparation involved in batch analysis.
 - reduce ground support requirement.

Aerosol characterization-Phoenix

u Major chemical components of PM_{2.5}



J. Watson et al., The 1989-90 Phoenix urban haze study. Vol. II: The apportionment of light extinction to sources. Final report. DRI Document No. 8931-5F1, 1991.

Aircraft techniques-currently available

u Optical Counter (PCASP)

- size distribution from 0.1 to 3 μm .
- derived surface, volume, and mass information

u Integrating nephelometer

- Aerosol light scattering
- derived mass information

u Aethalometer (particle/soot absorption photometer)

- black carbon content
- derived OC content

u Filter samples

- 10 to 20 min average concentrations of NO_3^- , SO_4^{2-} , Cl^- , NH_4^+ , Ca_2^+

Aircraft techniques - to be developed and improved

u Filter samples

- 10 - 20 min average concentrations of minerals using ICP-MS.
- 20 min average concentrations of extractable organic carbon using the GC-ECD-MS technique.
- 20 min average concentrations of EC and OC using the Thermal/Optical Reflectance Carbon Analysis technique.
- Individual particle analysis using EM equipped with energy-dispersing X-ray spectrometry.

u Key considerations in sampling of aerosols

- size segregation
- inlet design
- quantitative collection or removal of gaseous HNO_3