G-1 Summary



Objectives and Approach

Intercomparisons

Some Results

Photochemical age SOA formation Aerosol optical properties Aerosol nitrate O_3 production rates

"I will not corners" Bart Simpson

Data presented here is preliminary. Science is 1 to 4 weeks old.



fttp://ftp.asd.bnl.gov/pub/ASP Field Programs/

ASP G-1 Research Aircraft Facility Layout





PCASP, CAPS – PNNL, BNL: Senum, Hubbe State – PNNL: Hubbe PTRMS - EMSL: Alexander, Ortega AMS - Aerodyne, EMSL: Alexander, Jayne Peroxides - SUNY, BNL: Lloyd, Bowerman VOCs – York: Hubbe, Rudolf PILS – BNL: Lee CO, NO, NO₂, NO_y O₃, SO₂ – BNL: Springston, Senum PSAP, Neph, CNCs – PNNL: Group TSEMs – BNL: Wang MFRs – PNNL: Barnard SPSP – DMT, CIRPAS: Kok, Jonsson, Senum Balloons – PNNL: Zaveri, Hubbe Data – PNNL, BNL: Hubbe, Springston, Senum

Flight Plans and Winds



Winds at T1 and T2 from SSW Upslope winds along basin rim

OBJECTIVES

Characterize Source Region

Time Evolution of Aerosols in the Near-Field (0 to 12 hours)

Chemical composition Size distribution Optical properties

Photochemistry

 $\rm O_3$ productions rates and $\rm NO_x/VOC$ sensitivity SOA precursors

Chemical Signatures to Diagnose Boundary Layer Flows

Coordinate with King Air Lidar measurements

Approach

Repetitive flight plans with 10's of transects over T0, T1, and T2 Assemble statistics by location and for all plumes

Kinetics from Lagrangian Expt. when flow is from T0 to T1 to T2

More generally, use photochemical age and location to provide time scale Use CO as an inert tracer of urban emissions

Transects at multiple altitudes for determining basin flows

Compare Mexico City with U.S. urban areas

Box model calculations for $P(O_3)$ and NO_X/VOC sensitivity

Need partners for analysis and calculations

IT WORKED!

Dirty Air is More Interesting than Clean Air

Most equipment worked most of the time Good intercomparison and self consistency

T1 to T2 Lagrangian transport days with AM and PM flights

Age markers useful under less well defined transport conditions

Chemical mixtures different than observed in U.S. urban areas More of the same or new processes?

Missing: PM flights in urban basin in 2nd half of program

Intercomparisons

Winds: G-1, C130



CO: G-1, C130



Scattering: G-1, C-130



CO: G-1, T0



Stephen Springston G-1, Gao Chen C-130, Greg Huey T0

Aerosol Optical Properties



- Light scattering, absorption were 2 times Eastern U.S.
- Urban area routinely surpassed peak U.S. values
- Higher proportion black carbon in Mexico aerosol
- Mexico aerosol has lower ω_0 than U.S.

Aerosol Composition Comparison



Mexico City Urban



- Eastern U.S. episodes sulfate dominated
- Mexico urban aerosol organic dominated, with nitrate

Photochemical Age



NO_x/NO_y



Toluene/Benzene



NO_x/NO_y and Toluene/Benzene decrease with photochemical processing - at about the same rate. Graphs cover factor of 10 change. Fresh emissions (High ratio – low age) over T0 and West and SW Basin Air masses are older to North and East

SOA and Photochemical Age

Age = $- Log([NO_x]/[NO_v])$



[Organic Aerosol]/([CO] – 100 ppb)



Assume CO is an inert tracer of POA and SOA precursors Without SOA production [Organic]/[CO] is constant

Lowest [Organic]/[CO] ratio occurs in low age air masses over T0 and to W and SW

To the North and East, air masses are older and [Organic]/[CO] ratio increases 8-fold

Time Evolution of SOA and Light Absorption

Organic aerosol/CO

Light Absorption/CO





8 – fold increase in Organic with age

0.6

0.8

-Log (NOx/NOy)

1.0

1.2

1.4

°^γ 20 × 10

0.0

02

0.4

2-fold increase in Light Absorption with Age

Aerosol Nitrate

Aerosol NO_3^- and NO_z vs time



Gas-Aerosol partitioning of $NO_{3^{-}}$ can be followed on 10 s time scale

$[NO_3^{-}]/[CO]$ vs. $[NO_2]/[NO_y]$



Near emission source NO_3^{-}/CO increases from photochemistry Away from source NO_3^{-} evaporates

Ozone Production

Constrained Steady State Box Model Calculations



Peak $P(O_3) \approx 30$ ppb h⁻¹ over City and to W and SW Peak $P(O_3)$ occurs under VOC limited conditions

Mexico City, Phoenix, and Houston



For VOC limited conditions: $P(O_3) \approx (VOC/NO_2)_{reactivity} H Q(radical production rate)$

Extreme $P(O_3)$ as in Houston requires a higher VOC/NO_x ratio

Posters

Overview and Intercomparisons: Stephen Springston Aerosol Composition and Evolution: Yin-Nan Lee Ozone Production and Aerosol Evolution: Larry Kleinman Peroxides: Judy Weinstein-Lloyd PTRMS: John Ortega WRF Chem – Aerosols: Jerome Fast T1 – T2 Overview: Chris Doran KA Lidar: John Hair