Gas Phase and Aerosol Processing During Long-Range Transport: The Importance of Cloud Processing

Joost de Gouw & Charles Brock

1. Two case studies:

- SO_2-sulfate plumes from Asia observed over western U.S.
- Forest fire plumes from Alaska observed over eastern U.S.

2. Implications

Long-Range Transport & Chemical Transformation

What is the role of field intensives?

High level of (chemical) detail allows studies of:

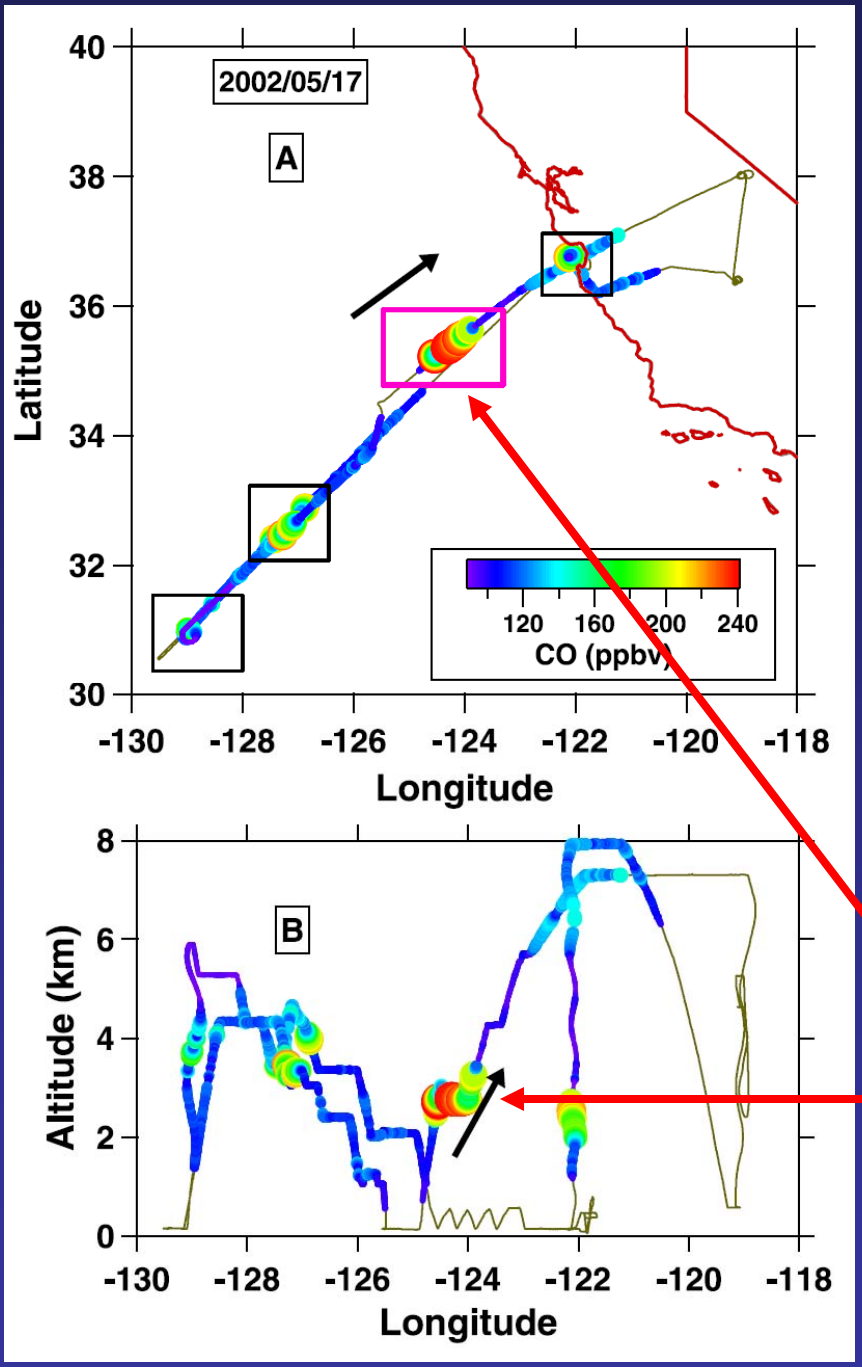
- Mechanisms of long-range transport
- Chemical transformation during the transport

What are the goals?

- Provide detailed test cases for global models
- Validated models $\Rightarrow$ quantification of the impacts

1. SO_2-sulfate plumes from Asia observed over western U.S. in 2002

[*Brock et al*., JGR 2004]

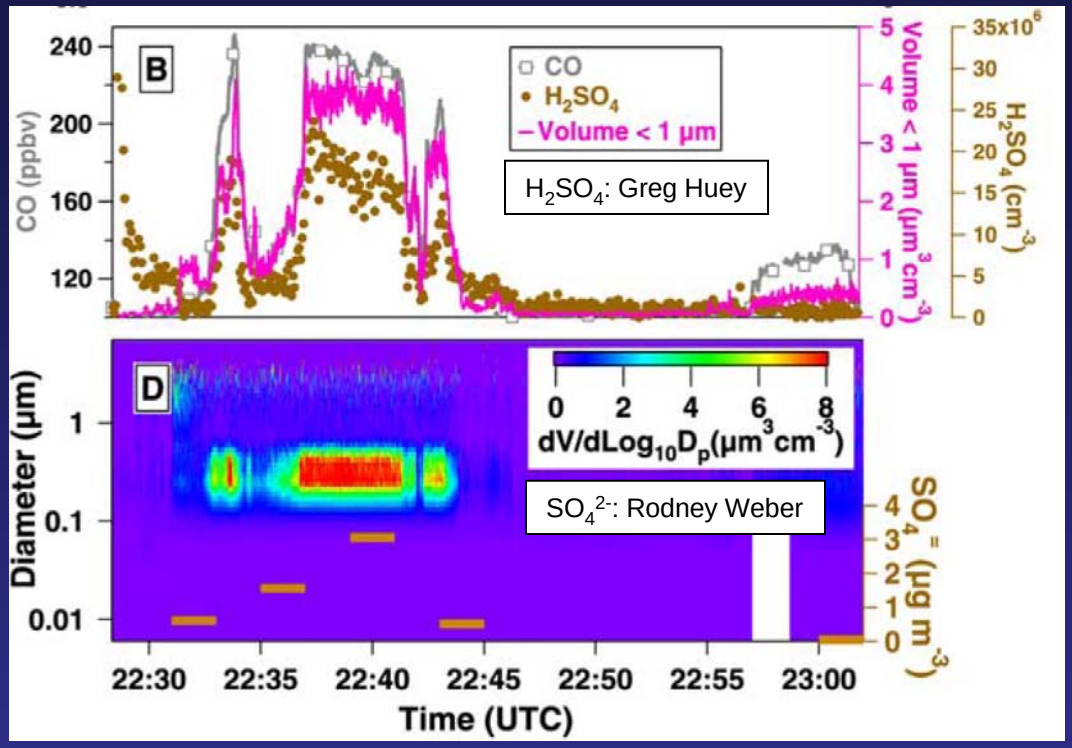


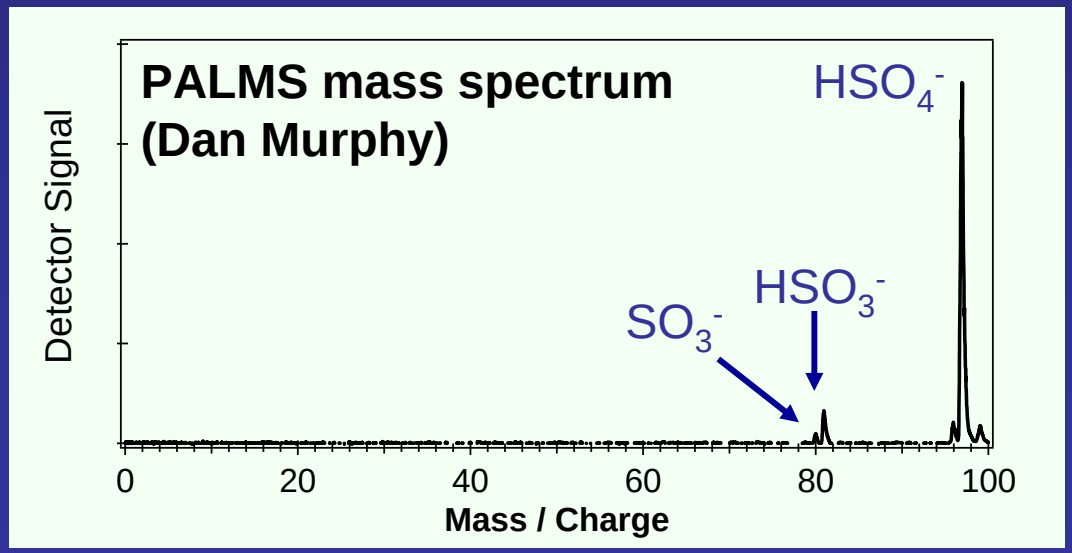
ITCT 2k2 Study

- Intercontinental Transport and Chemical Transformation study in 2002
- Long-range transport (LRT) of Asian emissions across the Pacific
- LRT observed on multiple days

Example from May 17, 2002: Enhanced CO in layer at relatively low altitude

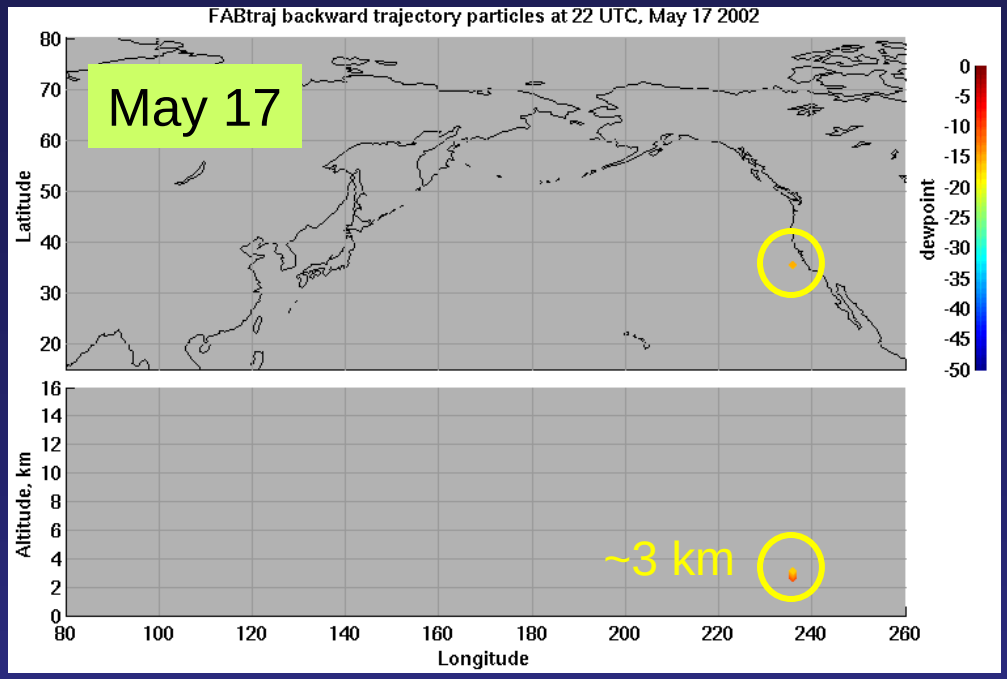
Aerosol Composition of the May 17 LRT Layer

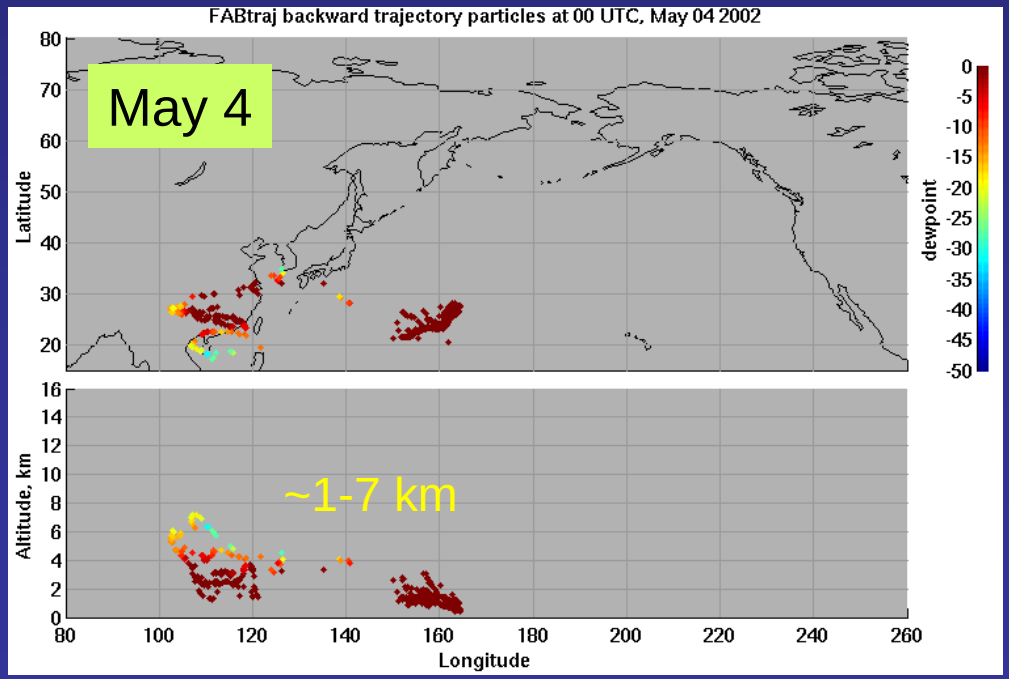




- Highest SO_2, SO_4^{2-} and H_2SO_4 in the free troposphere during ITCT 2k2
- Aerosol volume consistent with sulfate composition
- PALMS: almost pure sulfuric acid particles, as pure as in stratosphere

Why is there such a high fraction of sulfate?

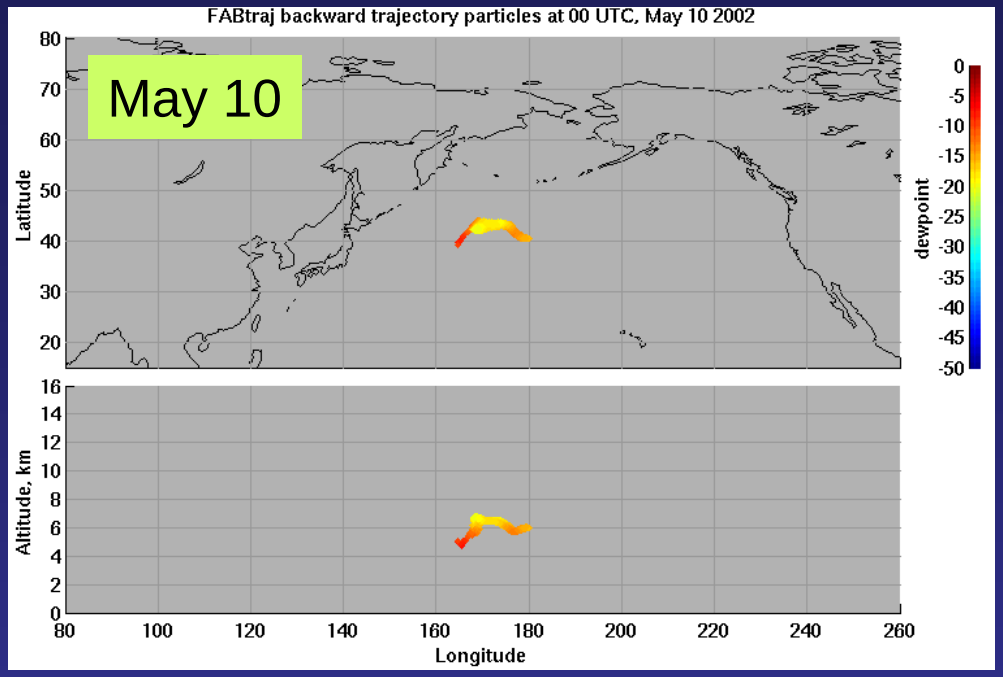


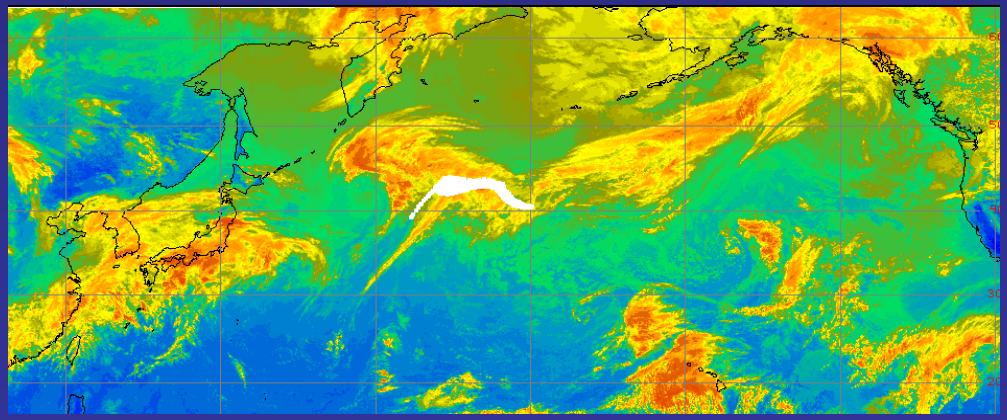


Back-Trajectory Analysis

- 567 back trajectories calculated from the location of the highest CO
- Fraction of trajectories was over China ~13 days prior to the measurement

Back-Trajectory Analysis





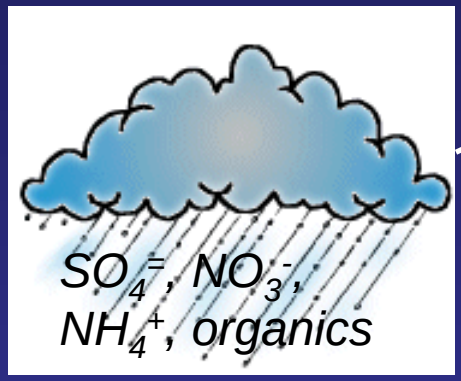
- 8 days prior to the measurement, back-trajectories were uplifted in a mid-latitude cyclone
- Cloud processing of the pollution plume must have occurred

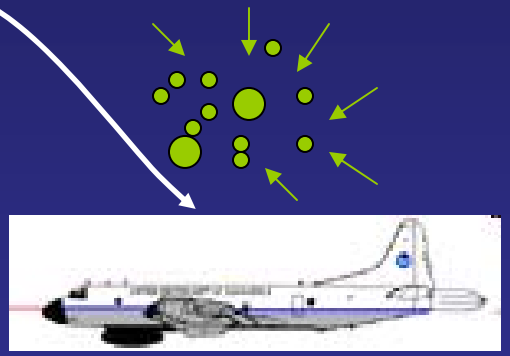
Conceptual Model for the Transport

2. Lifting & Scavenging
- Particles removed
- Some SO_2 remains

3. Descent & Chemistry
- $SO_2 \rightarrow H_2SO_4$
- particle nucleation & growth

1. Transport & Chemistry
- $SO_2 \rightarrow SO_4^{2-}$
- Some SO_2 remains
- Organic aerosol and nitrate formed

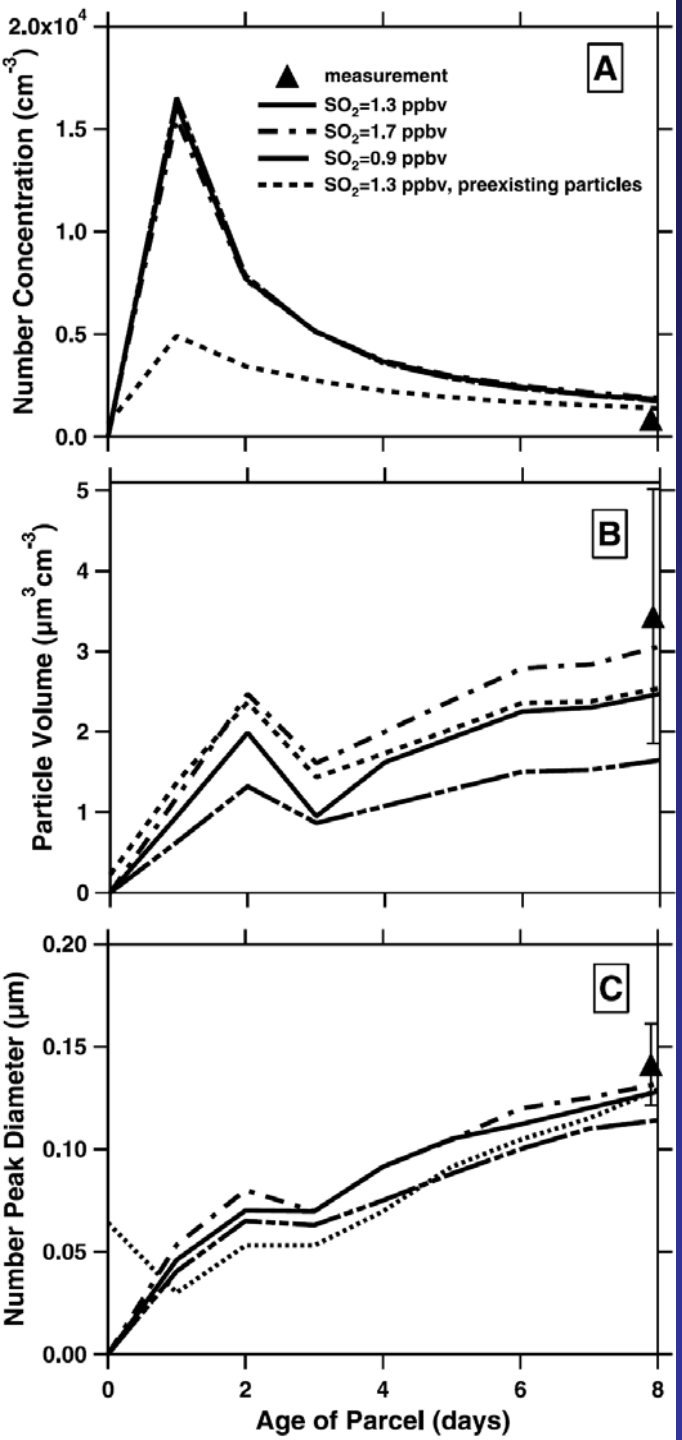




~6 days

~8 days

Could explain why particles are mostly sulfate



Box Model of Nucleation and Growth (Ned Lovejoy)

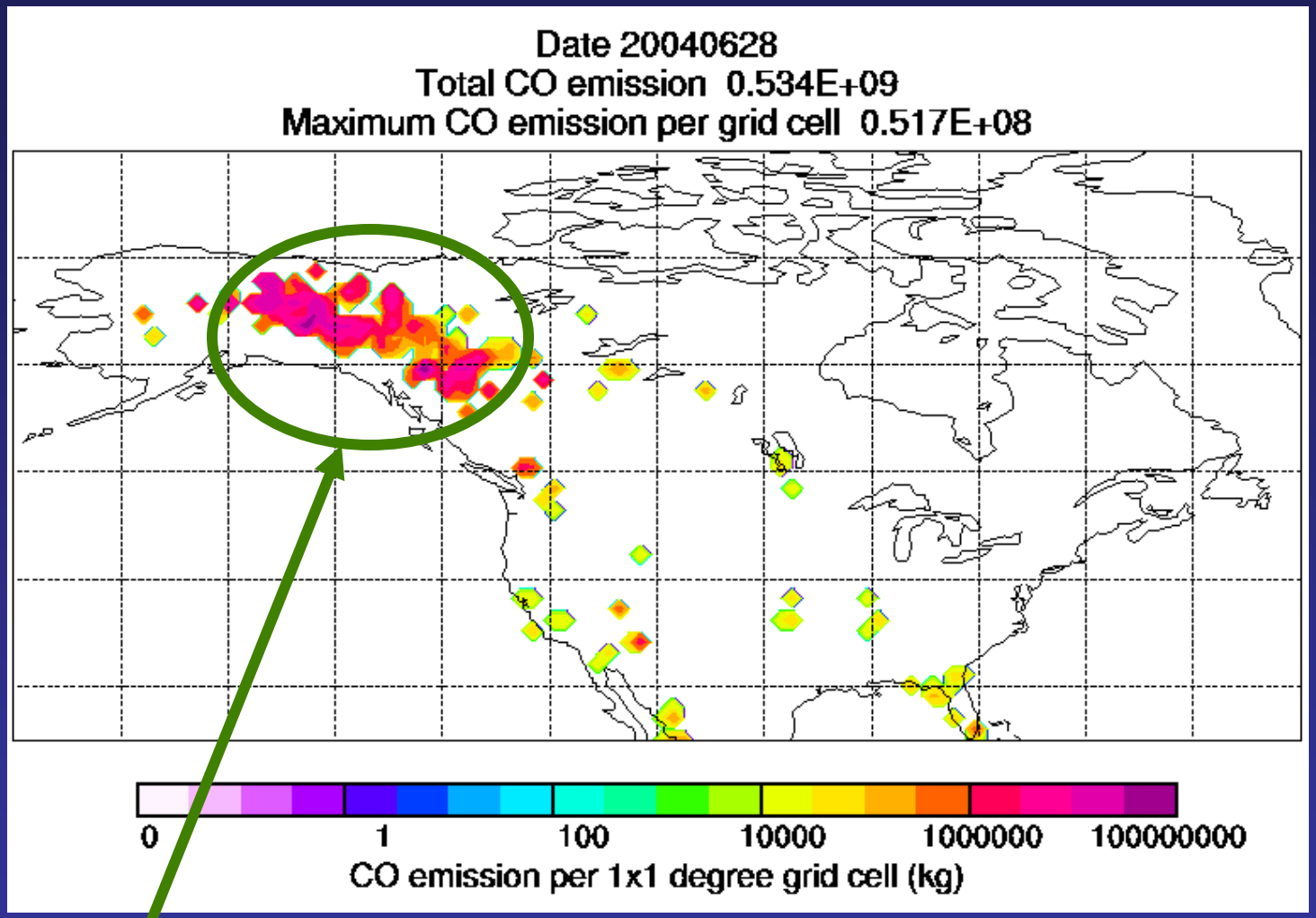
- Model begins at exit from cloudy air
- Simulates nucleation (ion-assisted), condensational growth and coagulation
- Conditions from trajectory simulations
- Initial SO_2 constrained by observed SO_2 and SO_4^{2-}
- OH required to produce observed particulate SO_4^{2-} ~3×10^6 cm^{-3} (NASA model: OH ≈ 2×10^6 cm^{-3})

Conceptual model consistent with particle size distribution and composition

2. Forest fire plumes from Alaska observed over eastern U.S. in 2004

[*de Gouw et al*., JGR 2006]

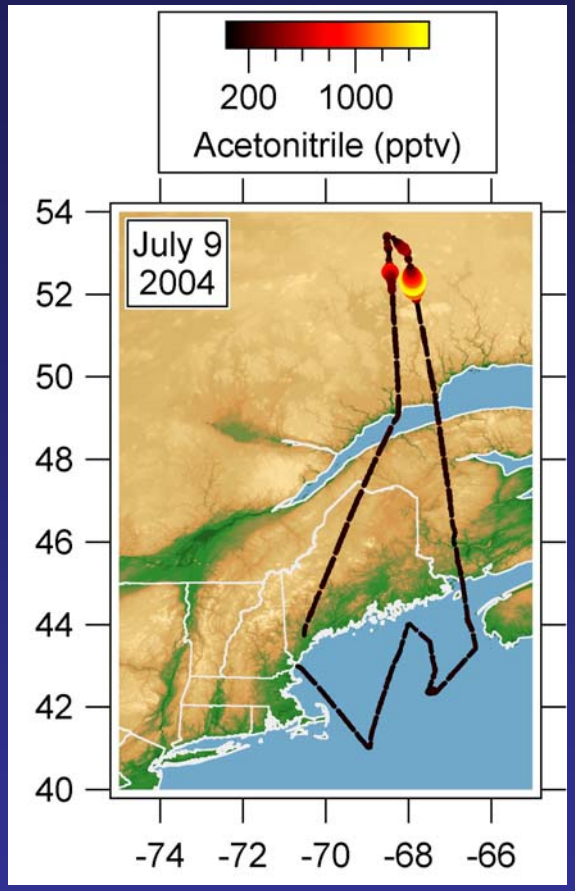
Forest Fires in Alaska and Western Canada in 2004

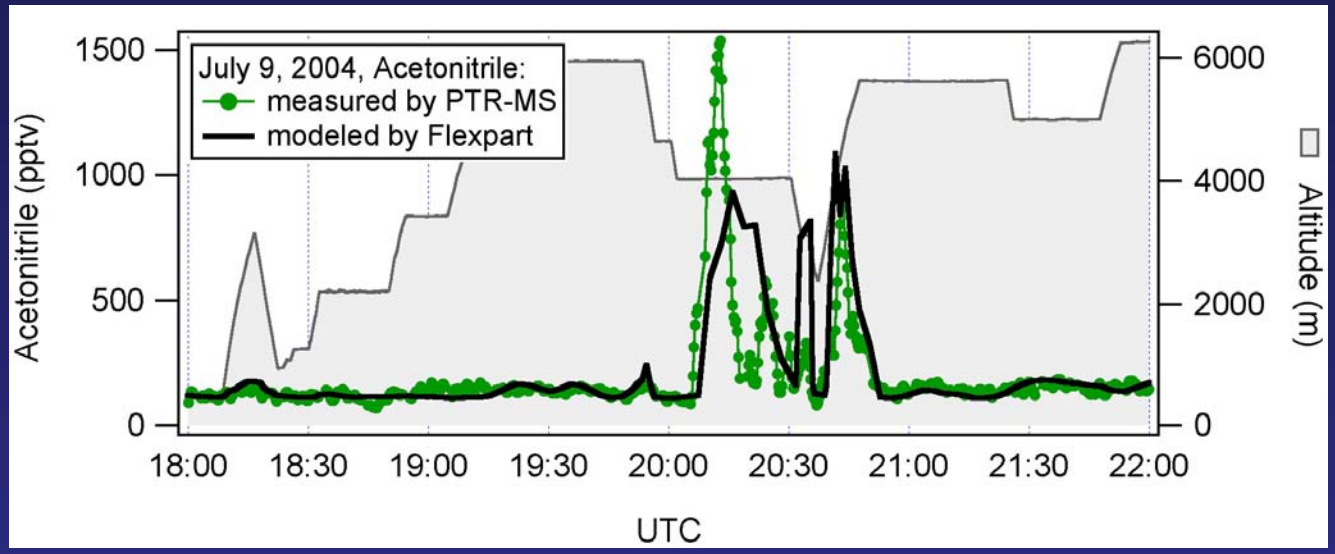


Fires late June and early July

Andreas Stohl, using data from MODIS & Center for International Disaster Information

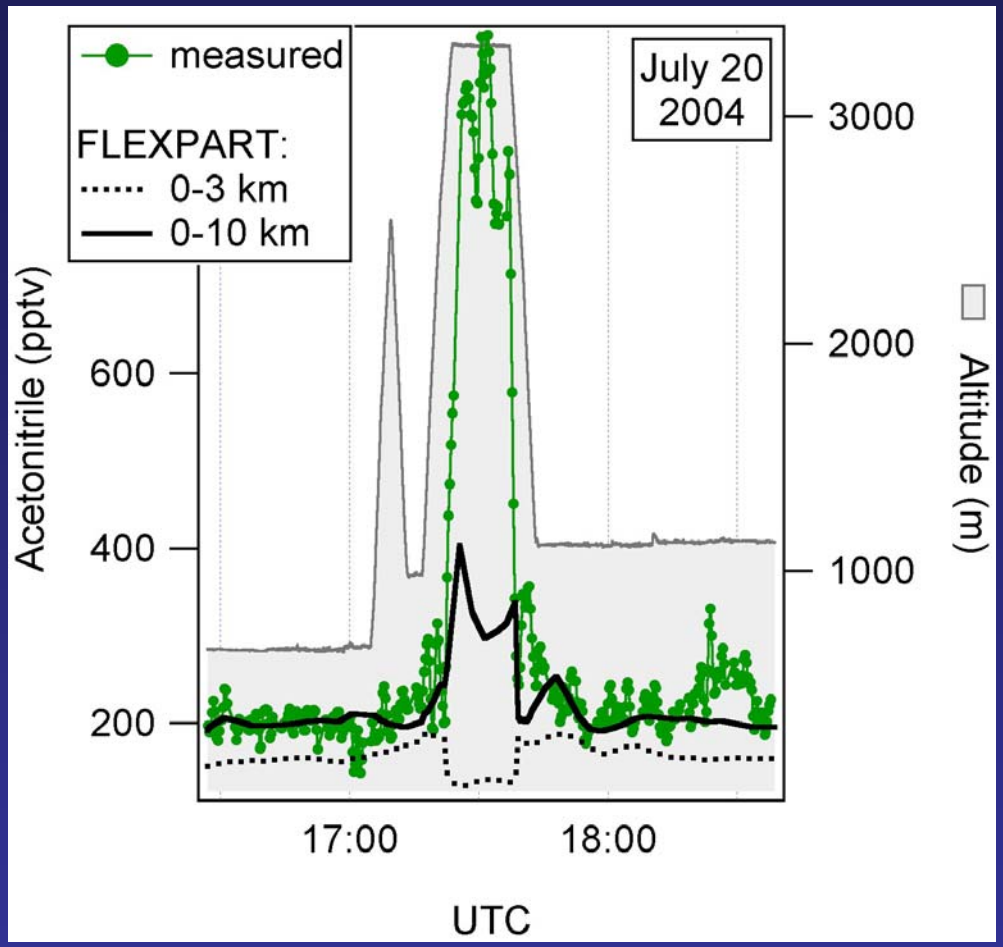
Observations of Fire Plumes From NOAA WP-3D

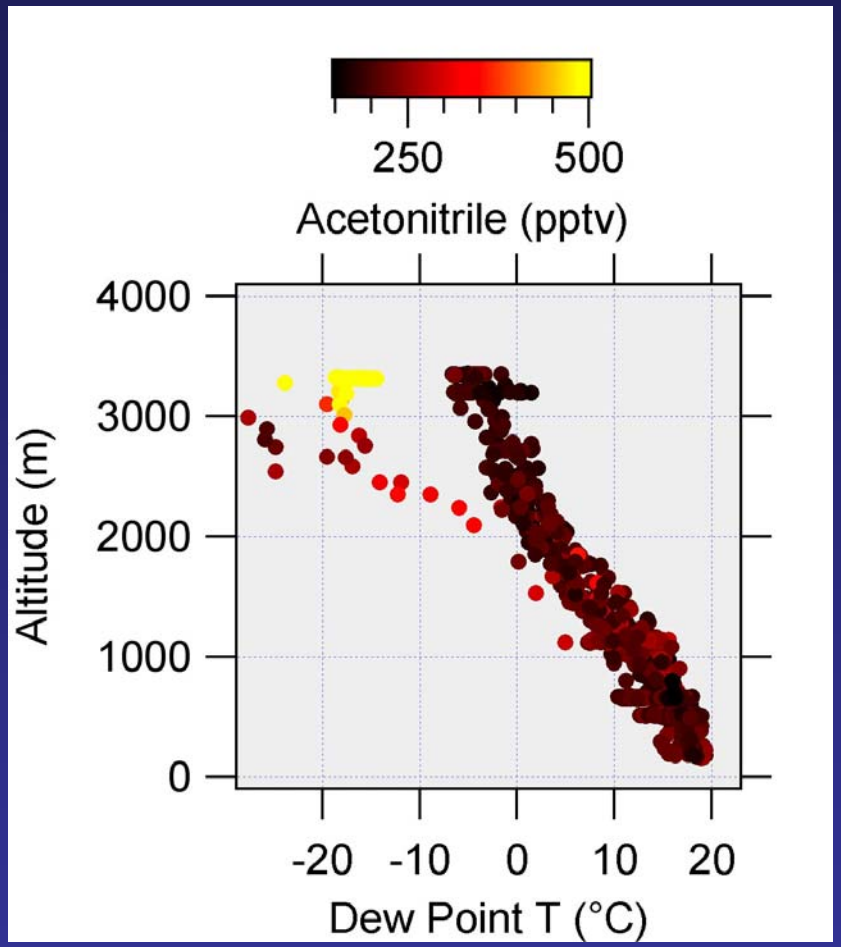




- Plumes targeted using GOES satellite images
- Acetonitrile (CH_3CN) is very useful tracer for identifying forest fire plumes
- Transport of the plumes was described well by the Lagrangian transport model FLEXPART

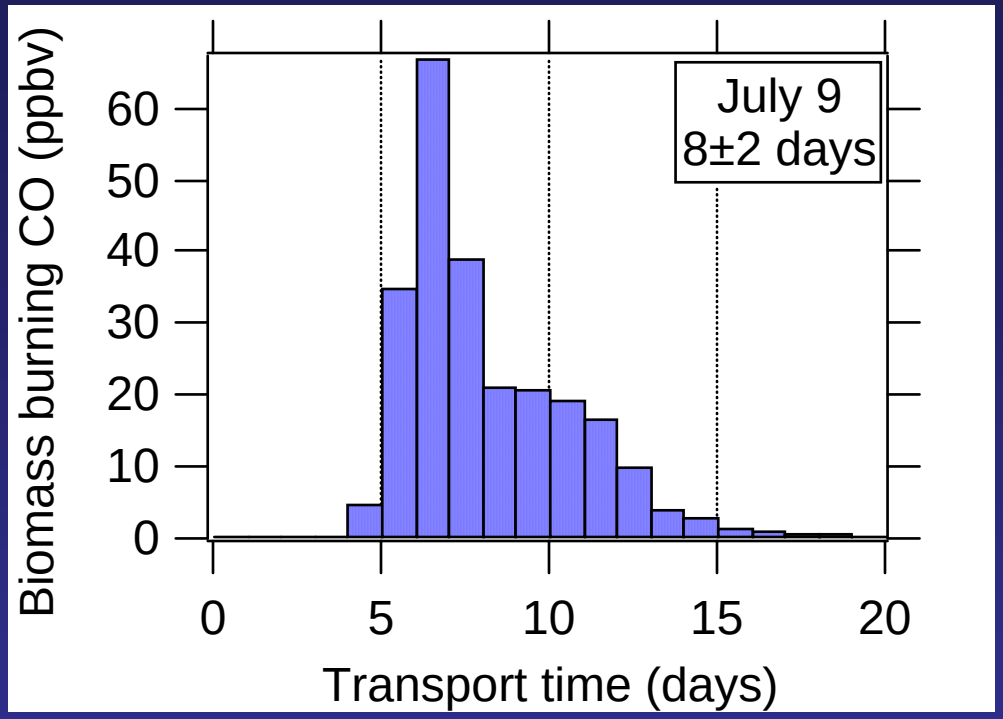
Evidence for Pyro-Convective Lifting



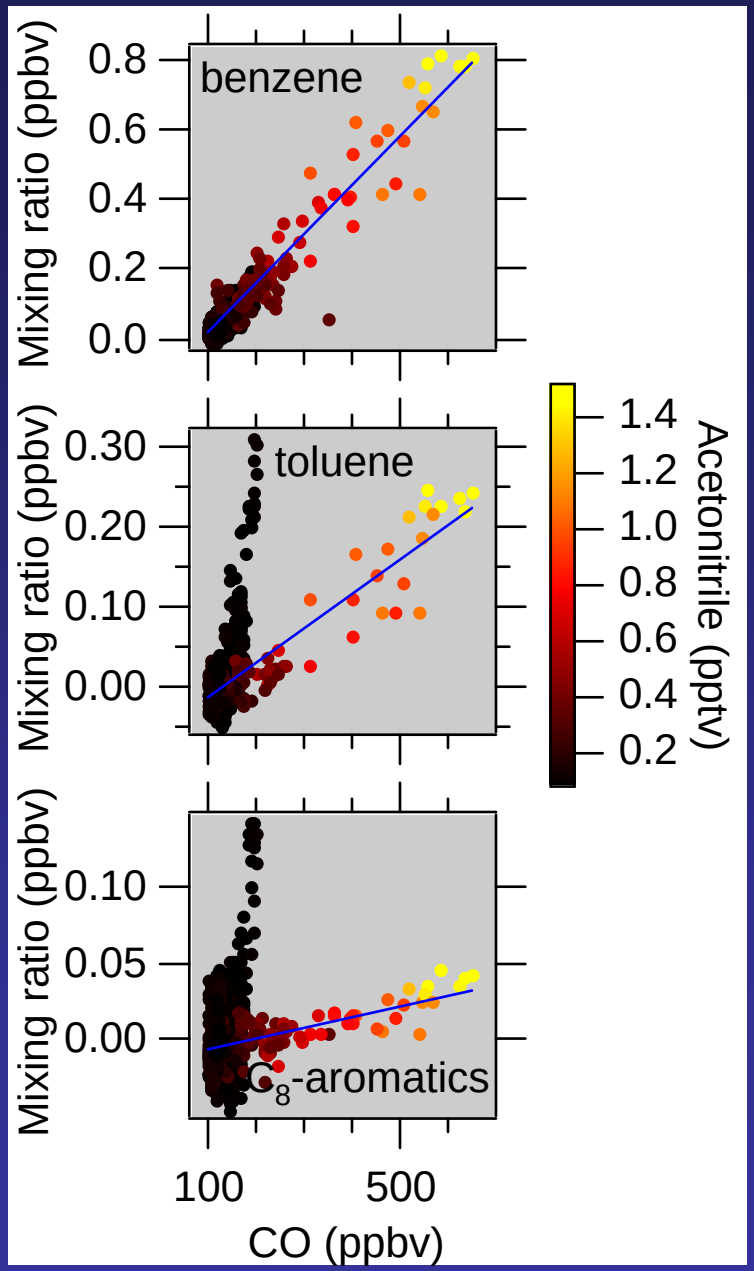


- Best description: emissions injected >3 km in FLEXPART
- Fire plumes had very low humidity
- Air masses were lifted and likely subjected to clouds

Chemistry in the Fire Plumes



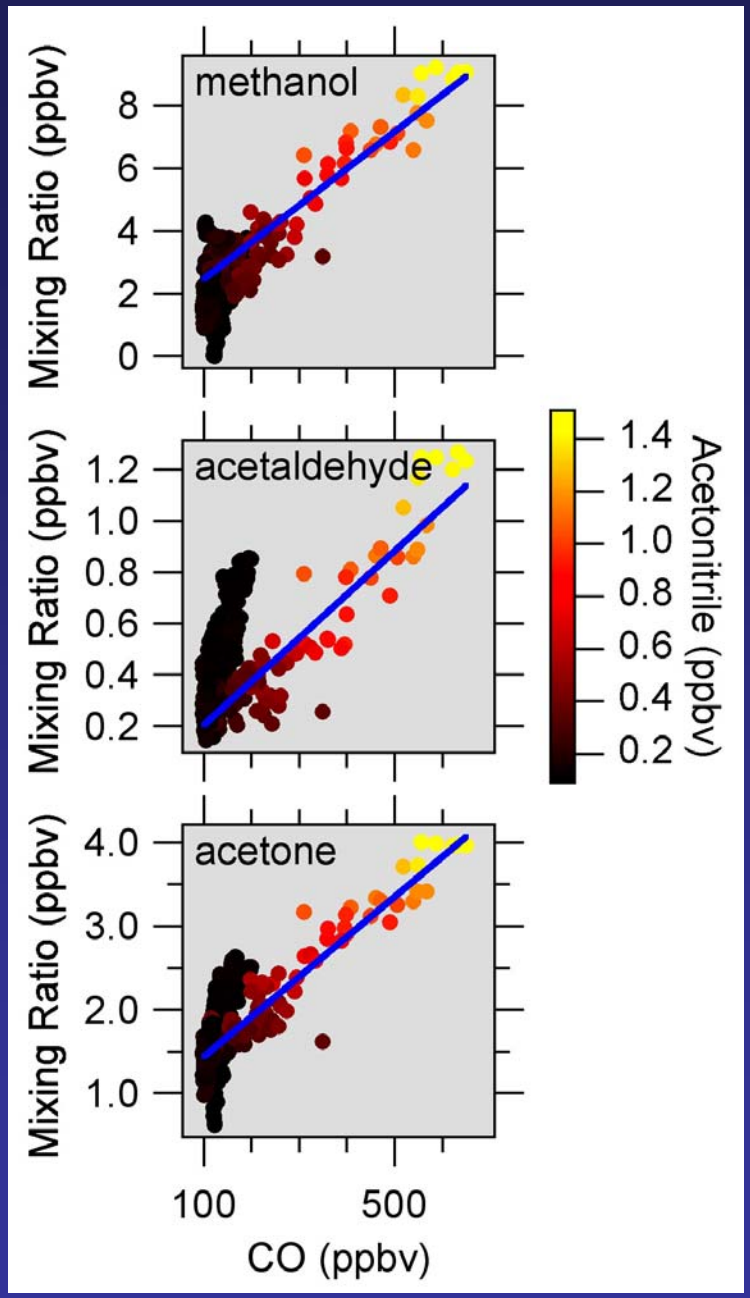
- FLEXPART transport times varied between 5 and 15 days
- Plume still contained significant levels of toluene and C_8-aromatics
  ⇒ <u>chemical removal is slow</u>



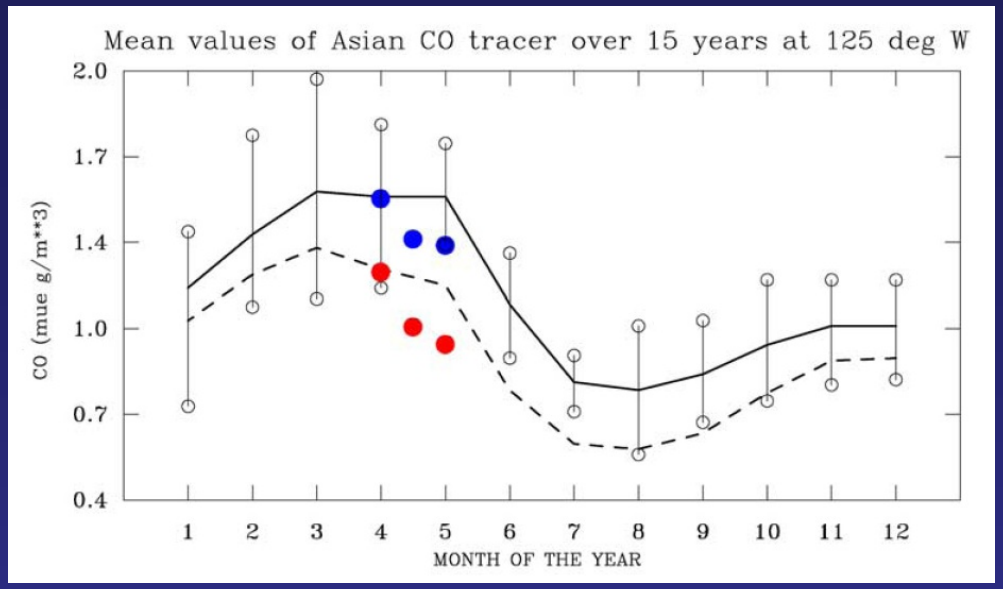
Slow OH Chemistry in the Plumes

- From VOCs: [OH] = 4.5×10^5 cm^{-3}
- Low humidity: $O^1D + H_2O$ is slow
- High CO and VOCs: OH lifetime is short
- NOx is tied up as PAN at high altitudes / low temperatures
- Photolysis is reduced close to the source
- Carbonyls were very high and could be relatively important HOx source

Fire plumes provided efficient transport of reactive material

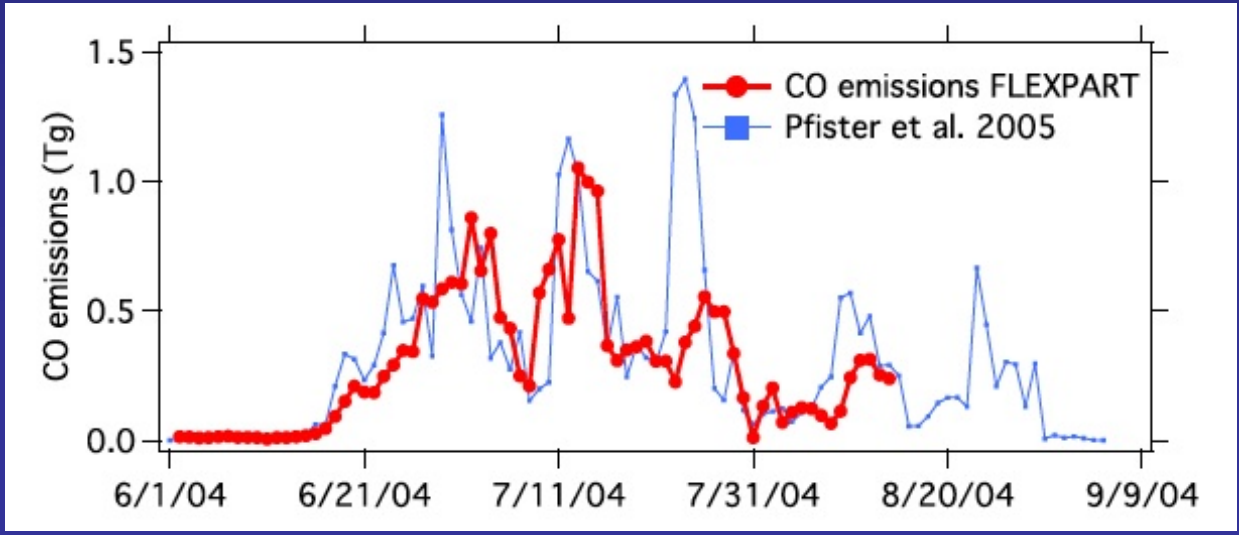


Implications of these Studies: Transport



Use of FLEXPART and measurements to estimate CO transport from Asia to North America [*Forster et al.*, JGR 2004]

Use of FLEXPART and measurements to estimate forest fire CO emissions [*Warneke et al.*, JGR 2006]



Summary

- Obtained new insights into transport mechanisms and chemical transformation:
  1. *Transport of sulfate across the Pacific*
     Implication: global distribution of aerosol
  2. *Transport of fire emissions*
     Implication: transport of reactive gases over large distances
- Transport model FLEXPART was validated, allowing:
  1. *Quantification of long-range transport of CO*
  2. *Estimates of CO emissions from forest fires*
- How well is cloud-modified transport represented in models?

Acknowledgements

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