Aerosol and trace gas processing by CRPAQS fogs

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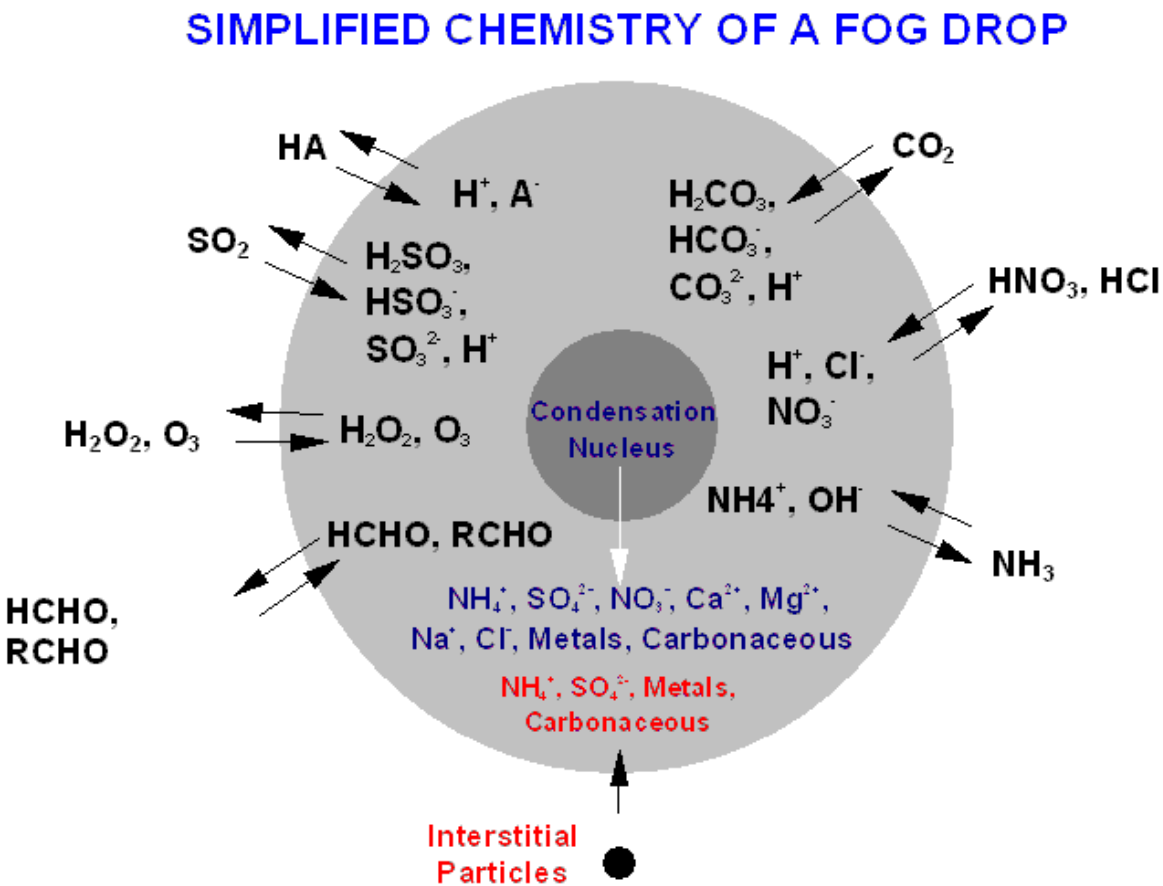
Outline

- Particle and gas scavenging by fogs
- SJV fogs
  - Past lessons
  - CRPAQS observations
- Aerosol and gas processing by CRPAQS fogs
  - Importance of organics
  - Deposition
  - New particle production - HMS
- Summary concepts and future research needs

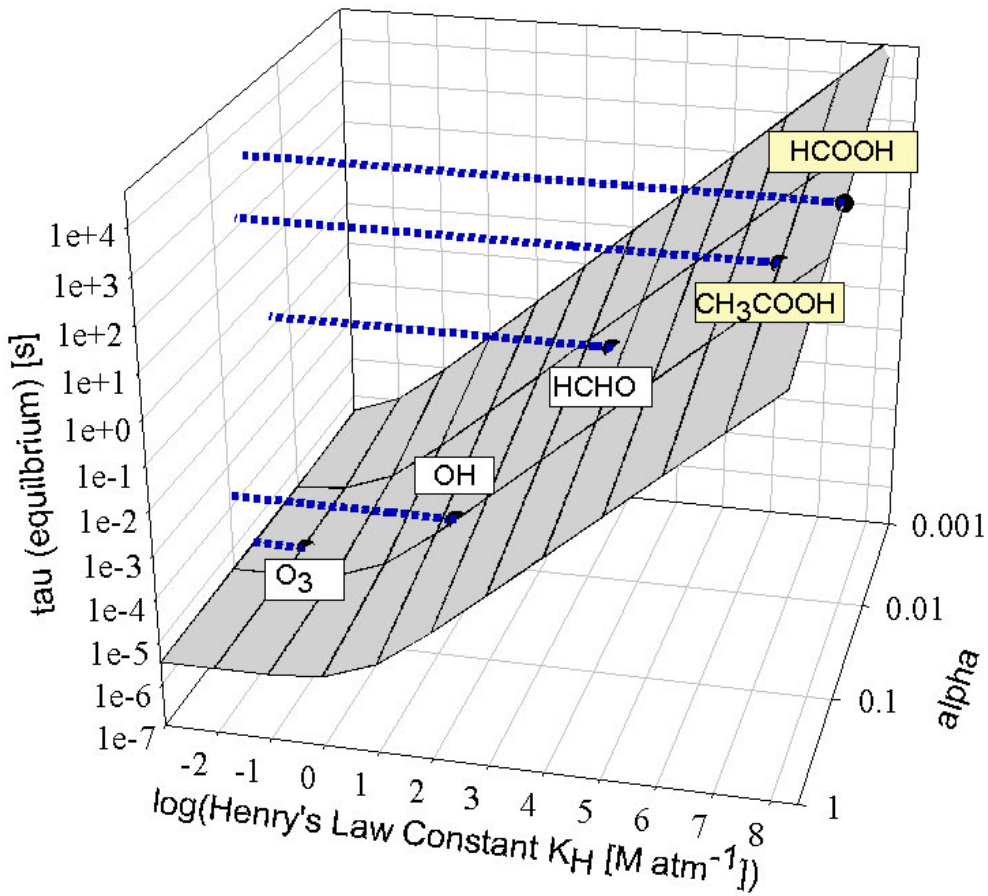
Particle and gas scavenging

- Particles scavenged by nucleation, diffusion, impaction, interception
- Soluble gases partition to drop



Gas-liquid equilibrium

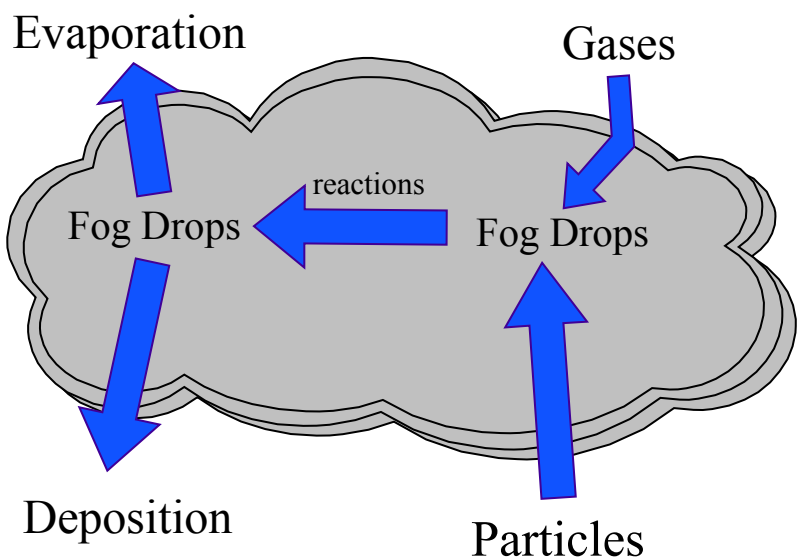
- Models and field observations suggest common lack of gas-liquid equilibrium
  - Highly soluble gases have insufficient time to equilibrate with large drops
  - Species derived from aerosol particles may be supersaturated in drops (e.g., Ricci et al., 1998)



Equilibrium time for pH 7 drops with r = 10 μm
Courtesy of B. Ervens, NOAA

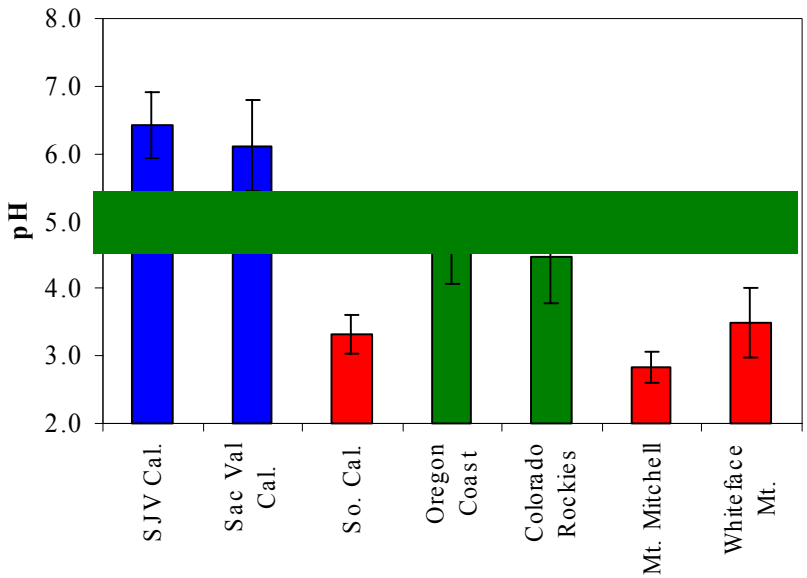
SJV fogs

- Dense, widespread radiation fogs occur during winter
  - Moist air trapped in valley by thermal inversion
  - Radiative cooling produces fogs
- Fogs affect particles by
  - Production of non-volatile solute mass
  - scavenging and deposition

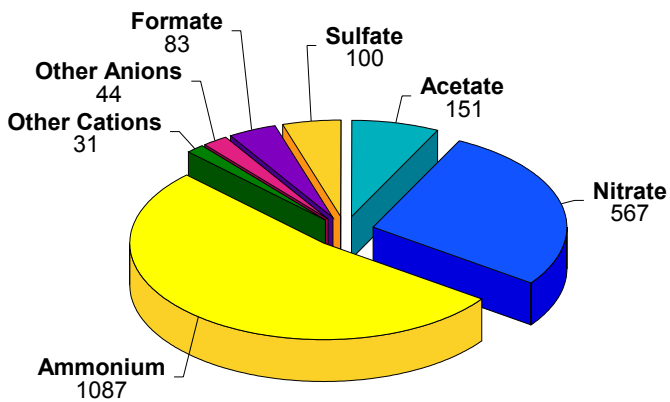


Past Studies of SJV fogs - I

- Nitrate and ammonium typically major species
  - pH high
  - Important organic carbon contributions
  - Nitrite and sulfate also present
  - Composition variable in time and space

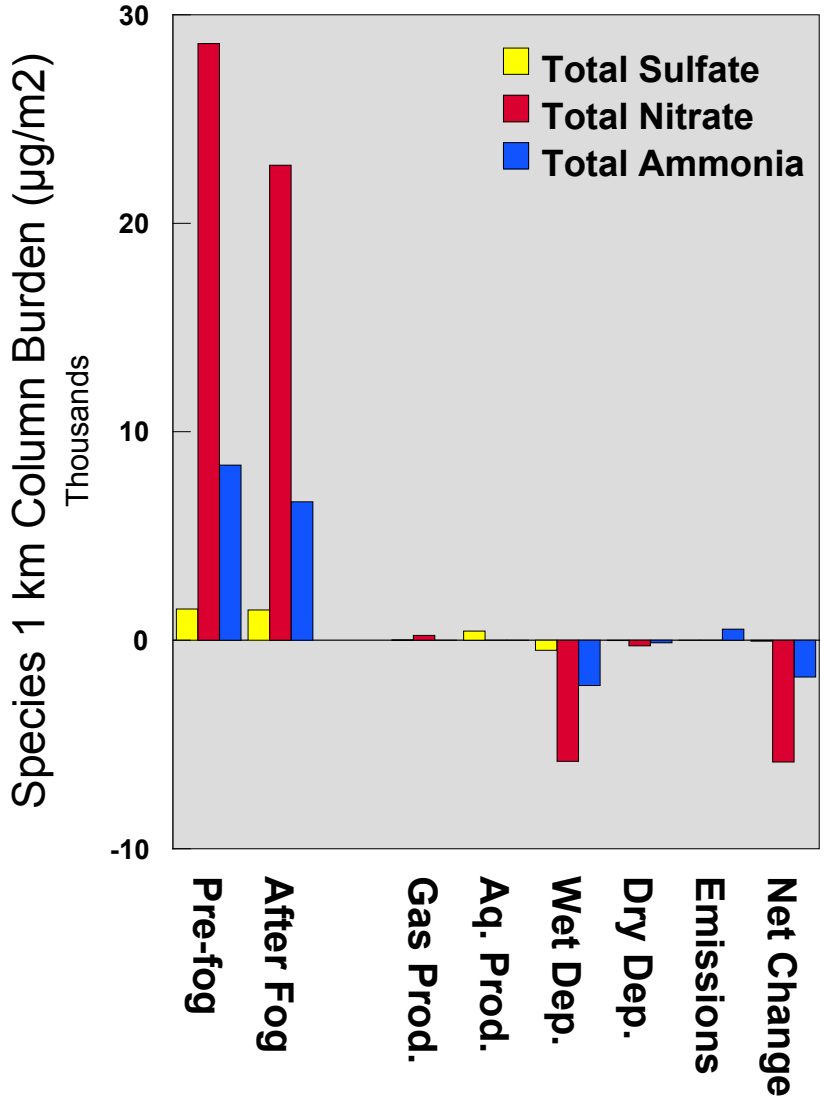


Major Ion Concentrations (μN)
Fresno Fog (December 10, 1995, 03:00-04:00)



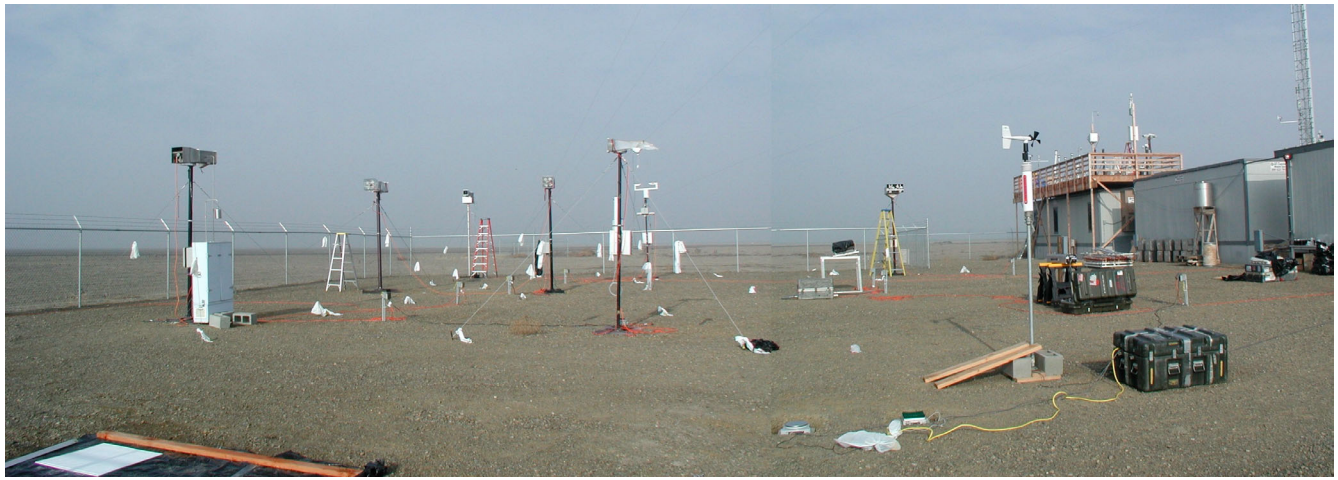
Past Studies of SJV fogs - II

- Deposition of inorganic ions important
  - What about OC?
- Sulfate production ~ balances sulfate deposition
  - Secondary organic aerosol production?



CRPAQS Fog Measurements

- Angiola
  - Bulk and size-resolved fog composition
  - Vertical fog profiles from tower
  - Fog deposition fluxes
- Other sites
  - Helm
  - McKittrick
  - Bakersfield

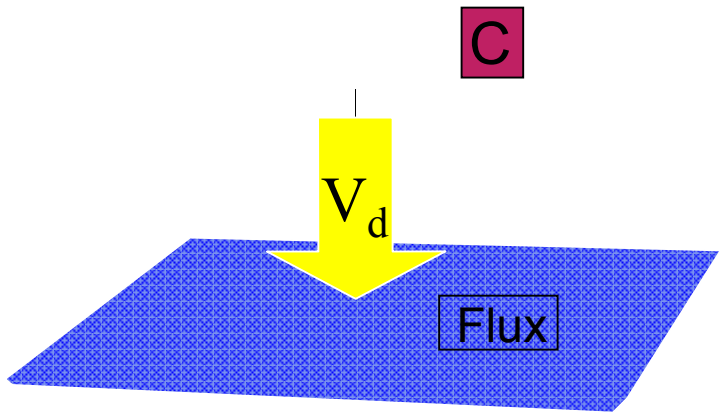


CRPAQS Fog Measurements - II

- Fog deposition

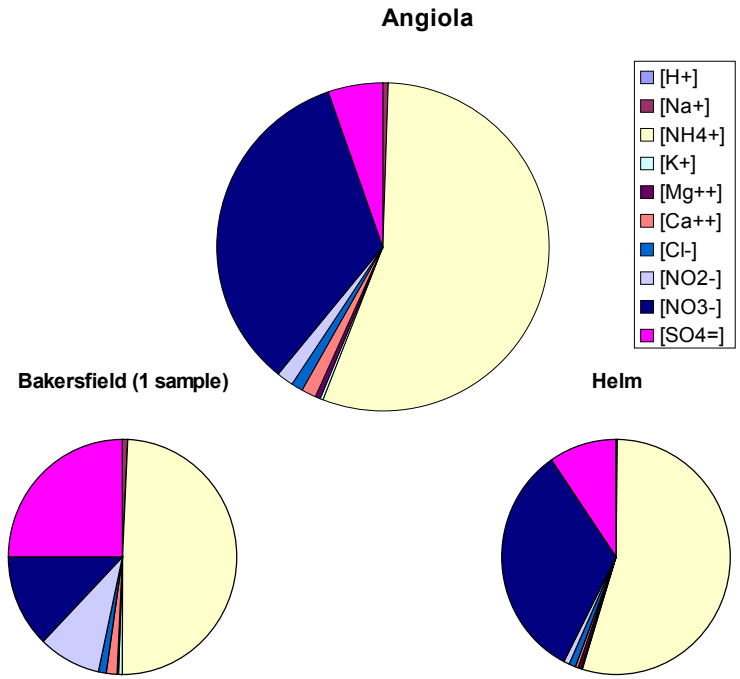
$$V_d = Flux/C$$

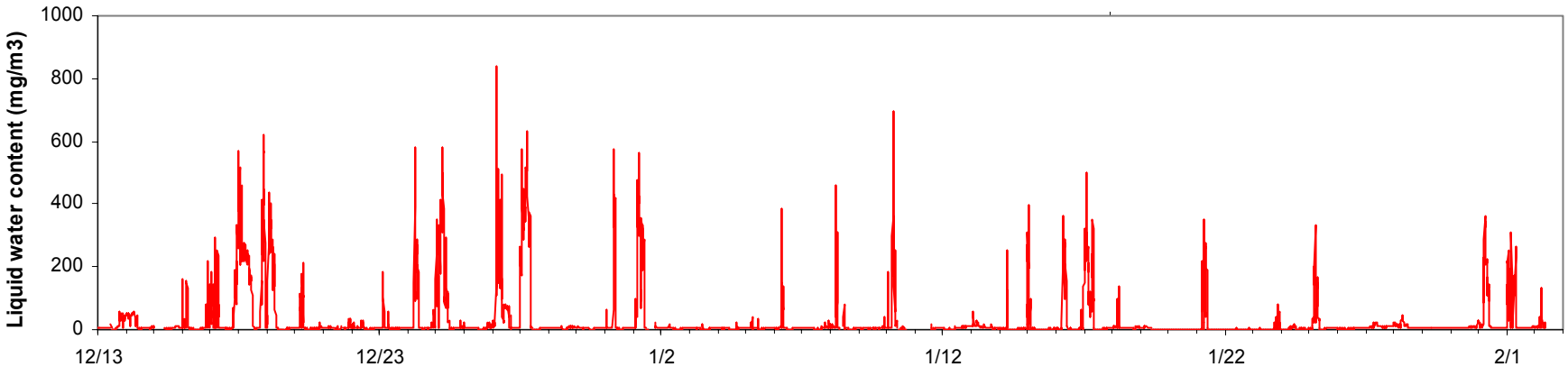
- Lab Analyses
  - Major ions and metals
  - Total/Dissolved Organic Carbon (TOC/DOC)
  - Organic composition
    - Organic acids
    - Carbonyls
    - Other trace species by GC/MS



CRPAQS Fog Findings

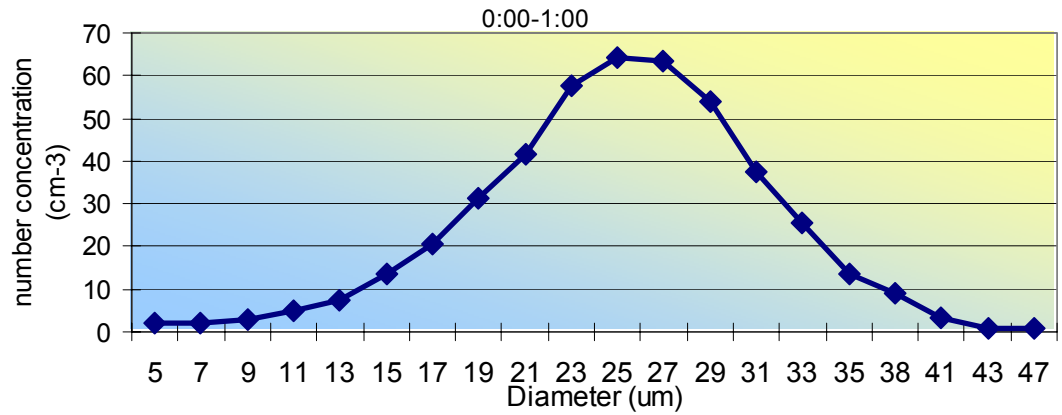
- Several fog episodes at Angiola and Helm
  - No fog at McKittrick
  - 1 event at Bakersfield
- Composition similar to past SJV fog studies

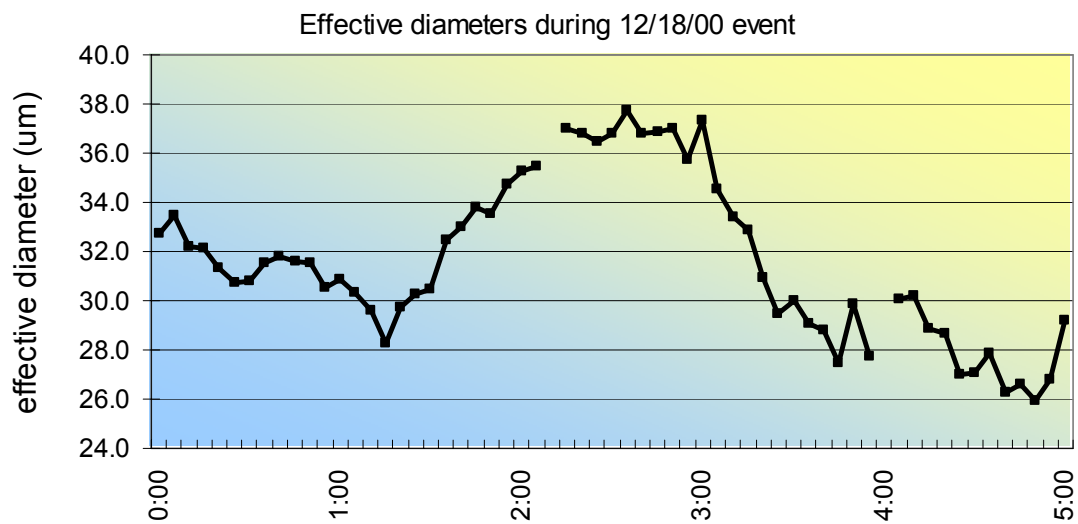




Angiola fog characteristics

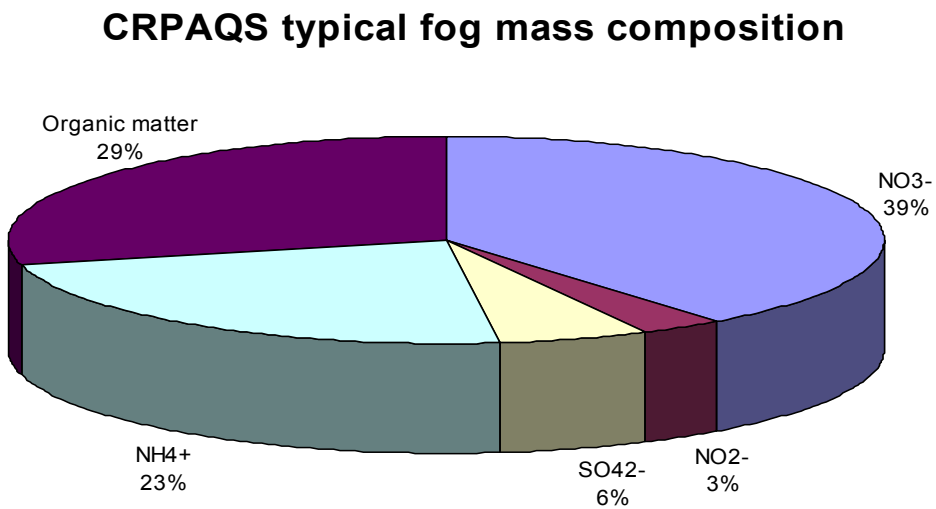
- Fog layer very shallow
  - Rarely reached top level of tower
- Fog drops very large
  - Drizzle formation from shallow fog
    - Strong radiative cooling of large drops
  - Fast deposition

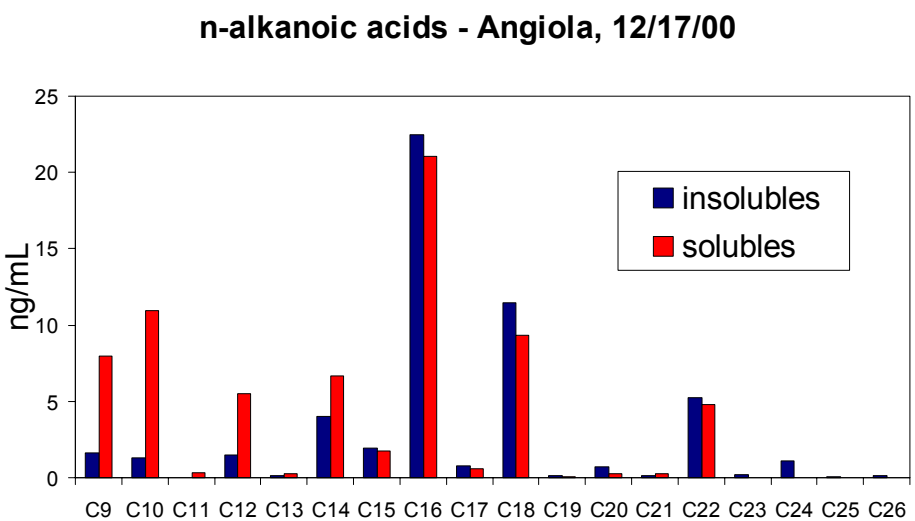


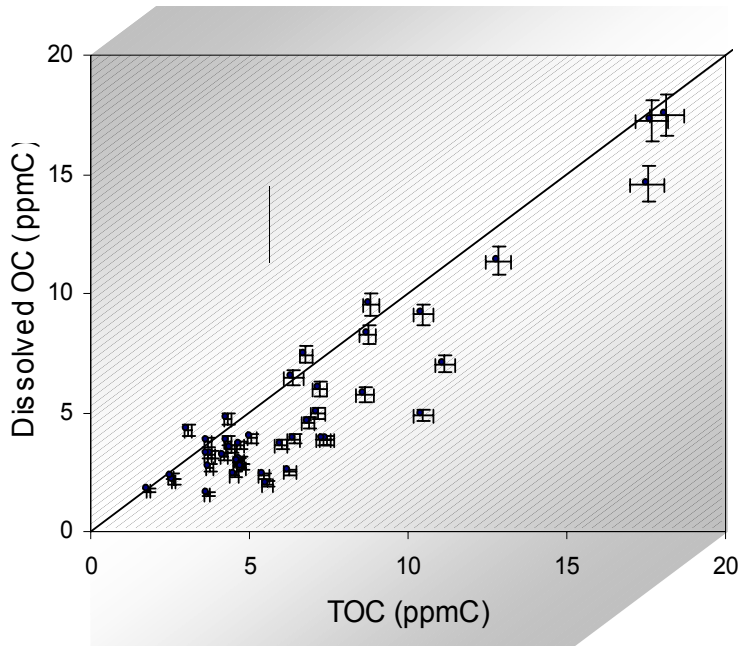


CRPAQS Fog Organics

- Organic carbon is key component of CRPAQS fogs
- ~75% of OC is dissolved
- Fogs process soluble and insoluble OC

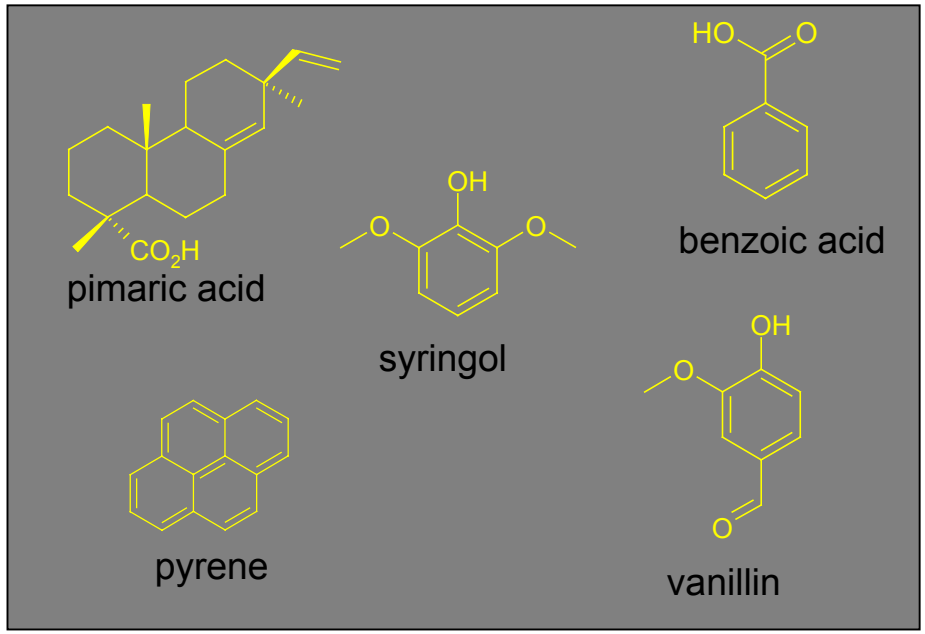


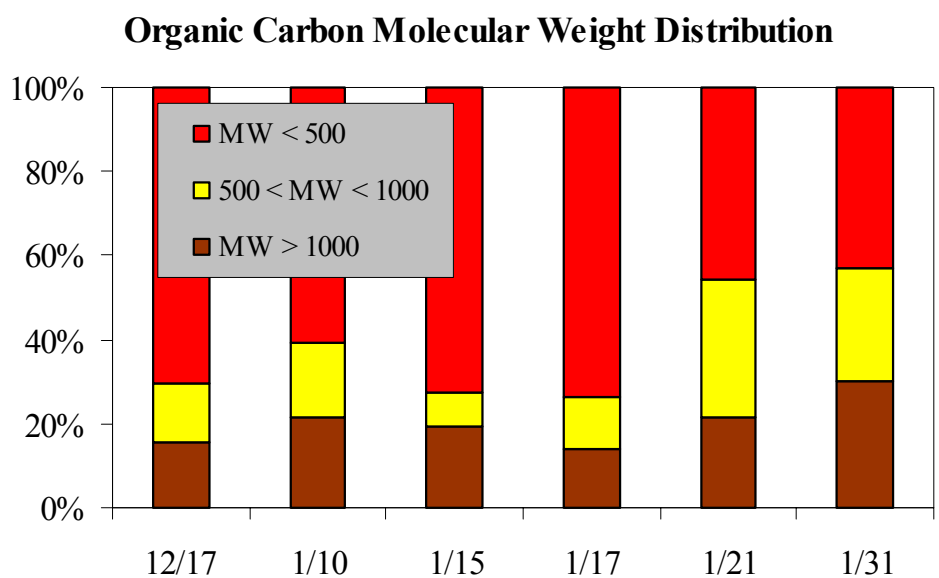




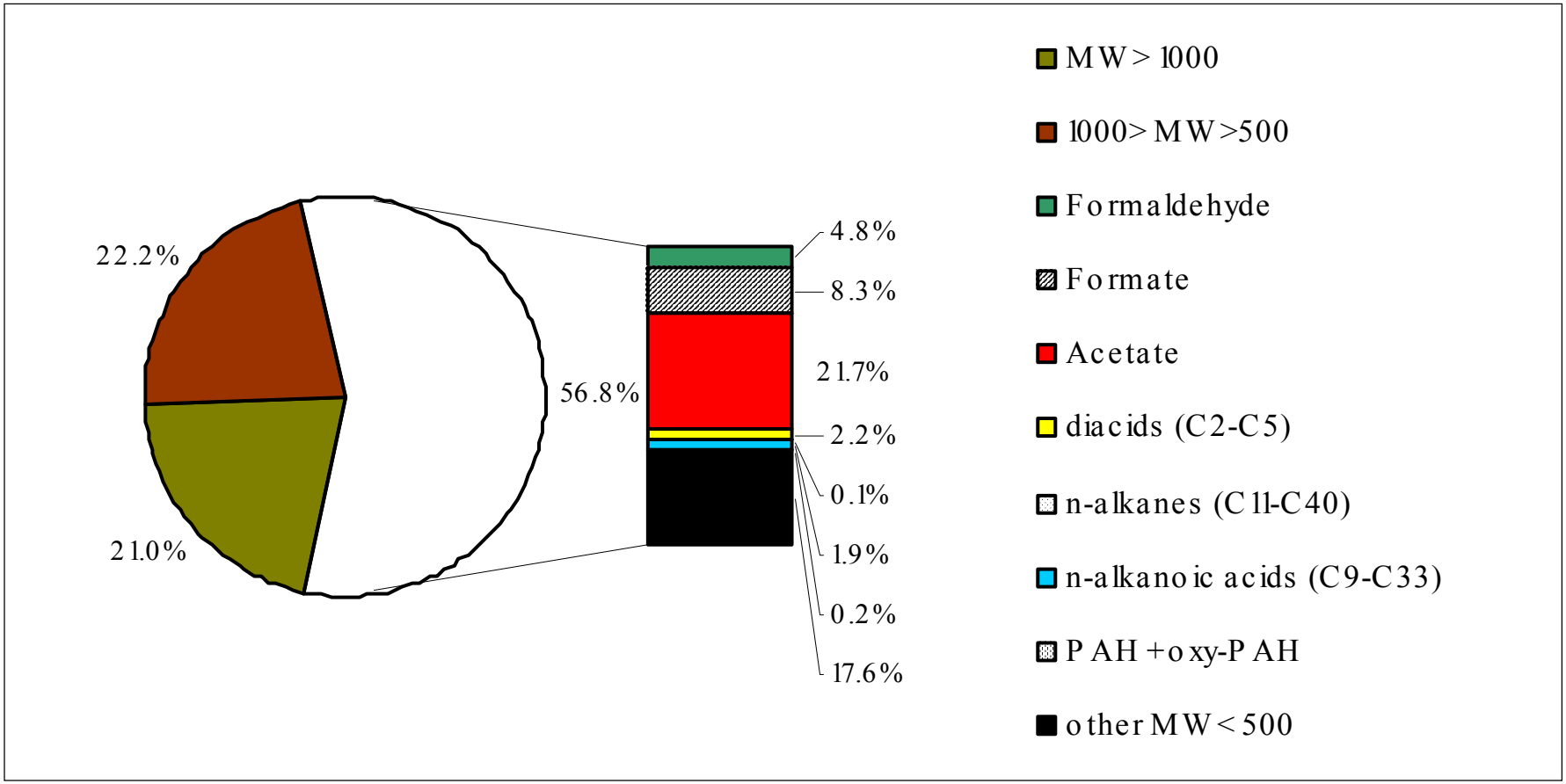
CRPAQS Fog Organics - II

- Many organic compounds present
  - PM source tracers
- Lots of high molecular weight material



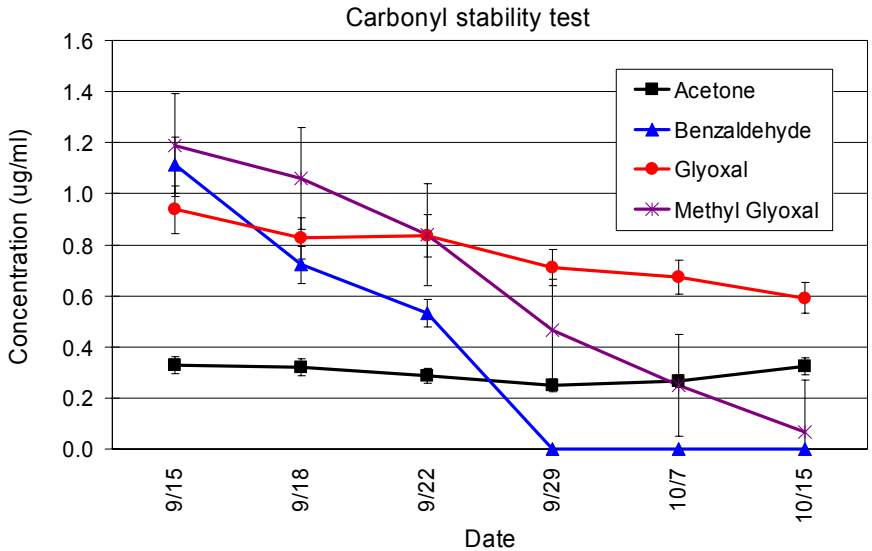


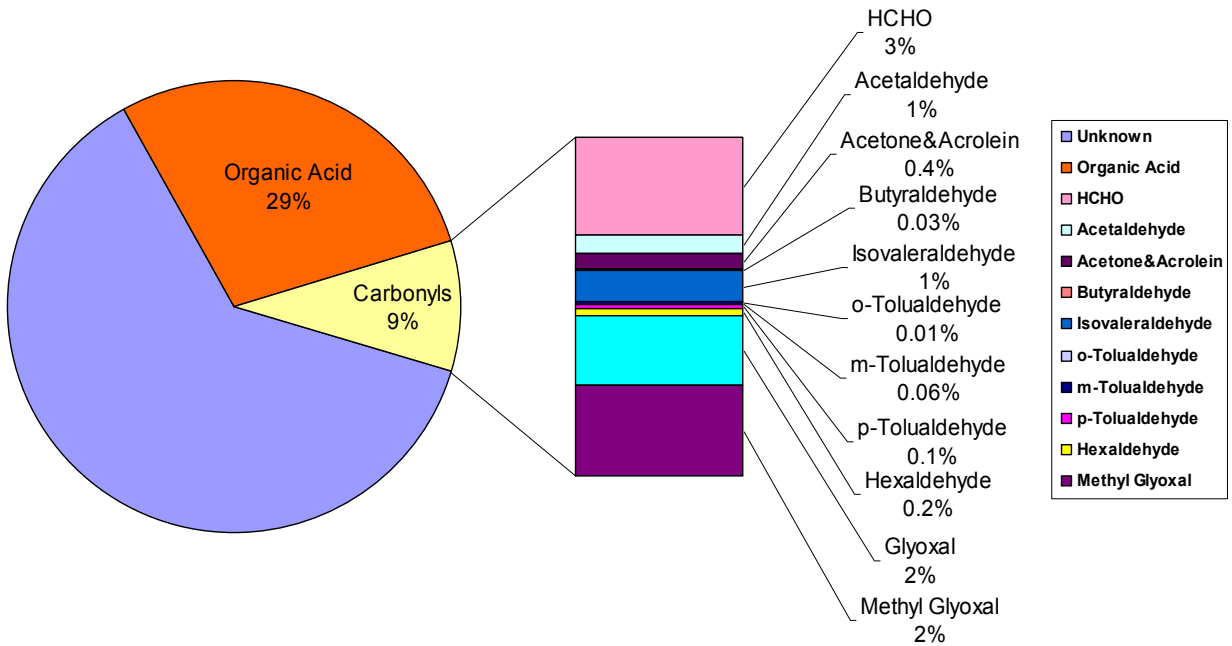
Fog Dissolved Organic Carbon Composition



Importance of higher MW carbonyls

- HPLC analysis of CRPAQS samples showed few carbonyls
  - Tests show rapid loss in fog
    - Not in H_2O
- Preserved Fresno 1/04 fog samples reveal large contributions from several carbonyls and dicarbonyls

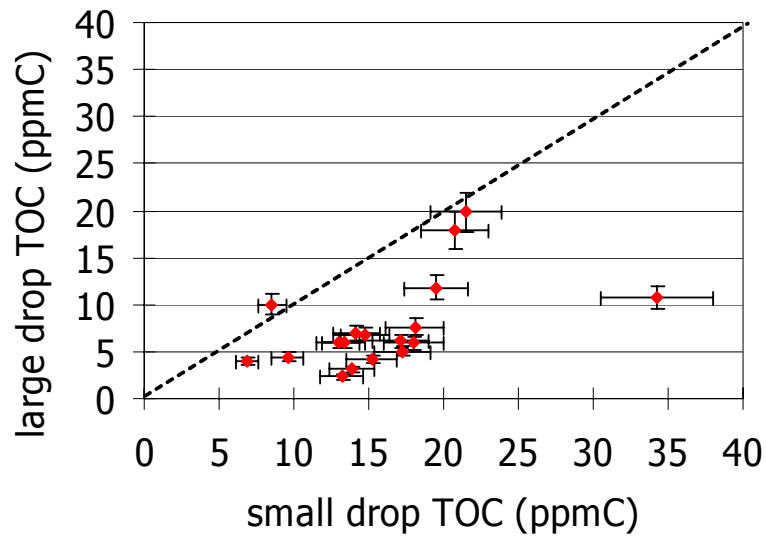


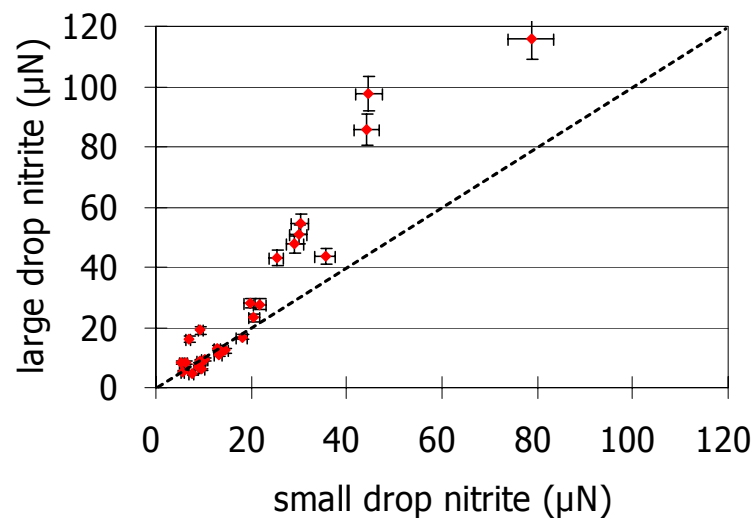


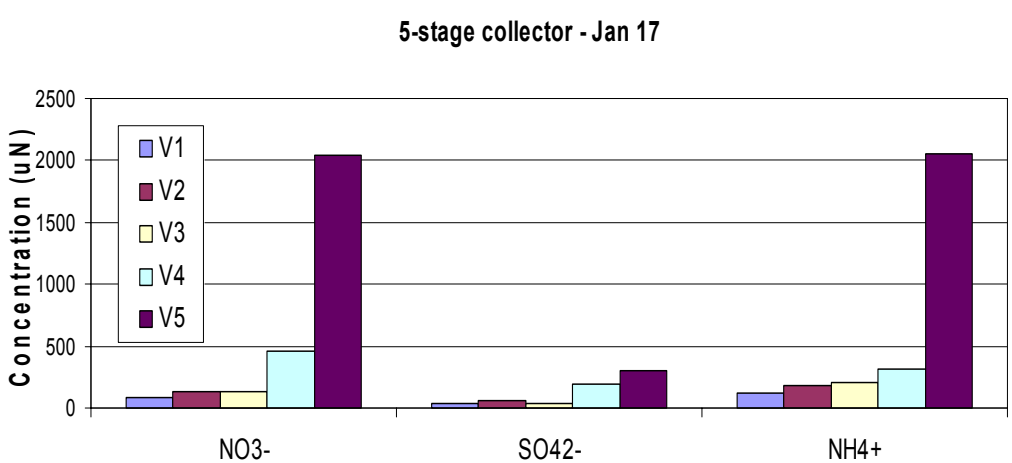
Jan. 2004 Fresno Fog DOC

Composition size-dependence

- Drop composition varies with size
  - Pattern varies between species
  - Most enriched in small drops

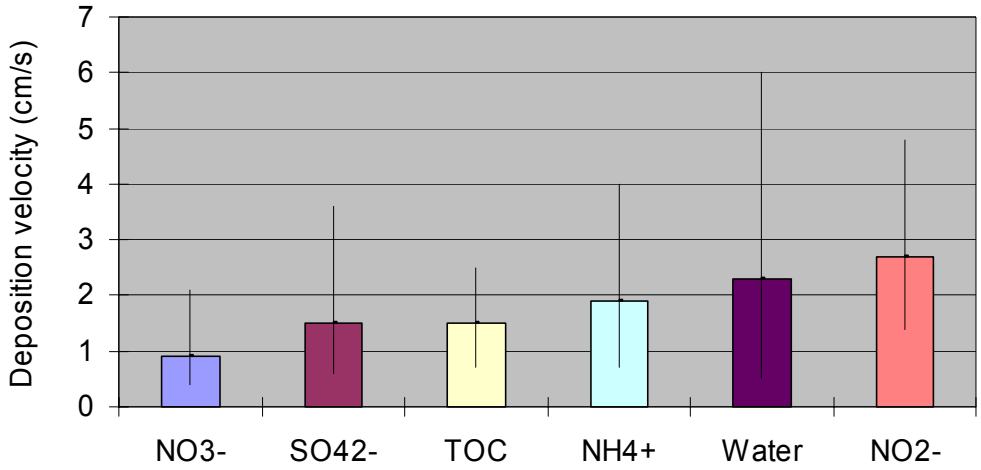


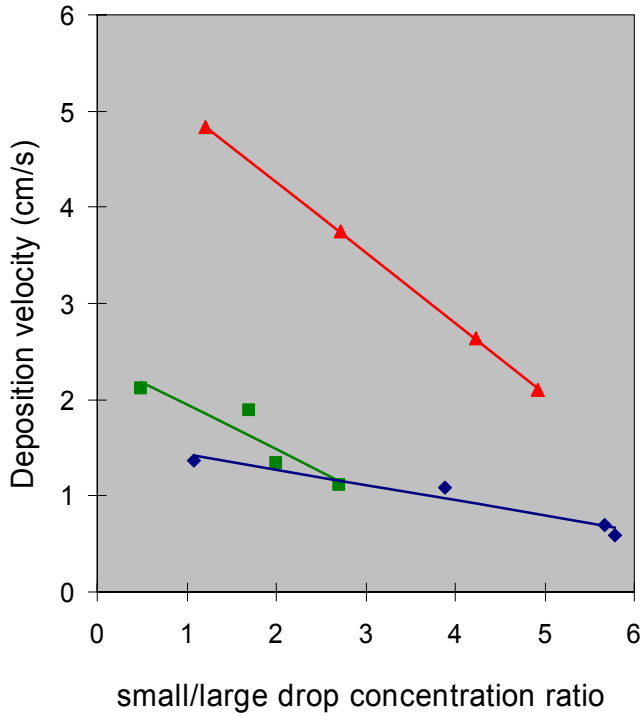




CRPAQS Fog Deposition

- Deposition velocities in CRPAQS fogs high
  - ~ 1-2 cm/s
  - >> $PM_{2.5}$
- Deposition velocity depends on solute distribution with drop size





CRPAQS Fog Deposition

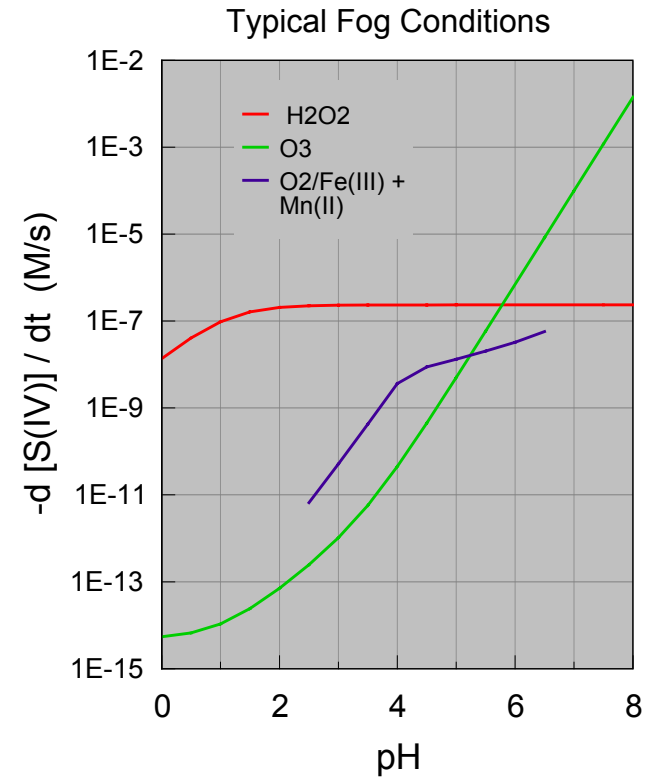
- Fog event fluxes range from 10s to 1000s of $\mu g/m^2$
- Assuming a 100 m deep fog, concentrations would decrease typically
  - ~ 0.5 $\mu g/m^3/hr$ sulfate
  - ~ 1 $\mu g/m^3/hr$ nitrate
  - ~ 1 $\mu g/m^3/hr$ ammonium
  - ~ 0.7 $\mu gC/m^3/hr$ TOC
- Remember, fog solutes can be volatile or non-volatile

Fog deposition

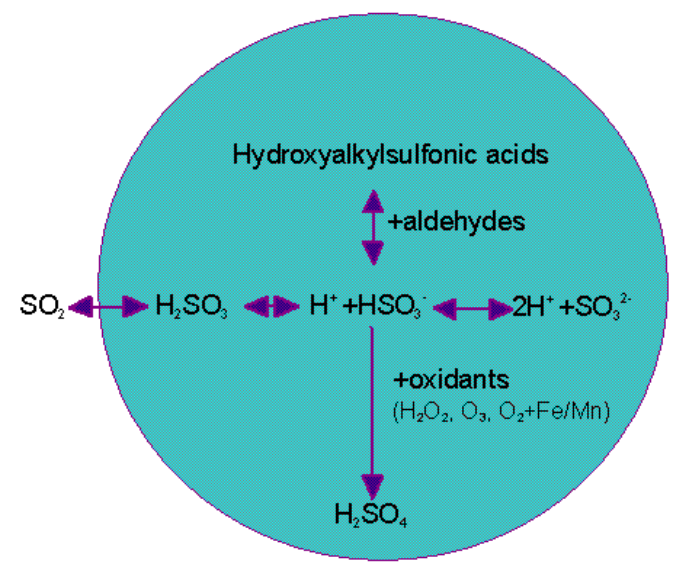
Sample Start Date	Sample Time (hour)	NO_3^- ($\mu g/m^2$)	SO_4^{2-} ($\mu g/m^2$)	NH_4^+ ($\mu g/m^2$)	TOC ($\mu gC/m^2$)
12/18/00	9.0	2246	1223	2627	952
12/19/00	2.3	127	50	203	72
1/15/01	2.0	51	22	71	75
1/17/01	7.8	393	174	526	309
1/21/01	3.0	774	173	448	312
1/25/01	2.5	37	26	70	66
1/31/01	3.8	592	251	463	452
2/1/01	1.7	96	71	101	113

Aqueous reactions and new particle production

- S(IV) reactions
  - Oxidation
    - by H_2O_2, O_3 and O_2/Fe(III)+Mn(II)

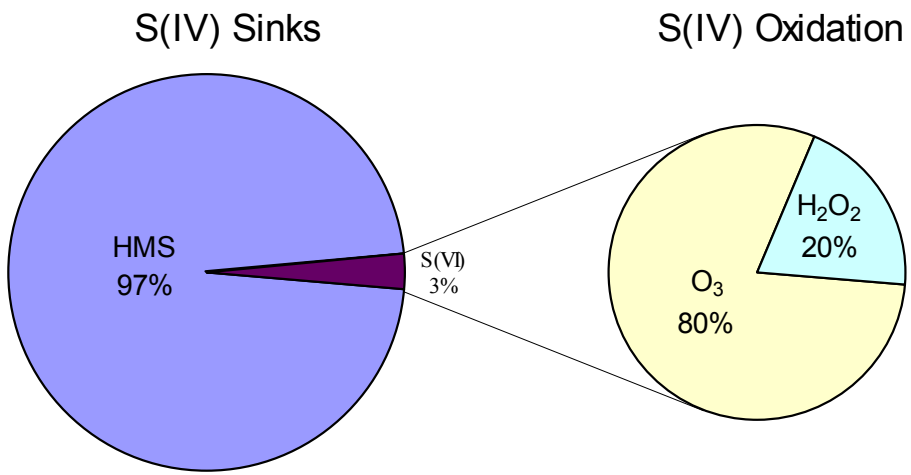


- S(IV)-aldehyde complex formation
  - e.g., HCHO + HSO_3^- ←→ $CH_2(OH)SO_3^-$



S(IV) simulations

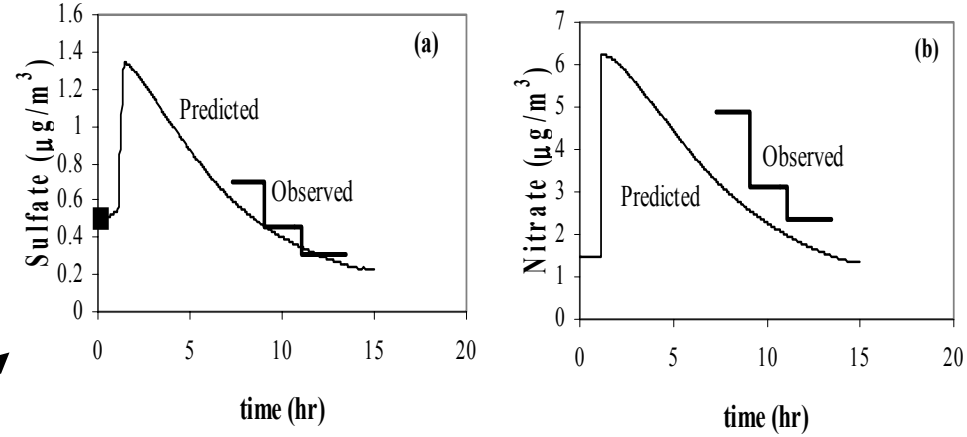
- Fate of dissolved SO_2 simulated for all sample periods with single drop model
  - Oxidation by O_3 and H_2O_2
  - Rxn with HCHO
- Most SO_2 expected to form HMS at high fog pH

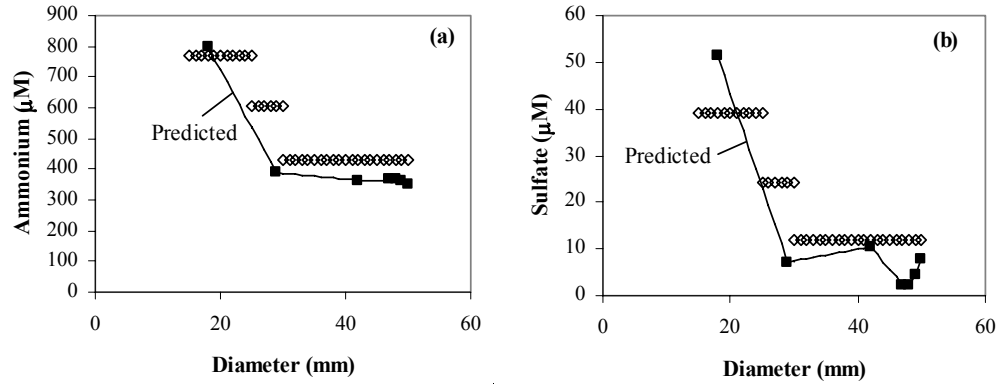


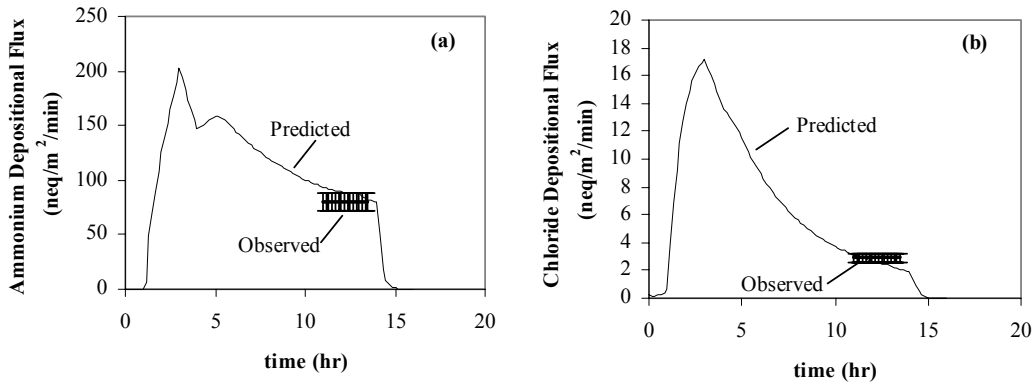
Large Drops

CMU Modeling
(Fahey and Pandis)

- Fog model reasonably predicts
  - Bulk fog composition
  - Size-dependence
  - Deposition fluxes







Acknowledgements

- CSU
  - S. Kreidenweis, G. Kang. J. Reilly, E. Sherman
- Carnegie Mellon
  - S. Pandis and K. Fahey
- National Science Foundation

Summary concepts and future needs

- Nitrogen species dominate fog composition
- Fogs are effective cleansers of the SJV atmosphere
  - Removal rates depend on species distributions across fog drop size spectrum
  - Sulfate removal balanced by production
- Organic matter comprises a large portion of fog solutes
  - Combination of volatiles and non-volatiles
  - Large amount of high MW material
  - Large OC deposition fluxes
- High time resolution aerosol and fog measurements
  - PILS + OC/EC in Fresno
- Better characterization of organic matter scavenged by fogs
  - Improved speciation
  - Source marker tracking
- Role of fogs in secondary organic aerosol formation

CRPAQS fog papers

- Herckes et al. (2002) Organic Matter in central California radiation fogs, *ES&T* **36**, 4777-4782.
- Ervens et al. (2003) On the drop-size dependence of organic acid and formaldehyde concentrations in fog, *J. Atmos. Chem.* **46**, 239-269.
- Fahey et al. (2004) The influence of size-dependent droplet composition on pollutant processing by San Joaquin Valley fogs, submitted.
- Overview paper for special issue (tbd)