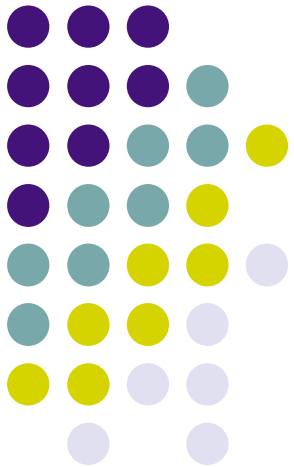
Cloud water chemistry during VOCALS-REx

VOCALS Meeting

Seattle, WA

July 12-14



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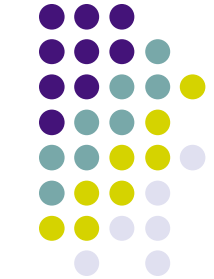
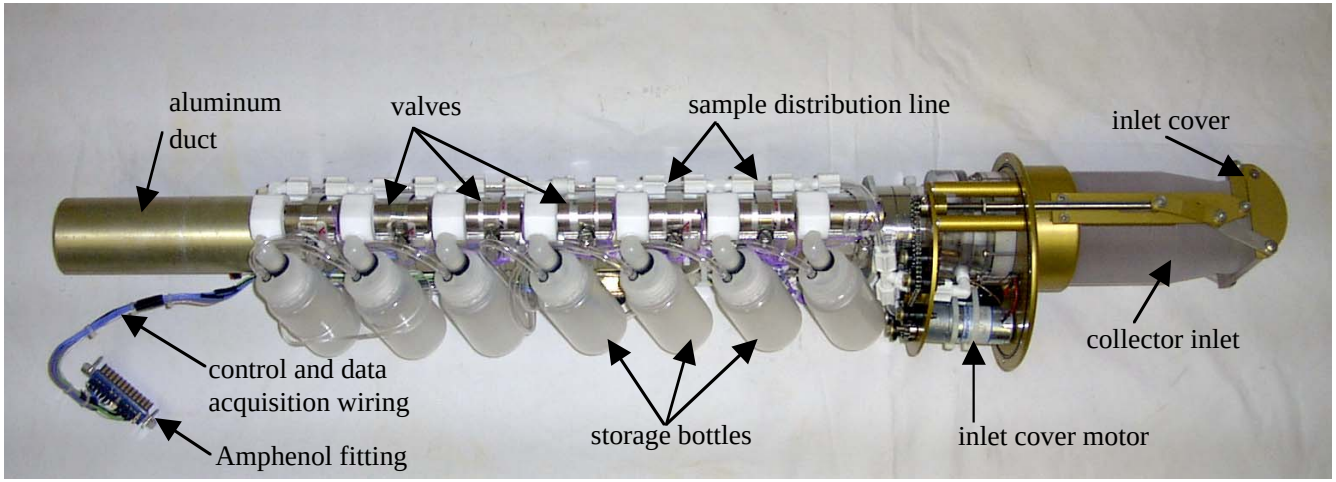
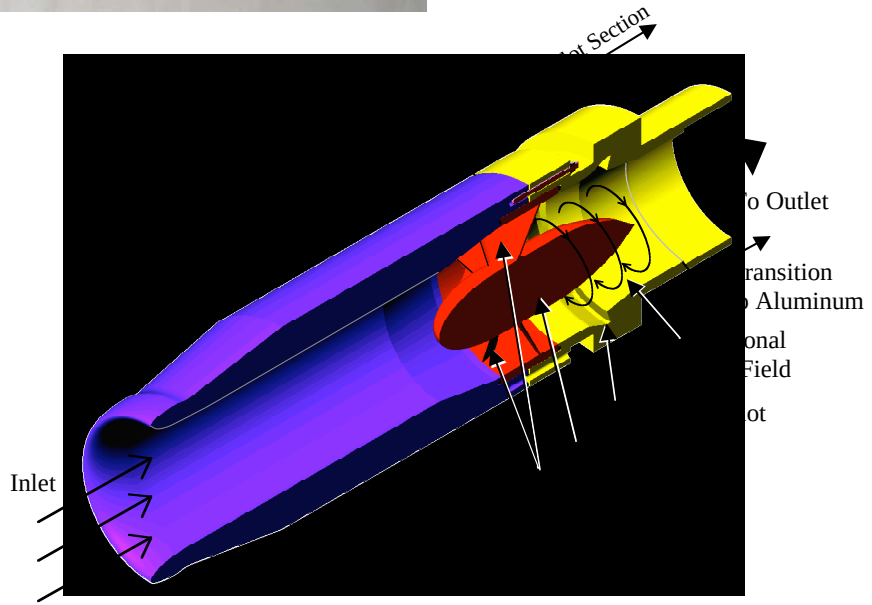
Objectives for cloud water collection



- Cloud water composition
  - Composition of CCN/important sources for the region
  - Sulfur oxidation pathways

Instrument





D_{50}=8 μm
This size was chosen to collect most cloud drops but exclude smaller, unactivated aerosol particles.

Collection Strategy

- Samples only collected in-cloud
- Cross section Missions
  - 2 adjacent in-cloud legs sampled together to get enough cloud water for analysis
  - On return portion of flight single samples may have been collected if enough space and sufficient cloud water collected per leg
- POC Missions
  - We attempted to sample cloud adjacent to POC and in POC clouds. Depending on LWC and understanding of the POC boundary these samples could be combined.

Composition Measurements

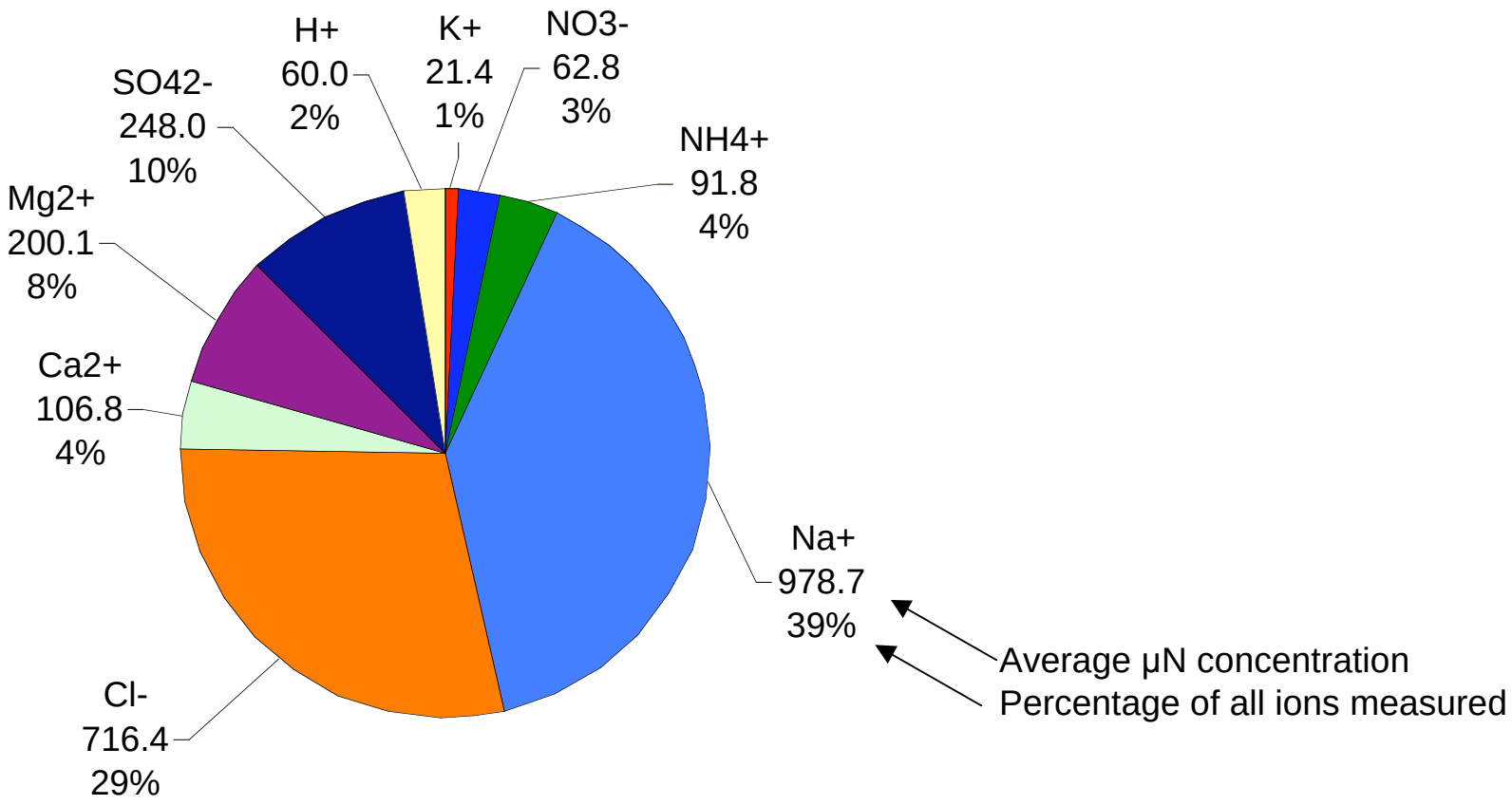
Measurement	Technique
pH	
General anions and cations (Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+})	Ion Chromatography
Total Peroxides	Spectrophotometric technique - fluorescence
Total Sulfur (IV)	Spectrophotometric technique - absorbance
Metals	Atomic Absorption Spectrophotometery
Organic Acids	Ion Chromatography
Formaldehyde	Spectrophotometric technique - fluorescence
Total Organic Carbon	Sievers Total Carbon

Depending on the amount of cloud water collected samples were analyzed according to the list above.

Outline of Results

- Relationships between species measured
  - Do we see expected ratios of species associated with sea salt? What is in excess/depleted?
- Averages of air equivalent concentrations – are there differences between POC and non-POC regions
- Spatial trends/variability of H_2O_2
- Sulfur Oxidation Rates
  - Which pathways are important?

Ion Species Summary



Ratio of ions to Na^+ - a sea salt tracer

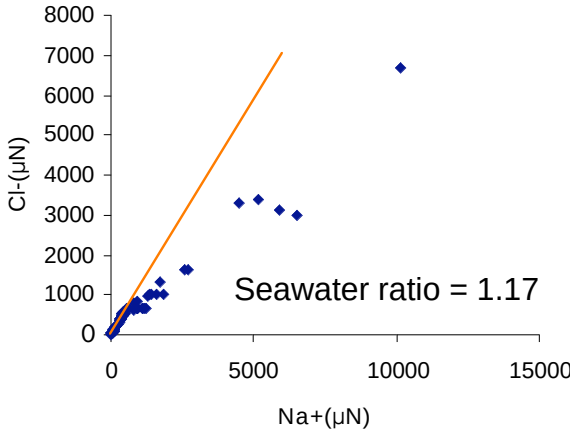
Na^+ is used as the tracer for sea salt because it doesn't react away to the gas phase as happens with Chloride.

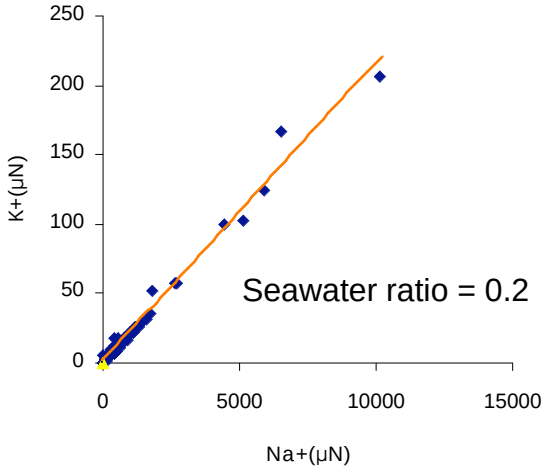
Example:

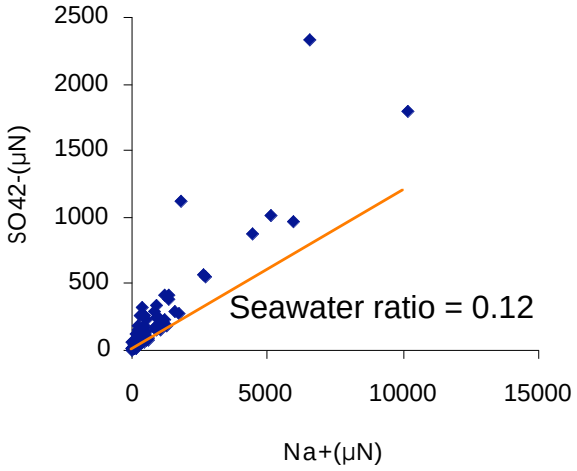
$HNO_3 + NaCl \rightarrow HCl(g) + NaNO3$

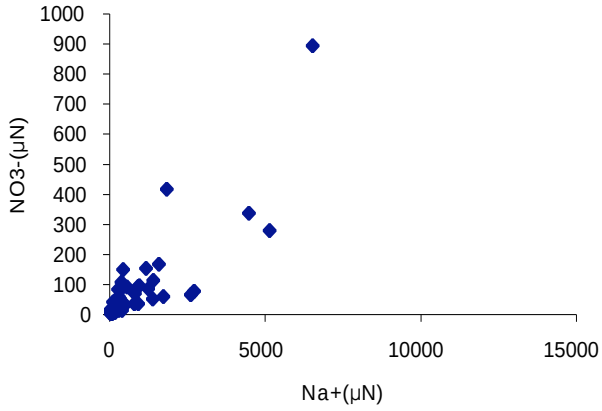
In the VOCALS samples we see:

- some depletion of Cl^-
- excess SO_4^{2-}

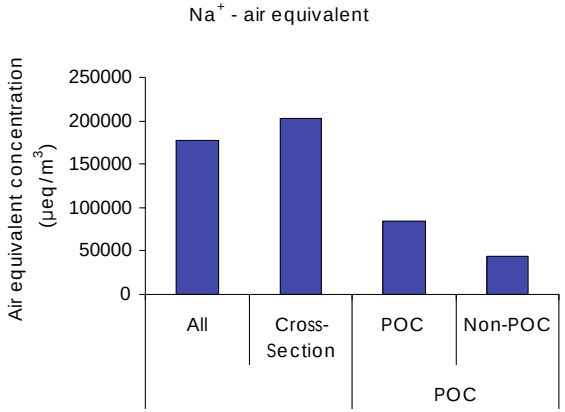


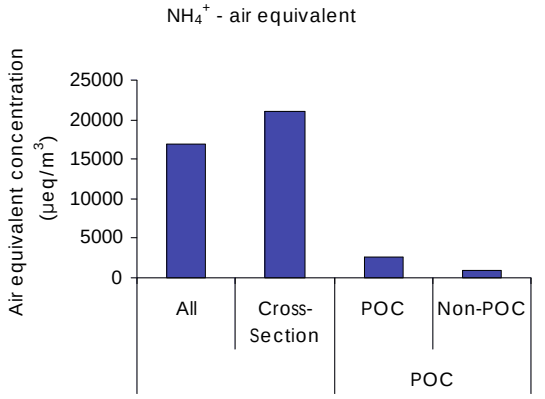


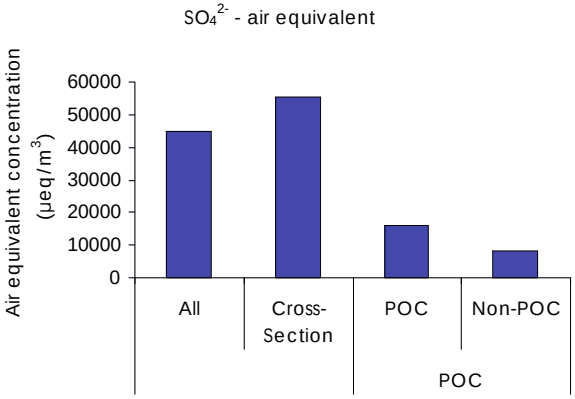


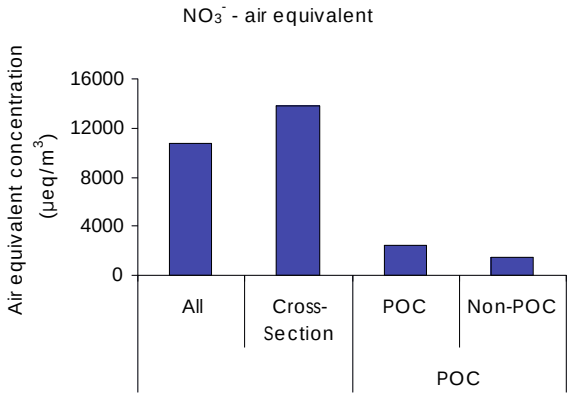


Examining the averages in POC and Non-POC regions



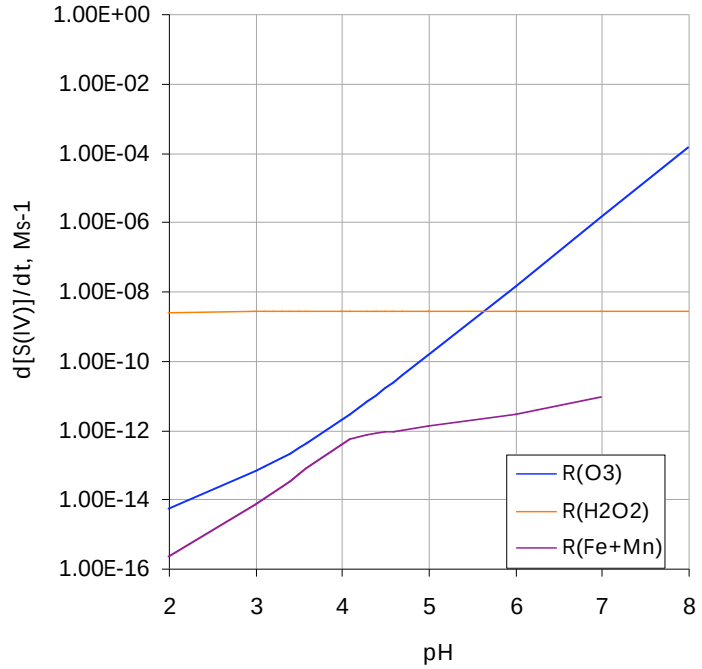






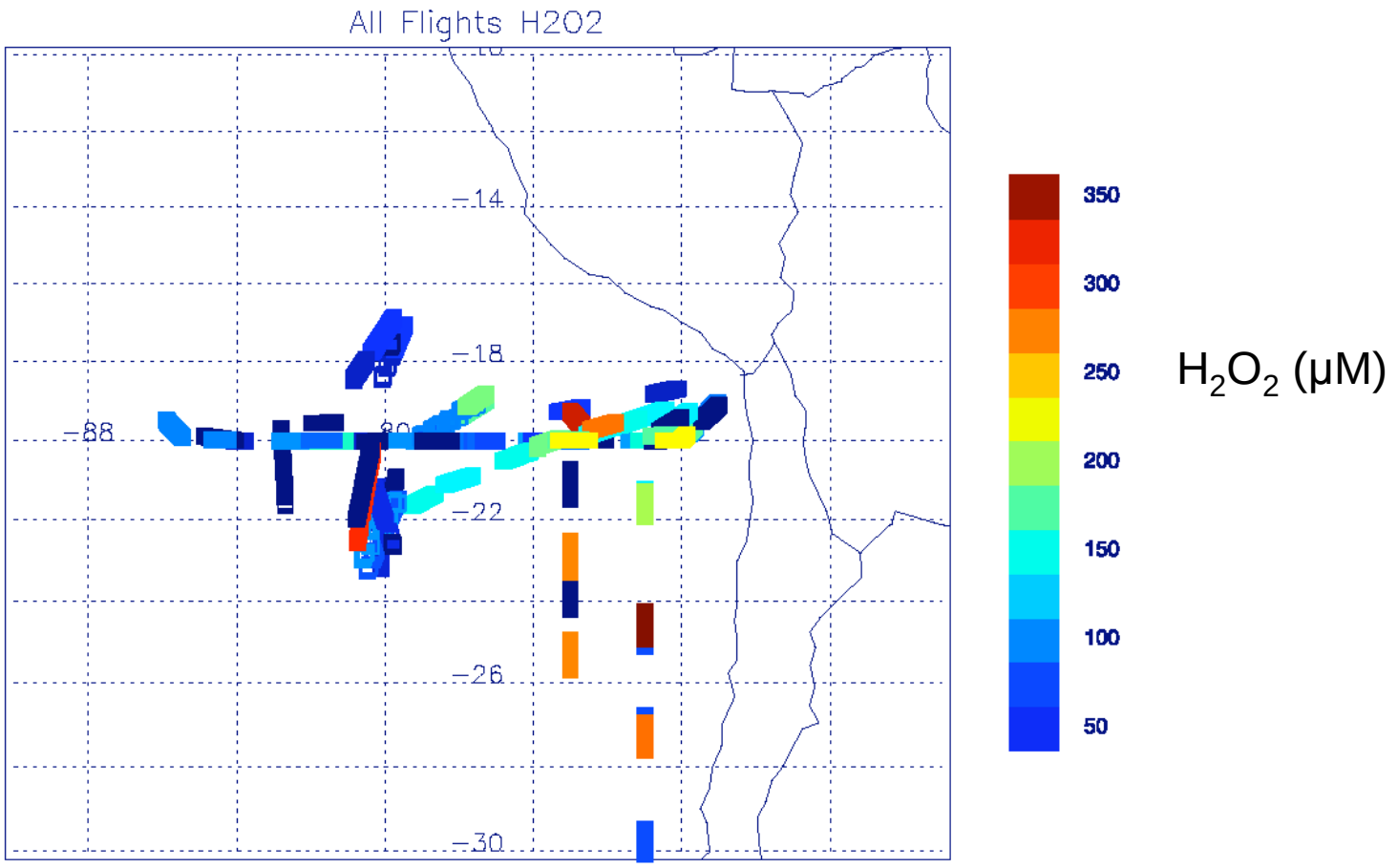
Sulfur Oxidation

- Oxidation of SO_2 is much faster in the aqueous phase.
- Important oxidants include:
  - O_3
  - H_2O_2
  - Trace Metal catalyzed autooxidation



SO_2 = 0.03 ppb
O_3 = 25 ppb
H_2O_2 = 1 ppb

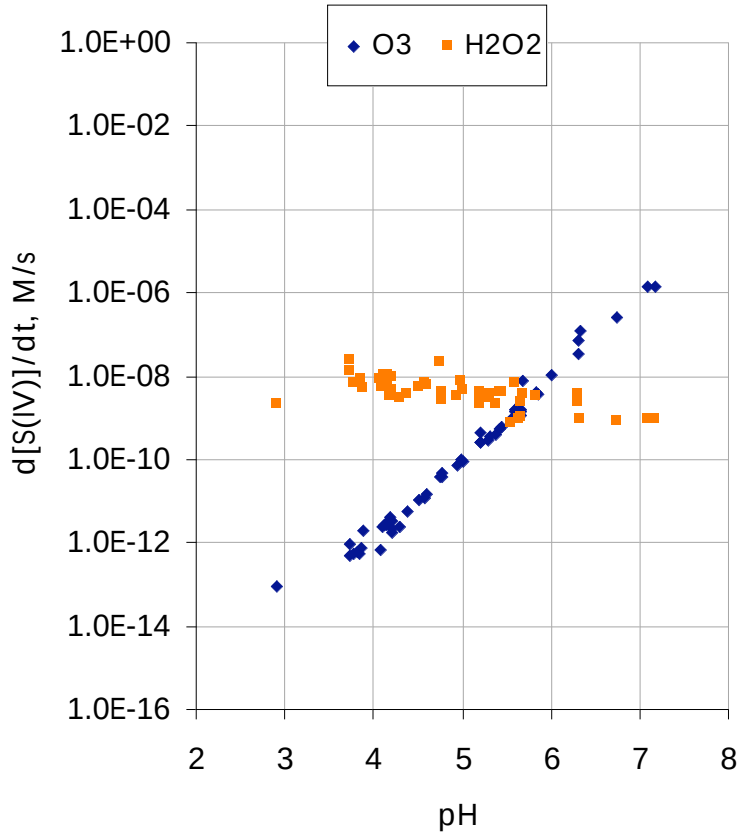
Spatial Variability of Peroxides



Estimated Sulfur(IV) Oxidation Rates

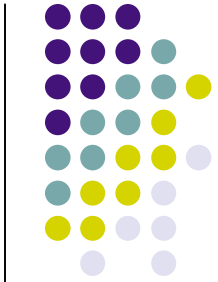
In cloud
O_3 concentration range: 10 – 60 ppb
SO_2 concentration range: 0.015 - 0.04 ppb
H_2O_2 range: 0.03 – 11 ppb

H_2O_2 was always in excess of aqueous S(IV)



Analysis of samples of concentrations of metals has not been completed.

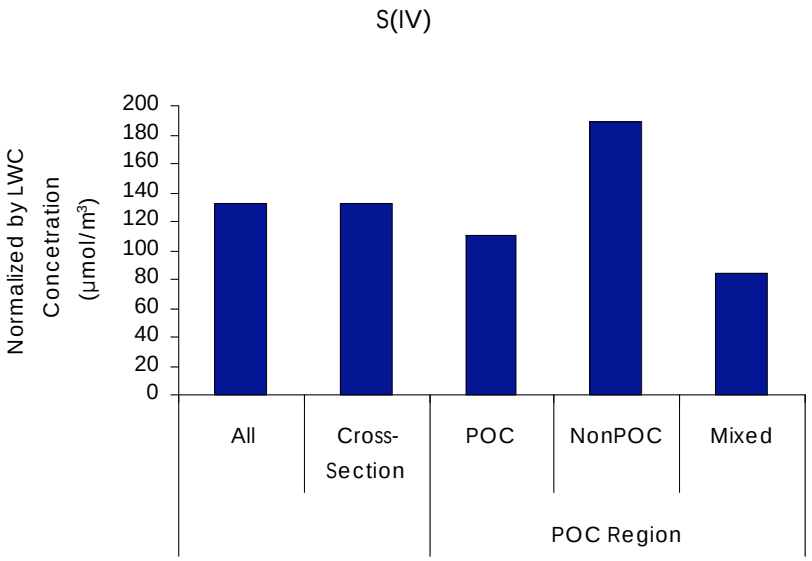
Preliminary Conclusions

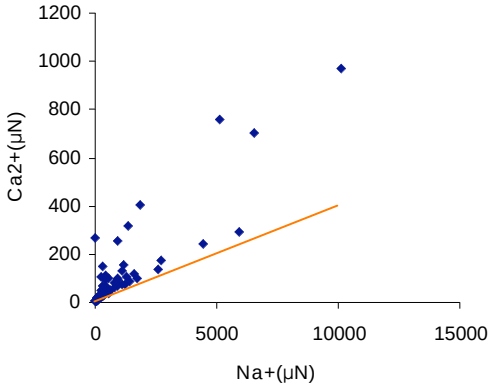


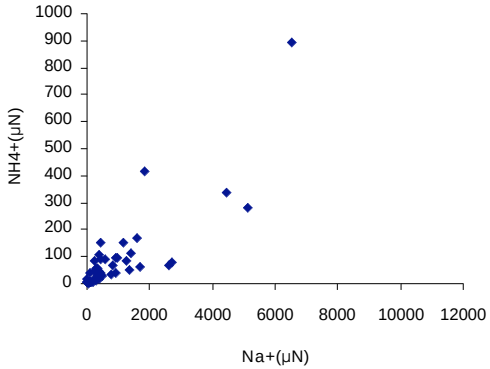
- Several ions were found to have similar concentrations relative to Na^+ - indicating a sea salt source.
  - Cl^- was depleted in may samples indicating replacement reactions with NO_3^- or SO_4^{2-}
  - Sulfate was measured in excess of the expected sea salt ratio. Indicating the presence of nss-SO_4^{2-}
- Present sulfur oxidation calculations indicate O_3 is the dominant oxidant at high pH and H_2O_2 is dominant at low pH.
- There are some differences in the chemistry of clouds in POC regions compare to outside. The explanations for the differences still needs to be investigated.

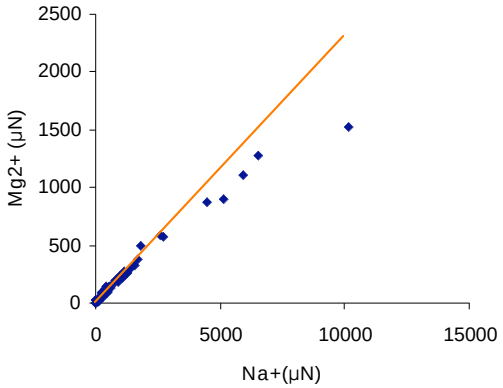
Acknowledgements

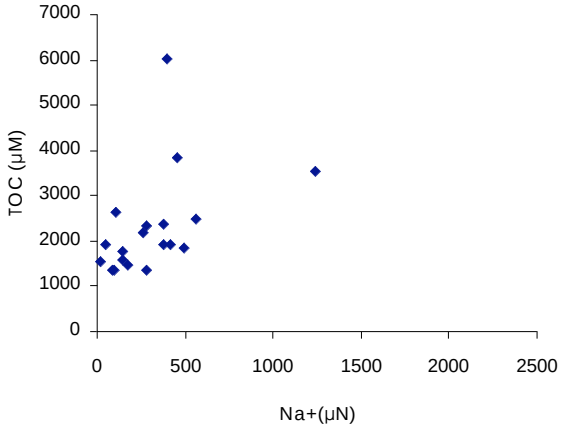
- NSF ATM-0745337
- RAF
- Derek Straub
- VOCALS people
- Aircraft data provided by NCAR/EOL under sponsorship of the National Science Foundation. http://data.eol.ucar.edu/

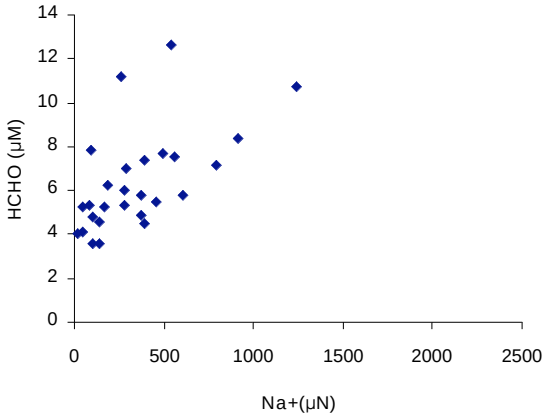

S(IV)
Normalized by LWC
Concetration
(µmol/m3)
200
180
160
140
120
100
80
60
40
20
0
All
Cross-
Section
POC
NonPOC
Mixed
POC Region

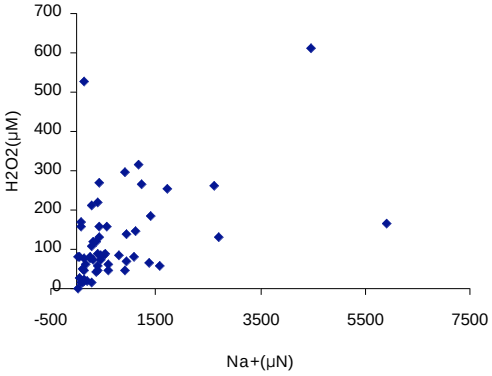

Ca2+(μN)
Na+(μN)
0
200
400
600
800
1000
1200
0
5000
10000
15000


NH4+(μN)
Na+(μN)
0
100
200
300
400
500
600
700
800
900
1000
0
2000
4000
6000
8000
10000
12000

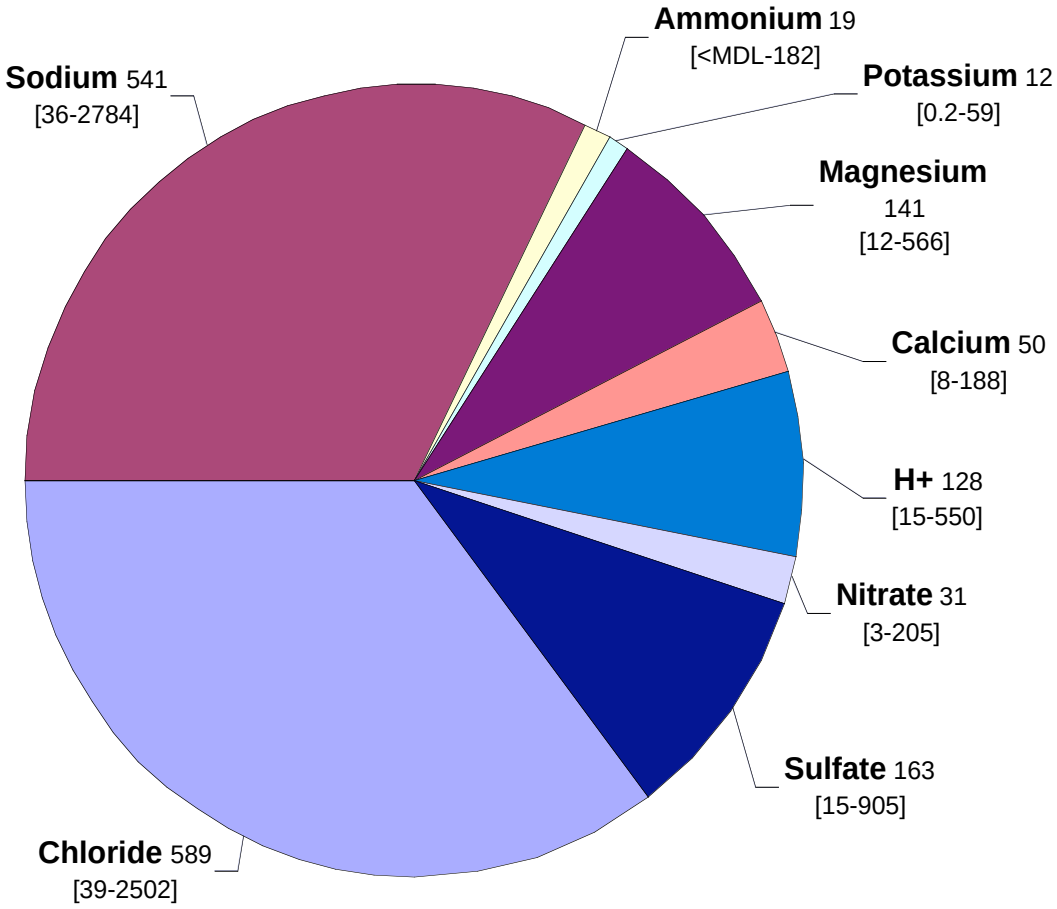

Mg2+ (μN)
Na+(μN)
0
500
1000
1500
2000
2500
0
5000
10000
15000


TOC (μM)
Na+(μN)
0
1000
2000
3000
4000
5000
6000
7000
0
500
1000
1500
2000
2500


HCHO (μM)
Na+(μN)
0
2
4
6
8
10
12
14
0
500
1000
1500
2000
2500


H2O2(μM)
Na+(μN)
0
100
200
300
400
500
600
700
-500
1500
3500
5500
7500

DYCOMS II


Ammonium 19
[<MDL-182]
Potassium 12
[0.2-59]
Sodium 541
[36-2784]
Magnesium
141
[12-566]
Calcium 50
[8-188]
H+ 128
[15-550]
Nitrate 31
[3-205]
Sulfate 163
[15-905]
Chloride 589
[39-2502]