

Overview and Significance

The Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) study was conducted in 2006 to identify the sources, transport, and speciation of atmospheric gases and aerosols throughout Colorado.

The research presented here will characterize the chemistry of particles by size in and around Rocky Mountain National Park, as well as furthering the general understanding of aerosol chemistry and their formation mechanisms.

Approach

Sites

- Main Site is located within Rocky Mountain National Park in a pristine natural area.
- Lyons Site is east of the national park in an urban corridor.



Data Collection

- Samples were collected at each site over a 48 hour period.
- The samples from Lyons were collected over a 36 day period in both the spring and summer.
- Only data from the Main Site summer samples will be presented (samples from the spring are missing).

Methods

MOUDI

- The aerosol samplers were collected with a Micro-Orifice Uniform-Deposit Impactor (MOUDI).
- The MOUDI separates aerosols into different size bins (10 or 12 depending on the model) and collects them on silicon coated aluminum substrates.



Ion Chromatograph

- Samples were extracted in deionized water and analyzed by ion chromatography (IC), which measured NH₄⁺, Na⁺, Ca²⁺, K⁺, Mg²⁺, Cl⁻, NO₂⁻, NO₃⁻, SO₄²⁻, and C₂O₄²⁻.
- The chromatograms were integrated and the areas converted into concentrations.

References:

- Jiang, Y., et al. (2014). Aerosol oxalate and its implication to haze pollution in Shanghai, China. *Chinese Science Bulletin*, 59(2), 227-238.
- Yu, J. Z., et al. (2005). When aerosol sulfate goes up, so does oxalate: implication for the formation mechanisms of oxalate. *Environmental science & technology*, 39(1), 128-133.

Results and Discussion

Part 1: General Composition

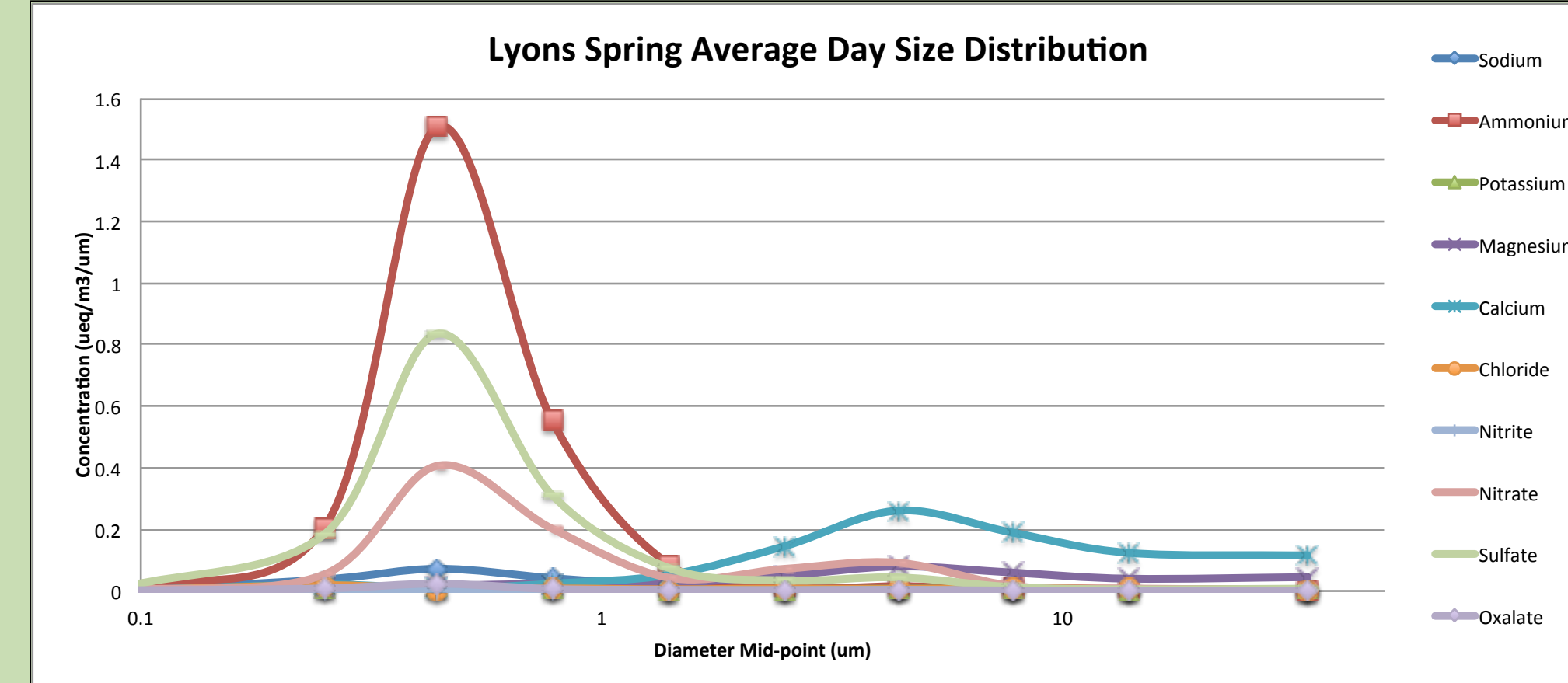


Figure 1: An average size profile for all measured species at the Lyons Spring site shows that the aerosols are concentrated in the 0.32-0.56 µm size range.

- On average NH₄⁺, SO₄²⁻, NO₃⁻, and Ca²⁺ are the most abundant species in both seasons at both sites.
- NO₃⁻ is unique because it is prevalent in both the fine and coarse modes.

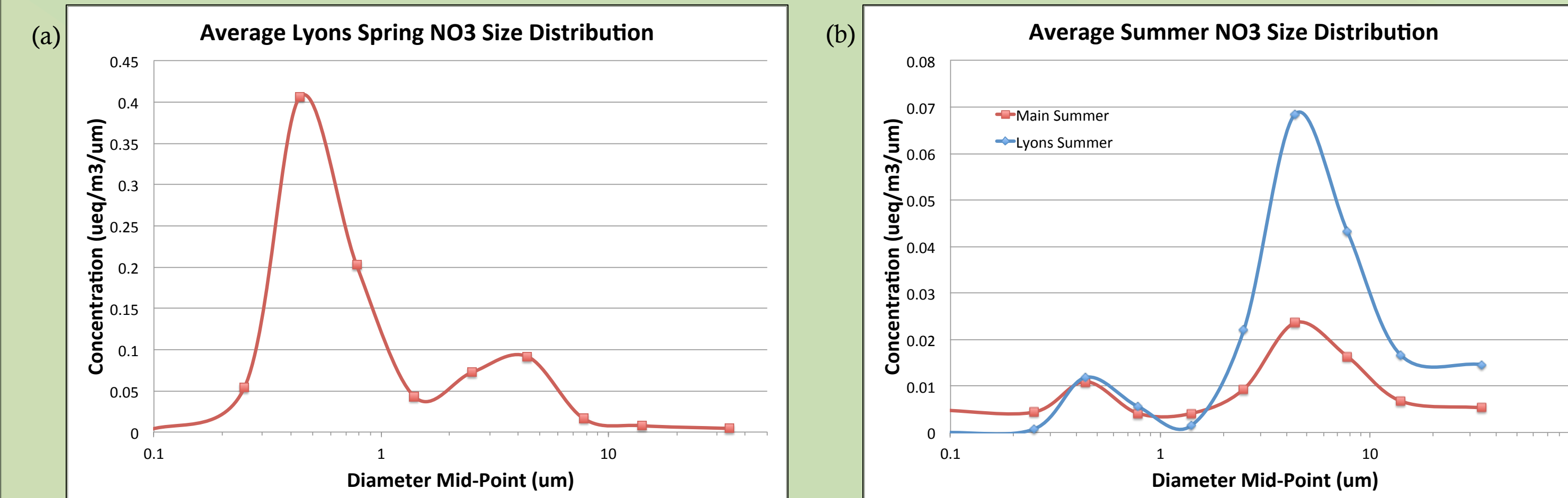
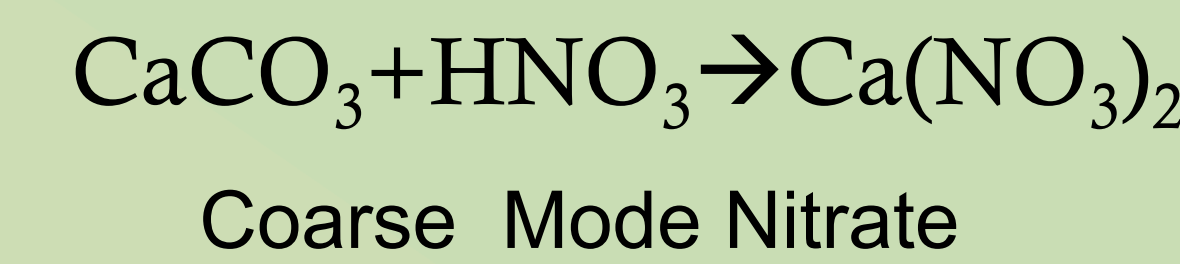
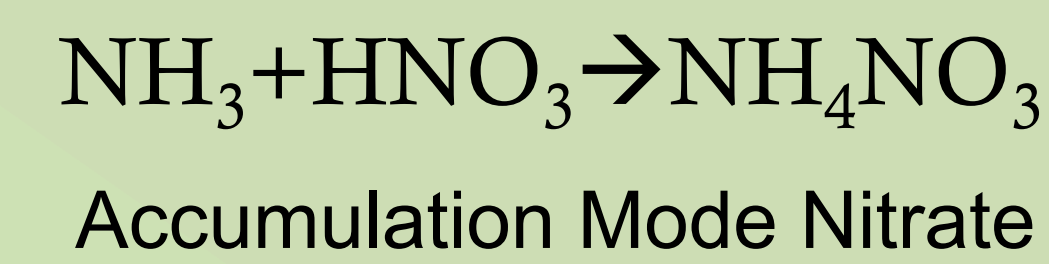
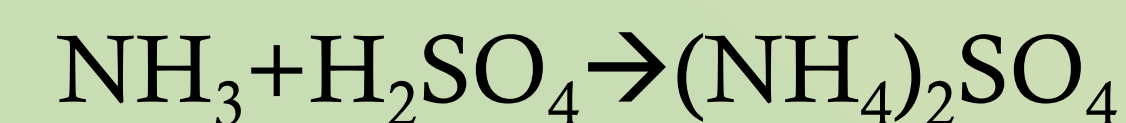


Figure 2(a and b): The average size distribution of NO₃⁻ at each site for (a) Lyons Spring and (b) Lyons and Main Site Summer.



Part 2: Ammonium Speciation

- Aerosols are neutral ($\sum \text{cations} = \sum \text{anions}$) and the dominant species should be in charge balance.
- Sulphate is preferentially paired with NH₄⁺.



- We observed that SO₄²⁻ and NO₃⁻ did not fully neutralize the NH₄⁺ (Fig. 3).
- Adding oxalate still did not fully neutralize the ammonium (Fig. 4).

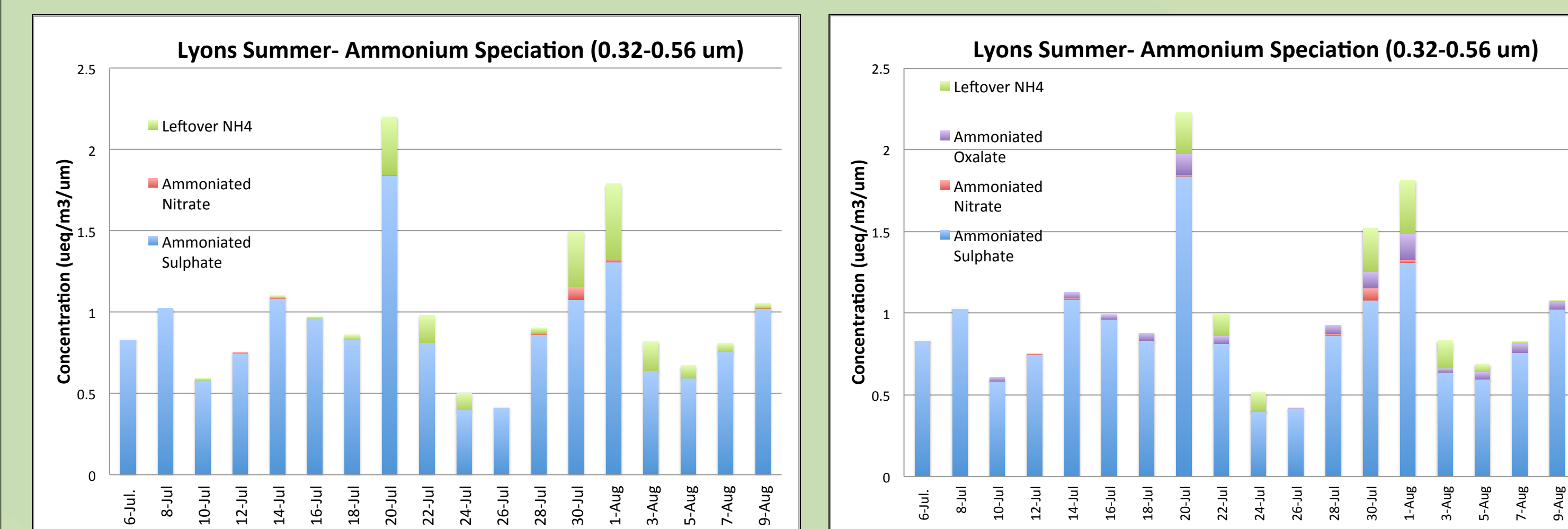


Figure 3: The ammonium speciation of the Lyons Summer shows that the majority of ammonium is neutralized, but some unpaired ammonium remains.

Figure 4: The ammonium speciation incorporating oxalate are shown for Lyons Summer. On some days there is still excess ammonium, so it must be pairing with another anion.

An unidentified anion must be pairing with NH₄⁺.

Acknowledgments

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Part 3: Oxalate- C₂O₄²⁻

- The MOUDI data shows that oxalate peaks in the 0.32-0.56 µm size range.
- Aerosol oxalate impacts cloud formation and radiative heating.
- Little is known about oxalate's size distribution and secondary formation pathways.

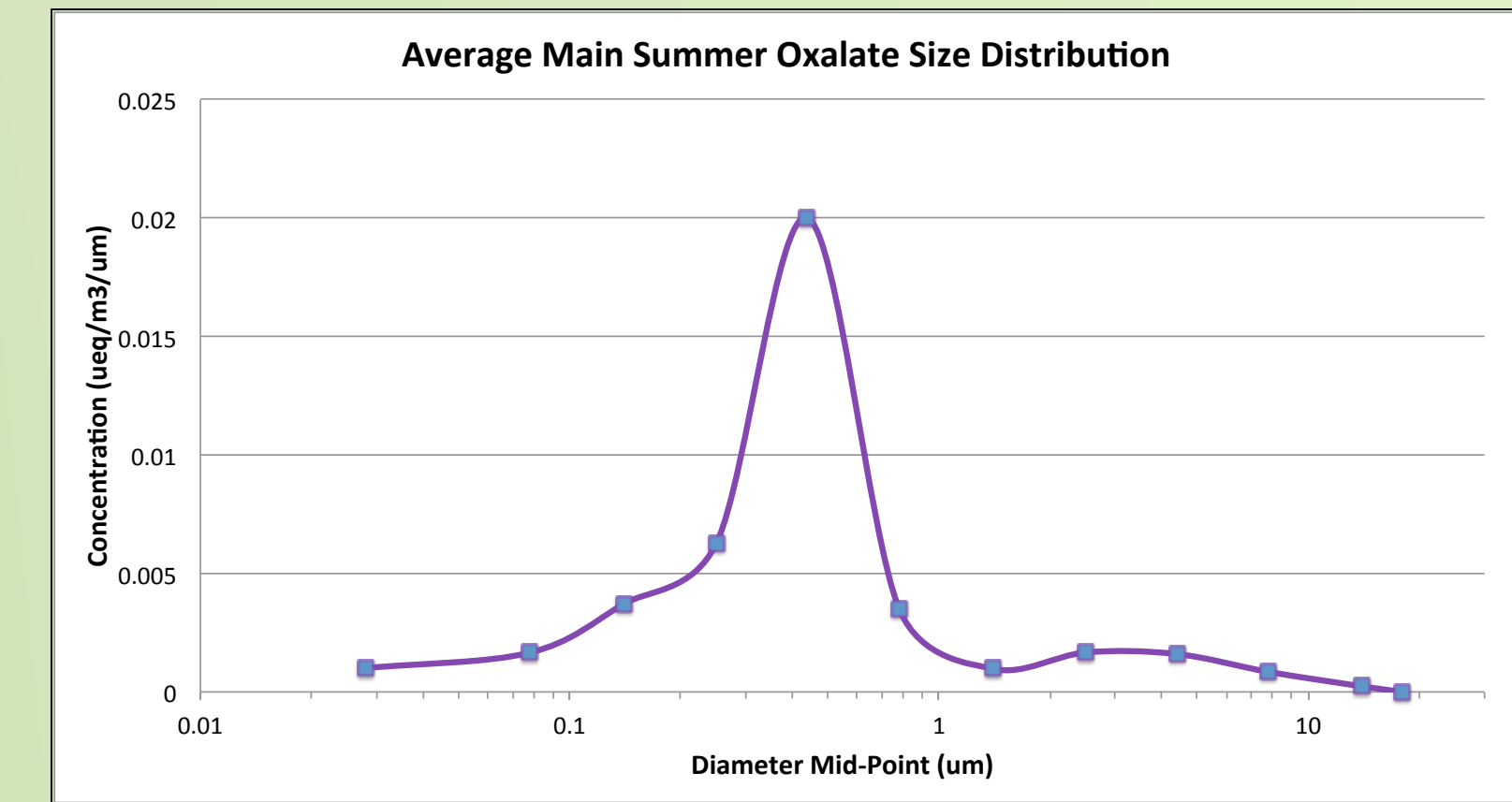


Figure 4: The average Main Summer oxalate size distribution has a peak in the 0.32-0.56 µm size range.

- Suggested pathways are photo-oxidation and in-cloud.

Secondary Formation Pathways

Photo-oxidation

- Lyons Summer has the most oxalate, perhaps because of the abundance of precursors and solar radiation.
- Supports a photo-oxidation formation pathway.

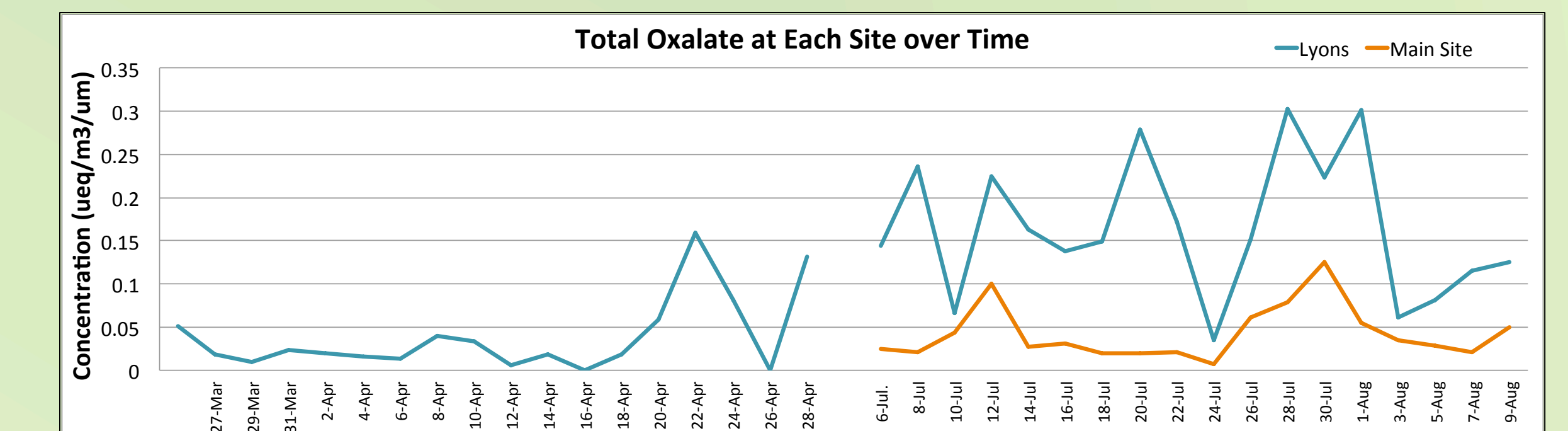


Figure 5: Total aerosol oxalate (all size bins) for each day in the spring and summer.

In-cloud

- Yu (2005) said that a strong correlation between SO₄²⁻ and C₂O₄²⁻ meant that they had the same formation pathway: in-cloud.
- Yu's R² range: 0.49-0.95
- Our R² range: 0.512-0.793
- Supports an in-cloud formation pathway

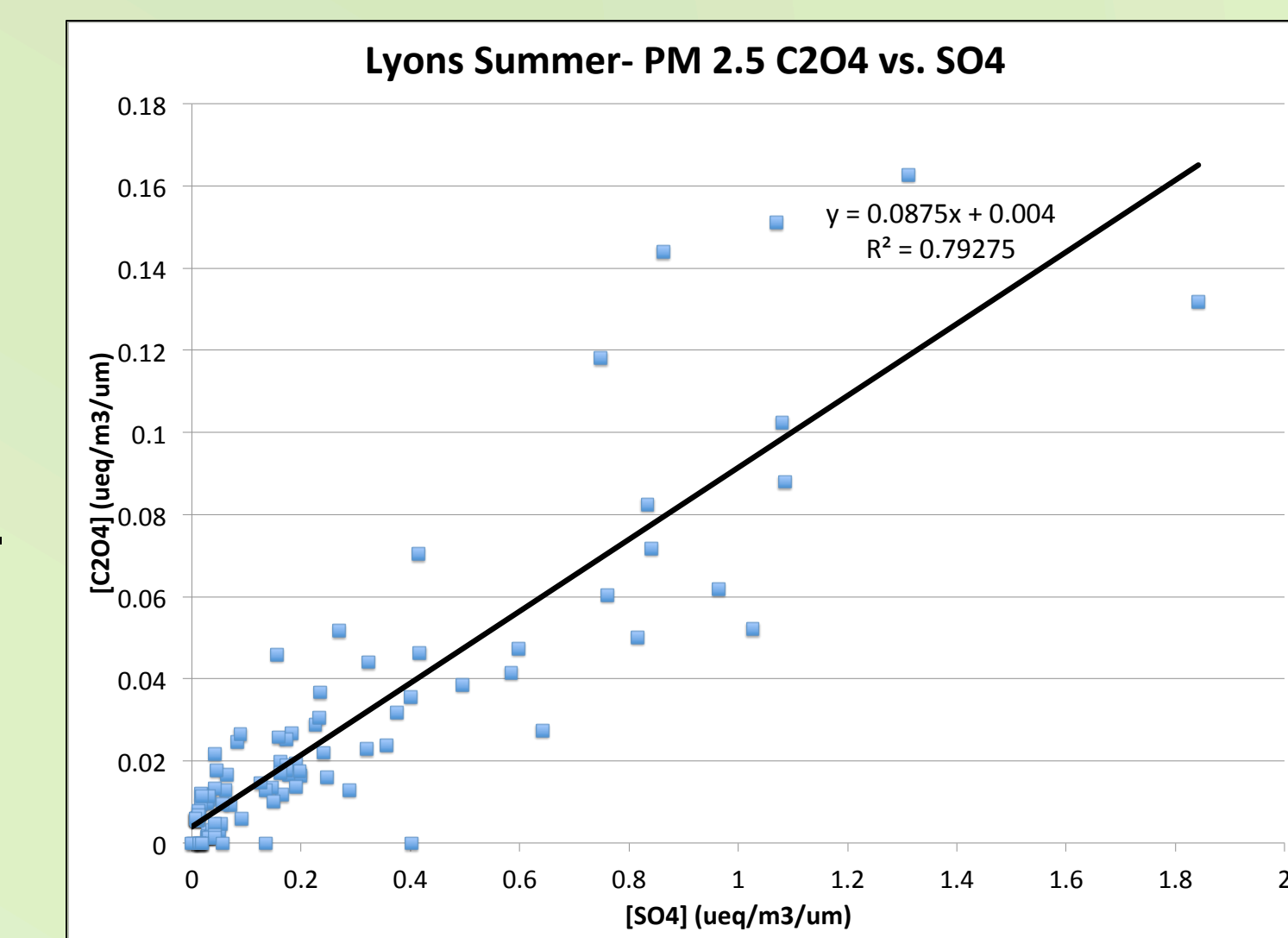


Figure 6: Relationship between oxalate and sulphate.

It is not clear which mechanism is dominant.

Conclusions and Future Work

Conclusions

- NO₃⁻ is prevalent in both the coarse and fine modes.
- SO₄²⁻, NO₃⁻, and C₂O₄²⁻ are not enough to fully neutralize NH₄⁺.
- Oxalate is primarily in the 0.32-0.56 µm size range.
- Higher levels of C₂O₄²⁻ when both precursors and sunlight are abundant support photochemical formation. High correlations between C₂O₄²⁻ and SO₄²⁻ support in-cloud formation.

Future Work

- Identify the other anion(s) pairing with NH₄⁺.
- Determine the dominant secondary formation pathway for oxalate.