Empirical Studies of Oxalic Acid Aerosol in Summer Cloud Water and Fine PM in the Northeastern U.S.

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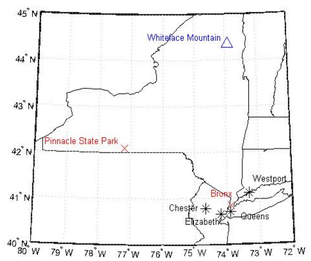
Introduction

Highly polar organic compounds (HPOC) comprise chemical mixtures found in cloud water and fine particles (nominal particle diameter < 2.5 micrometers, $PM_{2.5}$). An understanding of the chemical composition of HPOC is key to developing better knowledge of the role of these species on cloud life cycles, their sources, and the influence of organic carbon (OC) species on nanoscale to global scale atmospheric processes.

Here, we focus in particular on oxalic acid, the smallest diacid. Oxalic acid is the most abundant diacid and is highly oxygenated (O:C ratio of 2:1). It is very hygroscopic and is thought to be a good candidate to act as cloud condensation nuclei. We present oxalic acid concentration data in particulate matter (PM) samples from the New York City metro area, and in cloud water samples from the top of Whiteface Mountain in the Adirondacks. We discuss the motivation for focusing on oxalic acid, correlations of oxalic acid with other species in the samples, and implications of our findings.

Fine $PM_{2.5}$ & Cloud Water Collection

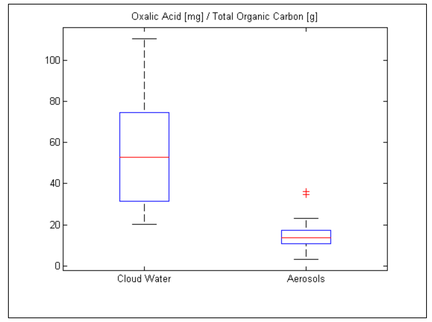
Fine PM samples were collected as part of the *Speciation of Organic Compounds for Source Apportionment* (SOAP) network. Samples were collected at 6 receptor sites from May 2002 to March 2007. Samples were obtained from three urban sites (Queens, NY and U.S. EPA Supersite; Elizabeth, NJ, and Bronx IS52), two upwind sites (Chester, NJ, and Pinnacle State Park, NY), and a downwind site (Westport, CT). Approximately 10 composites were generated for each site with 6 to 10 filters per composite. Filters were extracted half in acetone/dichloromethane and half in methanol (here, we focus on results from the methanol extraction). Cloud water samples (n=48) were collected during the summer of 2010 from Whiteface Mountain.



Filter collection sites from 2002-2003 are shown in black, while those from 2005-2007 are shown in red. The cloud water collection site is shown in blue.

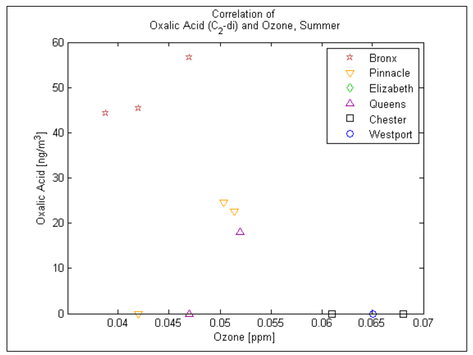
Motivation

Comparison of oxalic acid in cloud water and aerosol samples, when normalized by total organic carbon, showed that oxalic acid makes up a considerably larger percentage of the TOC in cloud water than in the particulate matter samples.

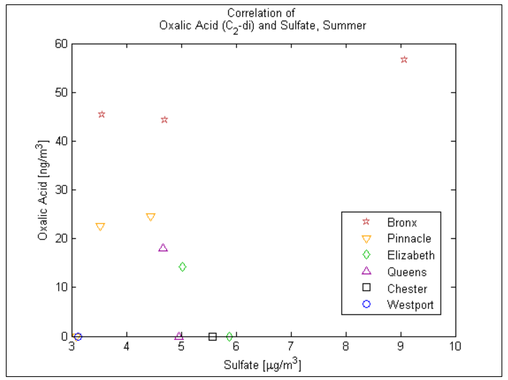


This suggests a potential additional source of oxalic acid in cloud water. We look at **the correlations of oxalic acid with two secondary species** (ozone in the gas phase, and sulfate in particles) to consider possible sources of oxalic acid. Ozone is formed photochemically, so a strong correlation with ozone would suggest direct photochemical formation.

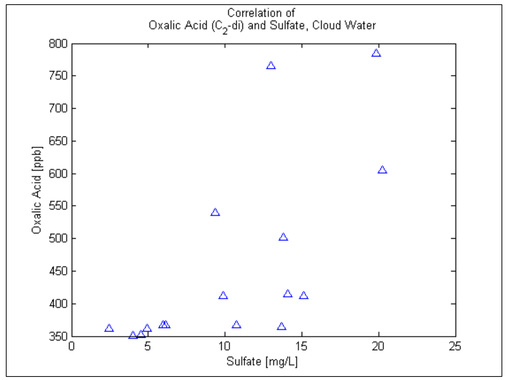
Correlations of Oxalic Acid with Ozone



Correlations of Oxalic Acid with Sulfate



Correlation of oxalic acid with sulfate in summer PM samples.



Correlation of oxalic acid with sulfate in summer cloud water samples.

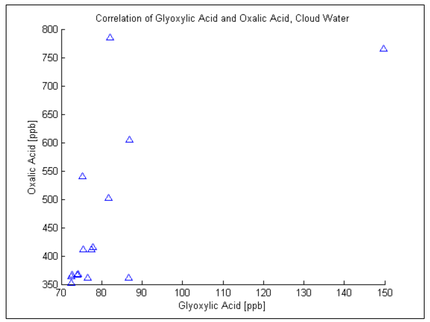
The R^2 values are **0.29** for oxalic acid and sulfate in PM, and **0.45** for oxalic acid and sulfate in cloud water.

Discussion

The correlation between oxalic acid and sulfate is not particularly convincing in the particulate matter samples. It is slightly better in the cloud water samples, but there is still quite a bit of variation. Given the fact that oxalic acid was more prevalent as a portion of total organic carbon in cloud water than in PM samples, it is surprising that the correlation with sulfate, a secondary species, was better in the cloud water than in the PM samples. This suggests that the sources of oxalic acid may vary between the two media, with perhaps a greater variety of sources in cloud water, but more homogenous formation in PM samples.

Additional thoughts – glyoxylic acid

Glyoxylic acid is a structurally similar compound to oxalic acid that was also quantified in this study. One source of oxalic acid is the oxidation of glyoxylic acid in the particle phase. The correlation of oxalic acid and glyoxylic acid in the cloud water samples is shown below. The R^2 value is **0.44**, suggesting that some of the oxalic acid may be associated with glyoxylic acid as a precursor, but other sources are likely present as well.



Next Steps

Future work will include further consideration of sources of oxalic acid via correlation with other potential precursors.

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