HIGHLY POLAR ORGANIC COMPOUNDS IN ATMOSPHERIC FINE PARTICLES AND CLOUD WATER: A STUDY IN THE NORTHEASTERN UNITED STATES

by

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A Dissertation submitted to the

Graduate School-New Brunswick

Rutgers, The State University of New Jersey

in partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

Graduate Program in Atmospheric Science

written under the direction of

Monica A. Mazurek

and approved by

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New Brunswick, New Jersey

May, 2013

ABSTRACT OF THE DISSERTATION

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Dissertation Director:

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Particulate matter is a ubiquitous component of Earth's atmosphere, but the degree to which it influences cloud formation and climate is not well understood. Highly polar organic compounds, or HPOC, are thought to be important in cloud formation due to their ability to attract water molecules. This study's goals included the quantification of HPOC in the atmosphere, study of correlations with sulfate and ozone to determine if the same production mechanisms are relevant, and study of temporal trends.

Two sample sets were analyzed: a set of particulate matter filters from in and around the New York City area collected from 2002-2007, and a set of cloud water samples from upstate New York collected in the summer of 2010. A lab method for the use of PFBHA was developed to facilitate analysis of compounds with an oxygen atom double-bonded to a carbon atom. This method was used in conjunction with BSTFA derivatization, which aids analysis of acids and other compounds containing a hydrogen atom bonded to an oxygen atom. Samples were analyzed with gas chromatography/mass spectrometry. The results focus primarily on four HPOC: cis-pinonic acid, glyoxal, glyoxylic acid, and oxalic acid. These and other compounds were

quantified in both sample sets. The concentrations of the compounds varied from season to season in the PM samples, but there was no clear seasonal cycle. Concentrations were typically highest at the urban sites. HPOC made up a larger portion of total organic carbon within the cloud water than in the PM, even though the amount of total organic carbon was higher in the PM. The correlation of HPOC with sulfate was considerably more pronounced in the cloud water samples, suggesting that, like sulfate, several of these compounds may be produced primarily within cloud droplets.

Acknowledgements

Many people have helped me along the way during my years at Rutgers. I would first and foremost like to thank my advisor, Professor Monica Mazurek, for her guidance and patience. I also appreciate Professors Mark Miller, Annmarie Carlton, and Eric Gonzales for serving on my committee. Min Li and Harmonie Hawley showed me the ropes when I first began, and they each made themselves available to discuss problems and questions with me even after moving on to professor positions at other universities. Professor Tony Broccoli was my first point of contact at Rutgers and continued to provide encouragement and good advice throughout my time here.

Dirk Felton and Oliver Rattigan (NYS DEC), Thomas McKenna and Charles Pietarinen (NJ DEP), and Alan Lester and Steve Bailey (CT DEP) collected and managed the SOAP filters. Jed Dukett and Phil Snyder from the Adirondack Lakes Survey Corporation collected the cloud water samples and provided supporting meteorological information.

I would also like to acknowledge the funding that supported me through my time at Rutgers. I am very grateful for the GAANN fellowship that was awarded to me for my first three years, the graduate assistantship that supported me in my fourth year, and the teaching assistantships in the departments of Chemistry & Chemical Biology (fall) and Environmental Sciences (spring) in my final two years. This work would not have been possible without them. Additionally, research projects through NASA's Graduate Student Summer Program (2008) and Student Airborne Research Program (2009) gave me the chance to branch out and develop my research skills in new settings.

I thank my friends in the department for all the intriguing conversations, food, softball games, and laughs over the years. Last but not least, I thank my husband Jeremy for his unwavering support.

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List of Acronyms

AMS = aerosol mass spectrometer

AQS = Air Quality Standard (EPA benchmark)

BSTFA = N,O-bis(trimethylsilyl)trifluoroacetamine (compound used to react with –OH groups in alcohols or carboxylic acids)

CCN = cloud condensation nuclei

CW = cloud water

DCM = dichloromethane (cleaning solvent for GC/MS machine and general lab glassware)

EC = elemental carbon

GC/MS = gas chromatography/mass spectrometry; also refers to the machine that performs these analysis processes

HPOC = highly polar organic compounds

NO_x = sum of NO (nitric oxide) and NO_2 (nitrate) in the gas phase

OC = organic carbon

PFBHA = O-(2,3,4,5,6)-pentafluorobenzyl hydroxylamine (compound used to react with aldehydes and ketones)

$PM_{2.5}$ = particulate matter with a diameter of less than 2.5 microns

PPB = parts per billion

PPM = parts per million

RRF = relative response factor (slope of line in calibration curves)

SOA = secondary organic aerosol

SOAP = Speciation of Organics for Apportionment of Fine Particulate Matter (project)

TC = total carbon (organic + elemental)

TOC = total organic carbon

VOCs = volatile organic compounds

1 Introduction

1.1 What is particulate matter?

One of the ubiquitous components of Earth's atmosphere is particulate matter (PM): solid and liquid particles suspended in the atmosphere, with a lifetime of hours to days. PM, also called aerosol, can be of natural origin, such as sea salt from ocean spray, dust, pollen, and resuspended soil. There are many anthropogenic sources of PM as well, such as diesel and gasoline exhaust, and smoke from coal-fired power plants and cooking operations [e.g. *Mochida et al.*, 2003; *Rogge et al.*, 1993]. In urban areas, the typical major components of PM include sulfate, nitrate, ammonium, elemental carbon, and organic carbon. PM can also be formed from the condensation of gas-phase species. Chemical compounds that are emitted directly into the atmosphere as solids or liquids are designated "primary" PM, while compounds that move from the gas phase to the particle (i.e., solid/liquid) phase are designated as "secondary". This distinction is particularly important for organic compounds in PM, which are discussed in more detail in Section 1.3. In the northeastern United States, organic compounds are more often secondary in origin than primary, with anthropogenic volatile organic compounds (VOCs) a larger source than biogenic VOCs [*de Gouw*, 2006].

1.2 Importance of PM

$PM_{2.5}$, or particles which have aerodynamic diameters less than or equal to 2.5 microns, is considered hazardous to human health because of its ability to penetrate the lungs and create cardiovascular problems. Prolonged exposure to such particles can result in increased mortality rates [*Schwartz et al.*, 1996; *Pope and Dockery*, 2006]. PM is an important, though not fully understood, component of Earth's radiation balance (Figure 1.1). Most particles scatter incoming solar radiation before it reaches the Earth's

surface; this cools the planet and is known as the aerosol direct effect, though a few light-absorbing species such as black carbon absorb solar radiation and warm the air around them. Increased PM concentrations also affect the radiation balance indirectly, by potentially increasing the number of cloud condensation nuclei available, causing more reflective [*Twomey*, 1977] and longer-lived clouds [*Albrecht*, 1989], both of which also result in less solar radiation reaching the Earth's surface. The overall scientific understanding of PM's role in climate is considered to be only medium to low [*IPCC* 2007; Figure 1.2]. The Northeastern States for Coordinated Air Use Management (NESCAUM) notes that key priorities regarding PM include confirming local sources and understanding the degree of its affect on public health [*NESCAUM* 2008], while the North American Research Strategy for Tropospheric Ozone (NARSTO) stresses the importance of understanding the factors contributing to regions with high levels of PM and finding source-specific solutions [*NARSTO* 2004].

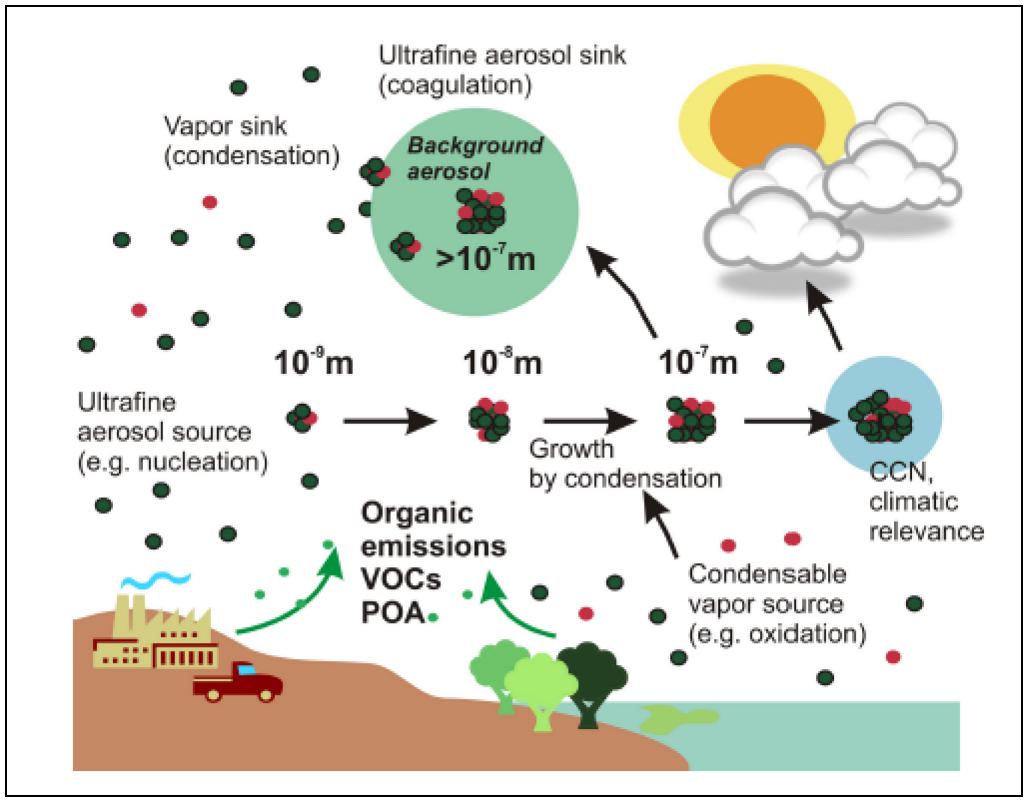

Figure 1.1. Particulate matter in the atmosphere. From Riipinen et al. 2011.

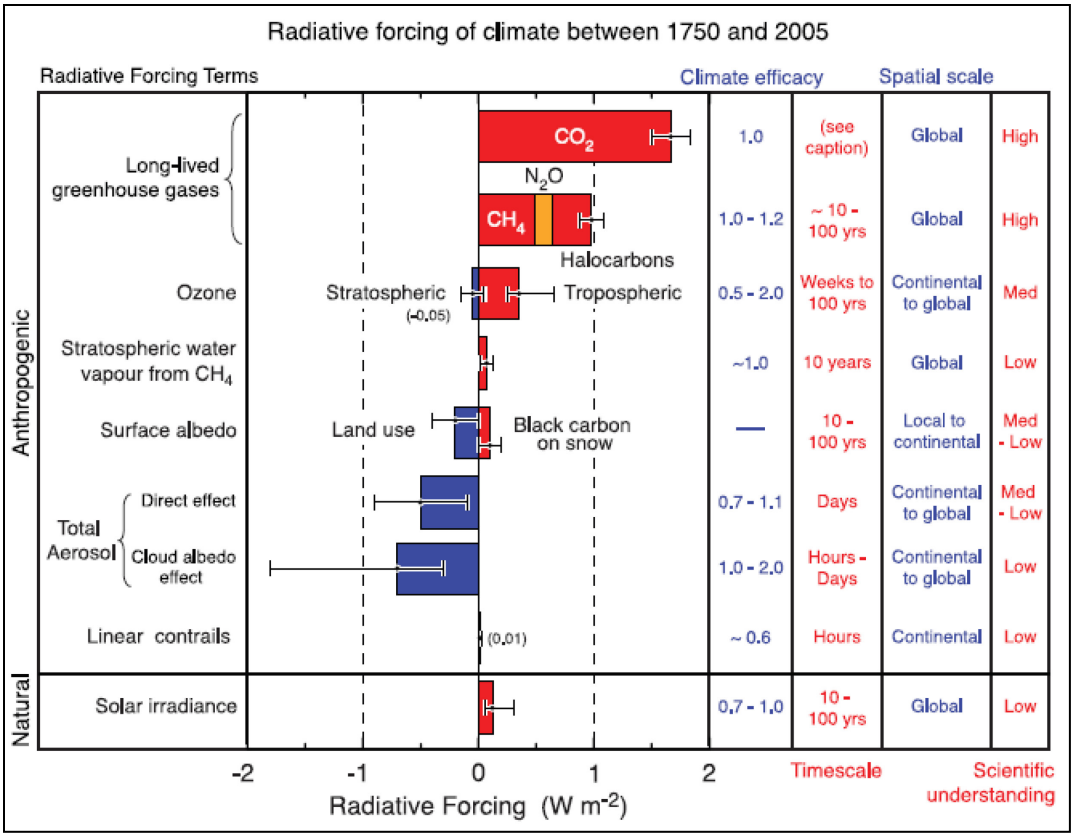

Figure 1.2. Radiative forcing of atmospheric constituents from IPCC 2007. Note that understanding of aerosol effects on climate is considered medium to low.

1.3 Highly polar organic compounds

Organic carbon (OC) accounts for 14-29% of total PM mass in urban areas; in pristine areas, this fraction can be as high as 90% [*Römpp et al.*, 2006; *Zhang et al.*, 2007]. Carbon is unique among the elements of the periodic table for its ability to form countless numbers of distinctive compounds with carbon itself as the "backbone" among different combinations of hydrogen, oxygen, the halogens, and other elements. There are millions of organic compounds, each having different thermodynamic properties depending on the functional groups present; it is thus important to identify which classes

of compounds are present in the atmosphere and what effects they have on Earth's radiation balance, cloud formation, and climate.

Polar organic compounds are organic compounds with an uneven distribution of charge. Oxygen-containing organic compounds tend to be among the more polar organic species, particularly when oxygen atoms are bonded to a carbon atom, as in aldehydes, ketones, and carboxylic acids. This configuration results in a lone electron pair on the oxygen atom due to its high electronegativity and thus a partial negative charge on the oxygen atom and an ensuing partial positive charge on an adjacent carbon atom. Such compounds, when present in the atmosphere, tend to attract water and thus serve as CCN [*Chebbi and Carlier*, 1996]. Since polar compounds may act as CCN, an understanding of their concentrations in the atmosphere is an important link to recognizing their role in atmospheric processes and processes which in turn, impact atmospheric water vapor interactions and Earth's radiation balance. Long-term perturbations in atmospheric cloud processes and radiative processes by organic compounds are believed to further impact the climate system.

Highly polar organic compounds, hereafter referred to as HPOC, are defined here to be those which contain two or more oxygen atoms. The compounds of greatest interest in this study tend to have oxygen to carbon ratios of 1:1 or higher, with oxalic acid (2:1 oxygen:carbon) being the most polar compound studied.

1.4 Key scientific questions

This study will attempt to answer the following questions:

1. **Which HPOC are present in ambient air samples and cloud water?** Do the two media differ in composition and relative abundance of individual HPOC?

2. **Are HPOC concentrations correlated with EC (elemental carbon), OC (organic carbon), and secondary gas and PM species (ozone and sulfate)?** Can these correlations, if they exist, be used to estimate HPOC concentrations in samples for which full organic speciation data are not available?

3. **Do HPOC concentrations in particulate matter vary significantly by season and site (urban vs. rural)?** If so, can their sources be established, and concentrations predicted?

2 Research Background

2.1 HPOC in the atmosphere

HPOC is omnipresent in the atmosphere. A comprehensive study by *Zhang et al.* [2007] analyzed aerosol data from 37 field sampling campaigns from around the world and found that oxygenated organic aerosol can make up 64% (in urban areas) to 95% (in rural and remote areas) of the total mass of organic aerosol. This is in contrast to "hydrocarbon-like" organic aerosol, which is less polar but emitted in urban areas from processes such as meat cooking. (All organics, in turn, made up an average of 45% of the total aerosol mass among the field campaigns, with the remaining 55% consisting of non-organic species such as sulfate, nitrate, ammonium, and elemental carbon).

The traditional method of measuring organic compounds, including HPOC, in PM in the atmosphere involves the collection of particulate matter on clean filters. Typically, a vacuum pump pulls air through the filter at a known flow rate, and the PM is collected on the filter. Later, the filters are "extracted" (collected particles are transferred from the filter to a liquid solution). The mass of target compounds can be calculated using gas chromatography/mass spectrometry, high performance liquid chromatography, or other analytical methods. The volume of air that passed through the filter can be calculated, and thus the concentration of compounds of interest can be calculated as mass per volume of air. Another method provides an alternative method of diagnosing the oxidation state of PM; rather than collecting PM samples on filters to establish concentrations of individual oxidized compounds, ratios of oxygen to carbon and hydrogen to carbon are calculated with an aerosol mass spectrometer (AMS) to give a general picture of how oxidized aerosols might be at a given time and place. Methods such as this, while limited in detail, are quite useful for examining the "big picture" of the

state of the atmosphere and for situations in which results are needed very quickly after sampling time, such as for air quality forecasting models.

Zhang et al. [2007] note that oxygenated organic aerosol can be both primary (emitted directly, such as in the case of biomass burning) and secondary (produced via chemical reaction or photooxidation of other organic compounds, either biogenic or anthropogenic in origin; e.g. *Simoneit et al.*, 1984; *Simoneit et al.*, 1999; *Mochida et al.*, 2003; *Rogge et al.*, 1993). In general, primary organic aerosol tends to be more hydrocarbon-like (i.e., less oxygenated), and due to the abundance of oxygen in the atmosphere, it tends to become more oxidized, either through formation of oxygen-carbon bonds or loss of hydrogen-carbon bonds, throughout its residence time in the atmosphere. The overall picture of an area's PM can be determined by studying the O:C and H:C ratios in the PM. *Aiken et al.* [2008] developed a method for diagnosing an overall O:C ratio from field AMS data, which was taken in and around Mexico City in 2006. Likewise, *Heald et al.* [2010] plotted O:C ratios against H:C ratios for a variety of field and lab samples, showing that the points tend to fall along a line with a slope of -1, implying movement toward higher O:C ratios and lower H:C ratios with age. In a similar manner, *Kroll et al.* [2011] suggest that the amount of oxidation in PM can be characterized by the average oxidation state of the compounds, estimated as two times the ratio of oxygen to carbon, minus the ratio of hydrogen to carbon. That study found that the oxidation state of atmospheric organic aerosol typically ranges from about -2 to +1, with the higher positive values found in more aged aerosol (Figure 2.1). Individual compounds can have a higher oxidation state, but the average over a sampling study would be unlikely to exceed +1. The authors also note that too much oxidation may be actually be a sink for organics in the particle phase, as they may become too volatile and evaporate. Compounds such as CO_2 that have a very high oxidation state (+2 in this case) could only be found in the gas phase.

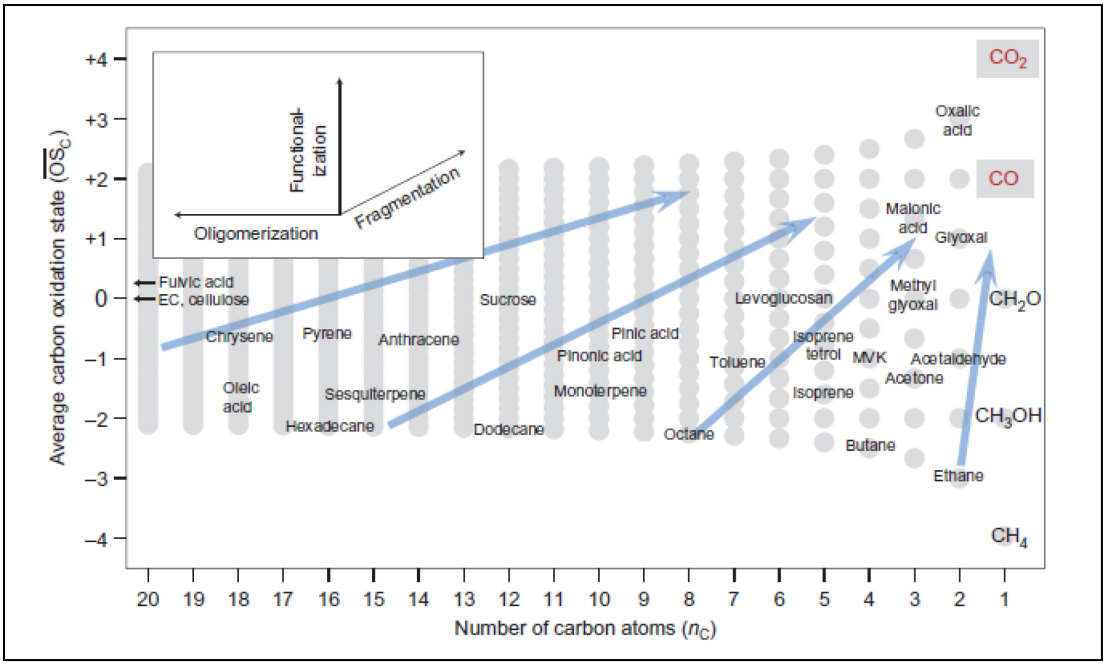

Figure 2.1. Size and oxidation state of common organic compounds in PM. The blue arrows show the tendency for compounds to become smaller and more oxidized over time. From Kroll et al., 2011.

In the previously discussed study by *Aiken et al.* [2008], the O:C ratio in Mexico City was shown to have a clear diurnal cycle, with the peak ratio of about 0.55 seen in the afternoon, suggesting photochemistry as an obvious source for many of the oxygenated species. However, the same study also performed positive matrix factorization on its data set and found four major components: hydrocarbon-like organic aerosol, fresh SOA, aged SOA and biomass burning OA. Of the four, the aged SOA had the highest O:C ratio (0.83 to 1.02), compared to 0.52-0.64 for fresh SOA, 0.31-0.42 for the biomass burning OA, and just 0.06-0.10 for hydrocarbon-like OA (which is typically found freshly emitted in urban areas). This study clearly shows that, as expected in an oxidizing atmosphere such as Earth's, increased oxidation is seen as aerosol ages.

2.1.1 Diacids

Diacids have been a focus of numerous PM studies all over the world. Figure 2.2 below presents a graphical summary of several recent studies that took place in or

around megacities, much like the $PM_{2.5}$ sampling campaign that makes up part of this study (Section 3.1). The data in the graph are from campaigns that took place in the summer. In these studies, oxalic acid, with two carbon atoms, has typically been found in concentrations far exceeding all other diacids, and its sources have been much discussed in the literature. *Kawamura and Kaplan* [1987] collected samples of exhaust from one gasoline and one diesel vehicle and found that the profile of diacids in the vehicle exhaust matched that of ambient air from Los Angeles. However, a more recent study by *Huang and Yu* [2007] compared simultaneous oxalic acid and elemental carbon (EC) concentrations from inside a tunnel and the outside environment. Since EC is a well-known product of vehicle exhaust, the authors sought a correlation between EC and oxalic acid in the tunnel. However, the oxalic acid concentrations were nearly identical inside and outside the tunnel, while EC concentrations were more than ten times higher inside the tunnel than outside, leading the authors to conclude that oxalic acid is probably not produced in large quantities from fuel combustion.

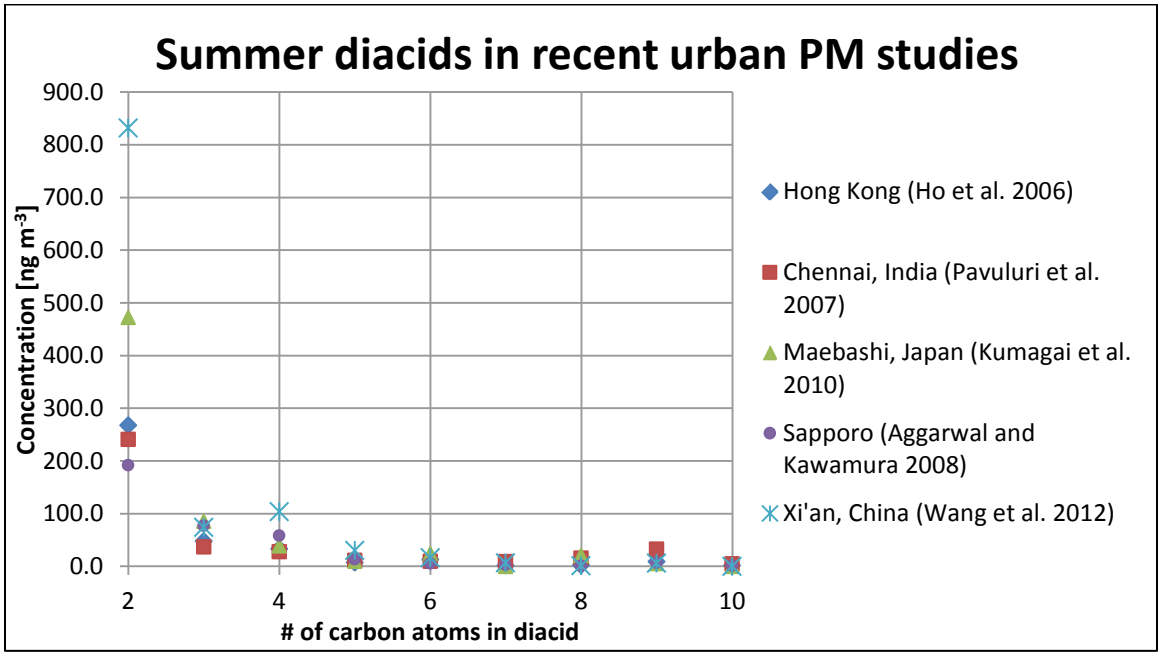

Figure 2.2. Summary of diacid concentrations in urban PM samples.

Pavuluri et al. [2010] report that oxalic acid was the dominant diacid found in Indian aerosols in both winter and summer, making up from about 60 to 75% of the total diacids, although the concentrations of larger diacids (C_5 to C_{11}) were about twice as large in summer as they were in winter. Oxalic acid is so prevalent because, in addition to possible direct emissions such as biomass burning ([*Yamasoe et al.*, 2000; *Narukawa et al.*, 1999]), it is thought to be the end product of many chemical reactions in the atmosphere. As previously discussed, many organics become smaller and more oxidized through their atmospheric lifetimes, eventually converting to oxalic acid. Oxalic acid is thought to be formed primarily in the aqueous phase, since its air-water equilibrium constant suggests that it would not be found in the gas phase [*Saxena and Hildemann*, 1996]. One of the suggested pathways is the conversion of glyoxal to oxalic acid (Figure 2.3 on page 15) in the aqueous phase.

After oxalic acid, diacids typically are seen in smaller quantities as the number of carbon atoms in the diacid increases. One notable exception is azelaic acid (C_9), which is thought to be produced in the atmosphere from biogenic sources (i.e., the oxidation of longer-chain monocarboxylic acids; *Kawamura and Gagosian*, 1987). Additionally, adipic acid (C_6) may be produced from anthropogenic cyclohexene, allowing it to serve as a marker for anthropogenic influence. The ratio of adipic acid to azelaic acid has even been used as an index to gauge the amount of "aging" an air mass has undergone (e.g. *Ho et al.*, 2006; *Yao et al.*, 2004). A study of diacids on remote Pacific island indicated that while short-chain diacids (C_2-C_7) had their origins in polluted air masses from Asia, longer-chain (C_8-C_{11}) diacids may have an oceanic source instead [*Mochida et al.*, 2003].

Diacid concentrations usually follow a seasonal cycle, with higher concentrations seen in the summer (e.g.,*Kerminen et al.*, 2000; *Li et al*., 2006; *Kourtchev et al.*, 2008). This is also consistent with the theory of photochemistry as a main source, though

anthropogenic sources such as meat cooking have also been identified [*Rogge et al.*, 1993].

Other studies have used the ratios of individual diacids to each other, or individual diacids to the total amount of diacids present, as estimates of source contributions; in addition to the previously noted malonic acid:succinic acid ratio, the ratio of adipic acid to azelaic acid (C_6 diacid to C_9 diacid) can help explain sources since adipic acid is thought to be formed photochemically, while azelaic acid is biogenic in origin (e.g. *Ho et al.*, 2006;). Such methods may also be helpful in determining sources in the New York megacity area.

2.1.2 Ketomonoacids and ketodiacids

Keto acids, acids which include a carbon atom double-bonded to an oxygen atom somewhere in the molecule, have been less frequently targeted in previous studies, likely due to the relatively lengthy lab work needed to derivatize both functional groups. One of the earliest studies on oxodiacid concentrations took place in Alert, Canada in 1987-88. *Kawamura et al.* [1994] found that diacid concentrations in the Arctic peaked twice a year, in fall and spring. The authors searched for two ketodiacids, oxomalonic acid and 4-oxopimelic acid, which were both found in peak concentrations in April coinciding with the end of winter darkness, lending credence to the idea that such oxygenated compounds are formed in the atmosphere photochemically rather than emitted directly. Each oxodiacid's mean concentration over the course of a year was less than 1 ng m^{-3}, while the C_2 to C_4 diacids had mean concentrations of 13.6, 2.46, and 3.73 ng m^{-3}, respectively. The authors propose that ketodiacids may be intermediates in a chain of reactions, leading to smaller and smaller straight-chain diacids; this would also help explain why oxalic acid, at "the end of the line" of diacids, is seen in such abundance compared to other diacids (as discussed in previous section). In support of

this idea, *Pavuluri et al.* [2010] found no seasonal differences in oxodiacid concentrations in the megacity of Chennai, India. Unlike the Arctic, India has little seasonal change in solar radiation, so ketodiacids were hypothesized to be constantly formed and destroyed via photochemistry.

2.1.3 Carbonyls

Carbonyls in the atmosphere have been studied in several different locations. *Destaillats et al.* [2002] searched for carbonyl compounds in the San Francisco Bay Area from filters collected during rush hour traffic. Acrolein, a product of incomplete combustion, is itself a precursor for compounds such as glyoxal and glycolaldehyde; in addition, like other α,β-unsaturated carbonyls, it is highly mutagenic. Acrolein was found in concentrations as high as 0.1 μg m^{-3}, which is in excess of California's established reference exposure level of ≤ 0.06 μg m^{-3}. Another study by *Ortiz et al.* [2006] looked at six bifunctional carbonyls in an urban area in Japan. The authors note that two of the compounds, pyruvic acid and glyoxylic acid, were particularly sensitive to the amount of UV radiation present in the sampling period, suggesting a photochemical origin for these two compounds.

2.2 HPOC in cloud water

Though there have been numerous studies of major inorganic ions in cloud water, studies of organic compounds in cloud water are less common. Though some projects have involved fast, in-situ collection and identification of organics from airplanes by use of an aerosol mass spectrometer, I focus here on studies involving collection and subsequent laboratory analysis.

2.2.1 Concentration data

One study by *Löflund et al.* [2002] in the Austrian Alps found that small acids and diacids made up around 11% on average of the total organic carbon found in their cloud water samples. They found no correlation between the individual diacids and TOC, although they did find a weak correlation between individual diacids and black carbon, with malonic acid having the highest R^2 value among diacids (0.464). Another mountaintop study from the Storm Peak Laboratory in Colorado [*Samy et al.*, 2010] found that cloud water diacid concentrations were highly dependent on wind direction; the magnitude of the sum of diacids, as well as the percentage abundance of individual diacids, varied according to the source region of the air mass from which the cloud evolved. Similar results were seen in a study by *Avery et al*. [2006]; they looked at organics in rainwater in North Carolina rather than cloud water, but also noticed that concentration of organic acids depended strongly on wind direction, with marine storms bringing the lowest volume of organic acids and storms from the south bringing the highest volume. However, the authors did not find any consistent dependence of individual organic acid concentrations on back trajectory.

A study in Shenandoah National Park focused on the partitioning of carbonyls, including glyoxal, between the gas and liquid phase [*Munger et al.*, 1995]. The authors found that glyoxal was in nearly equal concentrations in the gas phase and in the cloud water, suggesting that glyoxal quickly reaches equilibrium between the two phases. The study also examined two cloud water events, and found that glyoxal concentrations in the cloud water decreased over the course of the events.

2.2.2 Formation of HPOC in aqueous media

A few studies have looked directly at the differences in HPOC concentrations between PM samples and cloud water samples to determine the effects of in-cloud

processing of these compounds. *Sorooshian et al.* [2006] took samples from an aircraft in clear and cloudy air masses over Ohio and searched for both organic and inorganic species. The authors found that oxalic acid was found in much higher concentrations when clouds were present than in cloud-free circumstances. Furthermore, a high degree of correlation ($r = 0.8$ for 40 samples) was found between oxalic acid and sulfate. Since sulfate is formed in the aqueous phase, this strongly suggested that oxalic acid was primarily produced in the aqueous phase as well. A study by *Yu et al.* [2005] found similar results.

The formation of HPOC in cloud water has also been the focus of modeling studies. Studies by are summarized in Figure 2.3, which shows possible formation mechanisms for many HPOC. *Ervens et al.* [2008] model SOA formation at different initial ratios of VOC (isoprene)/NO_x. They found that the amount of SOA formed increased with the amount of NO_x. Further, when NO_x concentrations were low, isoprene tended to form organic peroxides which then entered the particle phase, whereas under high NO_x conditions, carbonyls were formed and then taken up in cloud droplets and further oxidized.

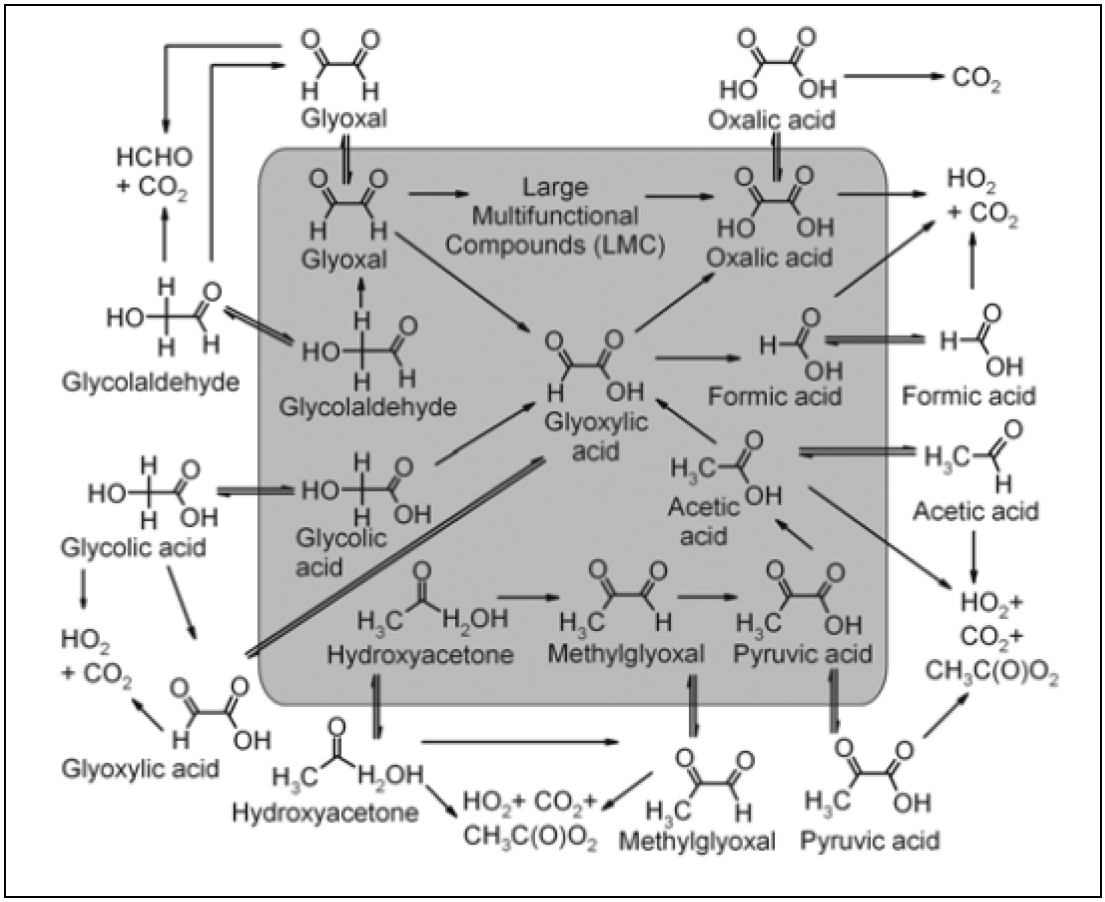

Figure 2.3. Formation mechanism for HPOC in the aqueous phase (shaded), gas phase (unshaded), and in between. From Ervens et al. 2008.

2.3 HPOC and climate

With HPOC defined, it is important to consider how the presence of HPOC in the atmosphere may affect radiation and climate. Modeling studies have been particularly useful in helping to clarify this relationship. As previously noted, aerosols may affect climate both directly (via the scattering of incoming solar radiation) and indirectly (through altering the properties and lifetimes of clouds). A study by *Shantz et al.* [2008] focused on how differences in particle composition affect their ability to take up water. They collected particle samples in forest and marine environments on the west coast of Canada and then modeled the ability of those particles to act as CCN, based on their size, number, and composition. They found that in samples from a forest, where

organics made up a large fraction of the collected particles (80-90% by mass), the number of droplets present was higher than in the contrasting marine samples, and the CCN growth rates were far higher than for the marine cases as well. This increased CCN growth rates were attributed more to the higher number of particles than the presence of organics, but the authors expected that organics did play some role in the increased water uptake. *Petters and Kreidenweis* [2007] defined the parameter κ as the hygroscopicity parameter; i.e., a single parameter describing the water uptake and CCN potential of a particle. Additionally, a κ value for a particle can be calculated from the κ value of the individual compounds that make up the particle. From lab studies, the authors calculated that organic species may have values as high as 0.5 (while the most hygroscopic compounds, inorganic salts such as ammonium nitrate, can have values as high as 1.4, and hydrophobic compounds have values of zero).

Furthermore, our knowledge of HPOC concentrations in the atmosphere is not perfect. As previously noted, the 2007 IPCC report characterizes scientific understanding of the effect of aerosols on Earth's radiation balance as medium to low. Additionally, modeled aerosol concentrations can be at odds with observed concentrations [*Heald et al.,* 2005 and *Volkamer et al.,* 2006]. The Heald et al. study focused on the northwest Pacific and suggests that chemical transport models lack a major source of organic aerosols there, which the authors guess comes from the oxidation of volatile organic compounds. Likewise, Volkamer et al. note that anthropogenic VOCs are typically neglected in models as a source of secondary organic aerosol (SOA) and calculate that this omission could be causing models to overlook a potential -0.1 W m^{-2} of radiative cooling at the top of the atmosphere.

3 Sampling Campaign Descriptions

3.1 $PM_{2.5}$ samples

The $PM_{2.5}$ samples used in this study come from the Speciation of Organics for Apportionment of Fine Particulate Matter (SOAP) project. SOAP took place in two parts. The first part, designated "SOAP 2002-2003", saw samples collected every third day from May 2002 to May 2003 at four sites: Chester, New Jersey; Elizabeth, New Jersey; Queens, New York; and Westport, Connecticut (*McDow et al.*, 2008). The second part, designated "SOAP-NY", saw samples collected every sixth day from October 2005 to February 2007 at two sites: Pinnacle State Park, New York and Bronx, New York. (Sampling sites are shown in Figure 3.1). In both cases, samples were obtained by loading a Tisch sampler with a baked-out quartz fiber filter and pulling air through the sampler at a rate of 113 L min^{-1} for 24 hours. Filters were kept within the holder cassettes, which were removed from the sampler at the end of the 24 hours and sent in a cooler to Rutgers. Filters were inventoried, removed from the cassettes, and stored in baked-out glass jars in a freezer until analysis. Each filter was cut in half, and the first part was analyzed in previous work on less-polar compounds (e.g. *Hawley*, 2008). The remaining portion was used in this study.

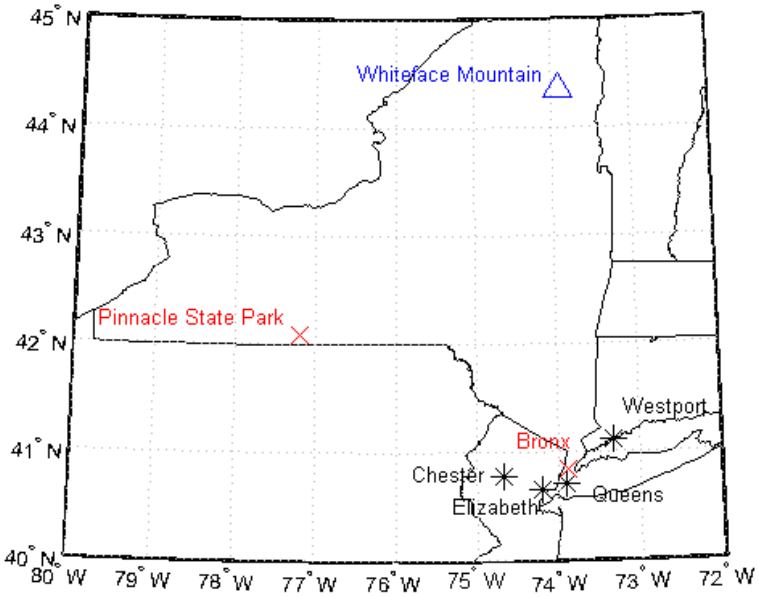

Figure 3.1. Locations of $PM_{2.5}$ and cloud water sampling sites. Sites from SOAP 2002-2003 are shown as black stars, sites from SOAP-NY are shown as red x's, and the cloud water site is shown as a blue triangle.

Field, trip, and lab blanks were collected as well. Field blanks, which are used to estimate the natural deposition of particles onto a filter, were obtained by placing filters in the sampler for 24 hours without turning the sampler on [*McDow et al.*, 2008]. Trip blanks consisted of filters that were shipped from Rutgers to the sampling sites and back again but were never removed from their storage casing, to determine if any contamination was occurring in transit. Additionally, one lab blank was created, which consisted of a baked-out, never-used filter that was extracted in the lab to check for any contamination points during lab processing.

Filters were not processed individually but grouped into seasonal or monthly "composites" to ensure that there would be enough mass to be detected by the GC/MS. For the first part of the SOAP project (SOAP 2002-2003), filters were composited by season such that each site's sampling days were maximized. For the second part of the

project (SOAP-NY), filters were grouped by calendar month instead. The complete compositing scheme can be found in Appendix C.

3.2 Cloud water

The cloud water samples analyzed in this study come from the top of Whiteface Mountain (44.37°N, 73.90°W, elevation 1483 meters) in the Adirondack Mountains of New York (Figure 3.2). The Adirondack Lakes Survey Corporation (ALSC) collects samples primarily for inorganic ion analysis. Samples are collected only when air temperature is above 2°C, wind speed is at least 2 m s^{-1}, liquid water content of the cloud is at least 0.05 g m^{-3}, and there is no precipitation. These conditions ensure that a large enough volume of water is collected for lab analysis, and that only cloud water and not rain water is collected. When all four conditions are met, the cloud water sampler automatically "pops up", as shown in Figure 3.3, exposing Teflon-coated strings to the cloud. As the cloud blows through the sampler, droplets collect on the strings and run down through plastic tubing and into plastic collection bottles in a refrigerator in the building (Figure 3.4). If any of the four conditions are not met, the sampler closes. A fresh collection bottle is automatically rotated into place at the start of each hour.

Samples were transferred from the original collection bottles to baked-out crimp-top glass vials ranging in size from 20 to 100 mL. These samples were sent to Rutgers in batches of 20-25 samples overnight in an ice-pack filled cooler and immediately inventoried and stored in a refrigerator at 4°C until processing.

This study focuses on samples from the summer of 2010. The first sample was taken on June 3 and the last on September 14. As noted, samples were automatically collected when meteorological conditions were right. The samples that we received at Rutgers represented days when a large amount of cloud water was collected; the ALSC research group used samples for their own work on inorganic ions first. If excess

volume was available, they sent it to us for organic analysis. A complete list of samples may be found in Appendix D.

Figure 3.2. Cloud water collection station, Whiteface Mountain. The cloud water collector is indicated by the arrow. Photo taken August 24, 2010 by the author.

Figure 3.3. The cloud water collector in collection mode. Photo taken August 24, 2010 by the author.

Figure 3.4. Cloud water collection bottles inside a refrigerator. The tubing at the top is directly connected to the cloud water sampler. Photo taken August 24, 2010 by the author.

4 Lab Processing

4.1 PFHBA method development

Previous work has focused on quantifying polar compounds such as sugars and woodsmoke products from the half of the $PM_{2.5}$ filters that were extracted in acetone and DCM, using BSTFA as the only derivatizing agent [*Hawley* 2008]. Some of the compounds that were targeted in that work, particularly keto-monoacids, were not found in the samples. There are three possible explanations for this: the derivatization technique still left these acids too polar to elute through the GC/MS; they were not removed from the filter in the first place during extraction because acetone and DCM were not polar enough to remove them; or they were never present in the samples in measureable quantities in the first place. Most of the target compounds in this study were not previously searched for in the acetone/DCM extraction, but the same keto-monoacids as *Hawley* 2008 were targeted to see if they could be found unambiguously in the methanol extraction. It was necessary to find a way to derivatize keto oxygen atoms in compounds, and PFBHA was chosen as a suitable derivatizing agent since it is effective in derivatizing keto oxygen atoms but does not interfere with the BSTFA derivatization process.

Laboratory tests were carried out to determine the proper amount of PFBHA to add for a given amount of organic carbon (OC) in a sample. A PFBHA solution of approximately 20 mg/mL was created by dissolving 100.1 mg of PFBHA.HCl (Fluka; Steinheim, Germany) in 5 mL of methanol. A portion of this solution was further diluted to make a new solution of 0.2 mg/mL. To determine the proper amount of PFBHA needed to fully derivatize all carbonyl groups in a cloud water sample, three identical aliquots of 20 mL were taken from one cloud water sample. These three aliquots were concentrated as described below and received 0.015, 0.15, and 1.5 grams of PFBHA

per gram of OC, respectively, added from the 0.2 mg/mL PFBHA solution described above. The chromatogram resulting from the 1.5 gram trial was difficult to analyze due to excess PFBHA which eluted throughout the run and saturated the MS detector. The 0.015 gram trial did not saturate the detector, but the peaks of expected HPOC were often indistinguishable from background noise. The 0.15 gram trial appeared to be optimal, with clear, unambiguous peaks for target compounds and no saturation of the MS detector. An additional test of twice this amount of PFBHA (0.3 g) on a fourth identical aliquot of cloud water did not improve peak shape or area, suggesting that 0.15 grams of PFBHA per gram of OC is enough to derivatize all carbonyl groups for this sample set.

The TOC concentration was used to estimate the amount of PFBHA solution needed to process each CW sample. Initially, 20 mL of cloud water sample were added to two 10mL glass vials with Teflon-lined screw-top caps. The samples were evaporated to dryness under a 2 psi stream of pure nitrogen gas while contained in an aluminum heating block set to 65°C. 65°C was chosen to help speed up the evaporation, while still staying comfortably below 100°C to avoid boiling off the sample and potentially losing HPOC. Once the volume of the sample was 5 mL or less, the two vials' contents were combined into one vial and the sample was further concentrated to approximately 1 mL. The concentrate was then transferred to a 1.25 mL microvial fitted with a Teflon-lined silicon rubber screw-cap and evaporated to dryness. This step removed the water completely, leaving the organic compounds as a residue. The calculated amount of PFBHA (added as 0.2 mg/mL in methanol as described above) was added to each sample vial according to its TOC content, along with 5 µL of 100ppm $C_{30}D_{62}$ in methanol as internal standard. The mixture reacted at room temperature (25°C) for 24 hours.

After the PFBHA derivatization was complete, the samples were evaporated to dryness once again with nitrogen in the same microvial. It was essential that any

remaining water and methanol were removed from the sample to ensure that the BSTFA would react only with HPOC in the samples and not with either solvent. Excess BSTFA reagent was added to the sample residues following the method of Hawley for organic aerosol [*Hawley*, 2008]; the volumes of each reagent remained the same for each sample regardless of TOC content. Hexane (Fluka, Steinheim, Germany, 100 µL), pyridine (Fluka, Steinheim, Germany, 20 µL), and BSTFA with 1% TMCS (Supelco, Bellefonte, PA, 20 µL) were added to each sample under a stream of nitrogen to inhibit room moisture from entering the reaction vial. The samples were heated in an oven at 65°C for 35 minutes to speed up the BSTFA reaction. Any samples that were not run right away were stored at -20°C, with all samples run in the GC/MS within two days to prevent degradation of the BSTFA derivatives.

4.2 $PM_{2.5}$ samples

During the two SOAP campaigns approximately 700 individual filters were collected among the six sites for the SOAP 2002-2003 (13 months) and SOAP-NY (17 months) field campaigns. The filters were "composited", or grouped according to time of year within each site to create a smaller overall number of samples; this was done because individual filters were not expected to contain enough organic mass for analysis with GC/MS. In order to generate the four aliquots for the extraction process (Figure 4.1), each filter was sectioned into half. One composite contained between 5 and 10 half filters. The compositing schemes are given in Appendix C for the two SOAP field campaigns. The first SOAP compositing scheme was generated by the principle investigators, NESCAUM project manager, and state field program partners. The strategy was to have as much OC mass per composite with all the same successful daily sample filters present for each site. In the case of SOAP 2002-2003 the composites were compiled by season and subseason, giving 10 composites for each of the four sites

(Appendix C). For SOAP-NY, the project scientists and NY State collaborators agreed on 12 calendar month composites for each site, giving 17 monthly composites.

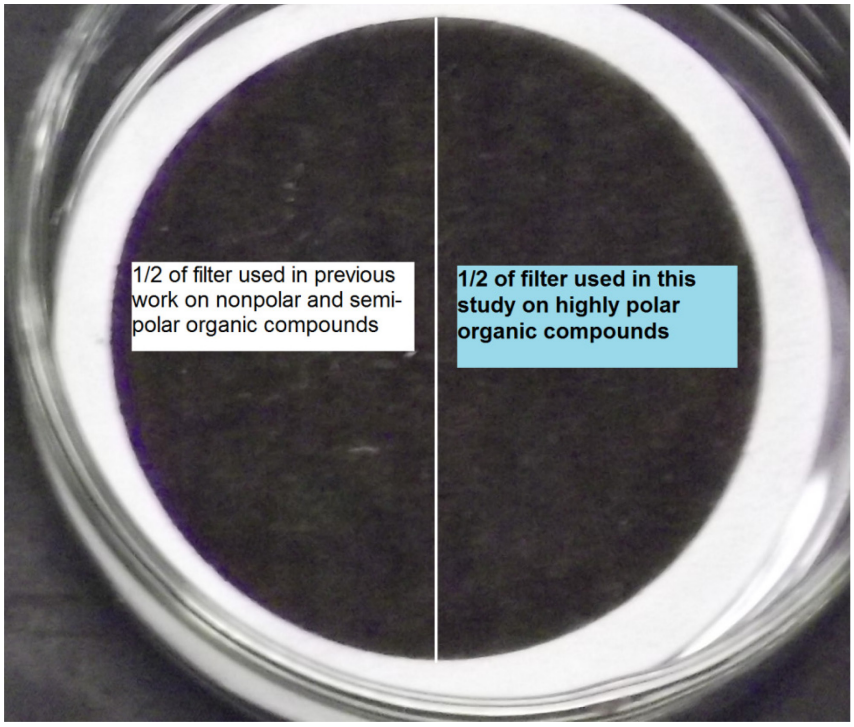

Figure 4.1. The remaining half of each collected filter was used in this study. The first half of the filter was extracted in acetone and DCM, while the half used in this study was extracted in methanol, a more polar solvent.

Before solvent extraction, the color of each filter was compared to a Glidden paint chip color card with shades ranging from white to gray to black. The total filter area that was extracted (usually half), and the number of EC/OC punches taken out for EC/OC analysis were recorded. For extraction, the composites were transferred into the glass Soxhlet extractors from the individual storage jars using clean tongs. 250 mL of HPLC-grade methanol was added to each Soxhlet extraction unit, and the filters were given 10 µL of 1010 ppm $C_{24}D_{50}$ and 8 µL of 1380 ppm deuterated succinic acid ($C_4D_6O_4$) as recovery standards. The heating mantles were then turned on and the extraction process proceeded for approximately 4 hours; this allowed the 250 mL of methanol to cycle through each extractor set approximately 4 times. After extraction, the Soxhlet units were removed and glass evaporators were placed on top of each flask to

reduce the extract volume to ~5 mL (about 8 hours). The concentrated extracts were transferred to 5 mL glass vials via a baked-out glass pipette. These extracts were placed in a Reactitherm concentrator unit equipped with a heating block set to 45°C and condensed further under a stream of pure nitrogen gas to a volume of less than 1 mL. These extracts were transferred to a 1.25 mL microvial with an open Teflon-lined screw cap. Samples were stored in the freezer (-20°C) until derivatization. Between each round of extractions, all extraction equipment except the condensers was washed with Alconox detergent, rinsed, dried, and baked out at 500°C for 8 hours. Each condenser was rinsed thoroughly with methanol to remove possible carryover between extraction sets. Laboratory blanks were run with each extraction set to confirm extraction process quality.

4.3 Cloud water samples

Sixty-eight cloud water samples and two field blanks were collected in summer 2010 sampling by scientists at the Adirondack Lakes Survey Corporation (ALSC). Sampling dates spanned June to September; see Appendix D for list of dates and times. Inorganic compounds, pH, and other bulk properties were measured by ALSC. Samples were placed in baked-out glass bottles and sent via overnight express shipping with cold packs to Rutgers and refrigerated at 4°C immediately. The lab processing procedure was similar to that of the $PM_{2.5}$ filters. 20 mL were taken from each sample and placed into two 10 mL glass vials for HPOC analysis. Each glass vial received 8 µL of 100 ppm $C_{24}D_{50}$ in methanol (for a total of 16 µL per sample) as a recovery standard. The two vials were placed under a stream of pure nitrogen at 2 psi, in a heating block set to 65°C, until approximately 1 mL of water remained per sample (the two separate sample portions were combined via clean glass pipette between the two vials when the total

volume was less than 10 mL). A lab blank was processed in the same manner using 20 mL of pure water purchased from Fisher Scientific.

4.4 Derivatization

During storage at -20°C, the $PM_{2.5}$ extracts saw small bits of filter and/or colloidal carbon (soot) separate from the liquid extract, resulting in approximately 10 to 100 mL of debris collected at the bottom of the microvial. These filter pieces could potentially clog the GC/MS injection syringe during sample analysis and required removal before chemical derivatization and GC/MS analysis. The extract liquid was decanted by pouring the sample through a small glass funnel into a new microvial. The liquid extract was easily transferred, leaving the small filter bits in the tapered bottom of the old vial. In some cases, residual sample extract that was clear of filter debris could not be transferred via pouring because it could not be removed easily from the lower microvial stem. In such cases, a single-use Eppendorf pipette was used to draw out the remaining sample liquid and transfer it to the new vial. The extracts were then condensed to ~100 µL under a stream of pure nitrogen gas, and 25 µL of 100 ppm 2-butanone and 25 µL of 100 ppm $C_{30}D_{62}$ (internal standard for GC/MS quantization) were added. Cloud water samples were likewise condensed to ~100 µL and were given 15 µL of 100 ppm of deuterated succinic acid as an internal standard. At this point, carbonyl groups (ketones, aldehydes, ketoacids) in the extracts were derivatized first with prepared PFBHA solution in methanol (Figure 4.2).

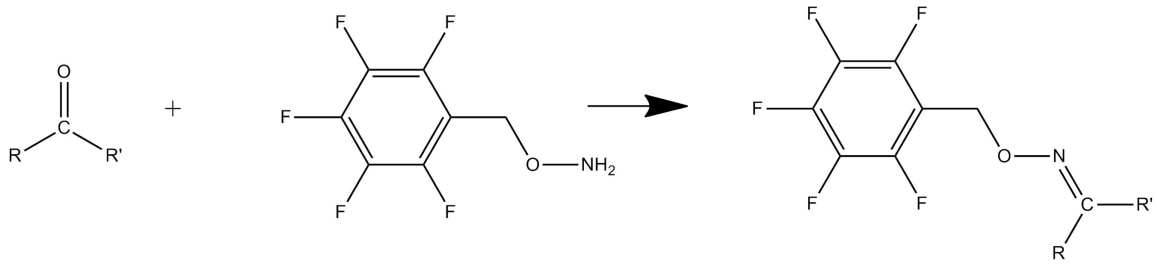

Figure 4.2. Reaction of a generic ketone with PFBHA.

The mass of PFBHA added per sample was determined by its organic carbon (OC) content. For the $PM_{2.5}$ samples, each individual filter's OC, calculated as μg cm^{-2}, was determined by sending a small punched area (1.5 cm^2) from each filter to Sunset Lab (Tigard, Oregon) for analysis. Thus, the total amount of OC in each composite was estimated easily from the returned results by calculating the total OC on each filter and adding up the values for each filter within a composite. For cloud water samples, the amount of OC per sample was measured and provided by ALSC. The proper ratio of PFBHA:OC was determined in laboratory experiments (Section 4.1) to be 1:138 mol:mol. Adding additional PFBHA per mole of OC beyond this ratio was not found to increase derivatization rates. This calculated excess of PFBHA reagent did not flood the MS source nor interfere with analyte identification and quantization. PFBHA was added to each composite as shown in Table 4.1 (for $PM_{2.5}$ samples) and Table 4.2 (for cloud water samples). Because there was so much less OC in the cloud water samples, they were derivatized using a much more dilute PFBHA solution, as noted in the column heading.

Table 4.1. PFBHA derivatization scheme for $PM_{2.5}$ composites.

OC in composite (μg)	PFBHA added (μL of 0.02 g mL^{-1} solution)
≤ 1344	10
1345 to 2688	20
2689 to 5376	40

Table 4.2. PFBHA derivatization scheme for cloud water samples.

TOC in sample (μg)	PFBHA added (μL of 0.0002 g mL^{-1} solution)
< 67	50
68 to 134	100
135 to 268	200
269 to 536	400

After adding PFBHA reagent, samples were left at room temperature for 24 hours to allow the PFBHA reaction to go to completion. The second derivatization step, conversion of free carboxylic acid and aromatic OH groups, was performed (Figure 4.3).

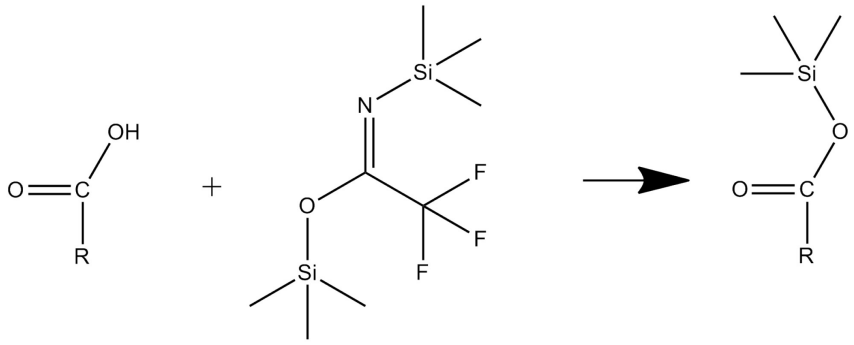

Figure 4.3. Reaction of a generic carboxylic acid with BSTFA.

All samples were evaporated to dryness under pure nitrogen gas, and BSTFA derivatization was performed by adding 100 µL of hexane, 20 µL of pyridine, and 20 µL of BSTFA to each sample, still under pure nitrogen gas. The three reagents always were added in the same volumes to all sample and blank extracts in both the $PM_{2.5}$ samples and cloud water samples, regardless of TOC content. The reaction vials were baked at 65°C for 30 minutes to accelerate the reaction. The derivatized samples were injected immediately the GC/MS using an autosampler. A 22-minute cleaning run consisting of dichloromethane was inserted between each $PM_{2.5}$ sample injection as a precaution to ensure no carryover occurred; cleaning runs were deemed unnecessary for the cloud water samples due to their low OC content.

4.5 GC/MS run and analysis

Once BSTFA derivatization was complete, the samples were run immediately in the GC/MS or stored in the freezer at -20°C and run within one week. GC/MS runs

consisted of injecting 1 µL of the fully derivatized solution (final volume 140 µL as noted above) into the instrument and following a prescribed program consisting of a six minute hold at 70°C, a ramping rate of 5°C/minute until the temperature reached 150°C, a three-minute hold, a ramping rate of 4°C/minute until the temperature reached 280°C, and finally a 22-minute hold. This method was developed to achieve maximum separation of the target HPOC while still maintaining strong peak shape. Typically, 5 to 10 samples were run in a row, and in the case of the $PM_{2.5}$ samples, an injection of DCM took place between each sample injection to provide extra column cleaning. The resulting chromatograms were saved to the computer and analyzed manually using the Shimadzu Postrun Analysis software that came with the GC/MS. Concentration values were calculated from peak area data in an Excel spreadsheet.

4.6 GC/MS chromatogram problems

4.6.1 $PM_{2.5}$ samples

The above GC/MS analysis method produced viable chromatograms for 84 out of the 109 $PM_{2.5}$ samples and blanks, from which target compounds were identified and quantified. The remaining 25 samples produced problematic chromatograms. The most common problem encountered was the absence of the $C_{30}D_{62}$ (internal standard peak m/z 66) peak, which occurred in 17 of the 25 problematic chromatograms. The $C_{30}D_{62}$ was the GC/MS internal standard for which the 5-point standard calibration curves of the target HPOC were established; without its presence in the chromatogram, it was impossible to convert the target compound peaks into units of ng m^{-3}. This may have happened due to sorption of $C_{30}D_{62}$ to the side of the microvial rather than mixing fully in the methanol. For the 17 sample chromatograms that had this problem, the peak area of $C_{30}D_{62}$ was assigned the average value of the $C_{30}D_{62}$ in the other, successful chromatograms run on the same day.

Another problem occurred for extracts with high mass levels of HPOC (i.e., those with the highest carbon content). These sample injections saturated the MS detector, causing it to shut off. The mass of compounds would elute for a period of 10 seconds, and then the GC/MS system would turn on the filament within in the MS source. Thus, any compounds passing through the MS with the filament off were not recorded in the chromatogram. This was not inherently a problem, since this tended to happen at the same early point in each run, and the 10 second shutdown window did not overlap with any compounds of interest. However, if the sample managed to flood the detector two additional times in the same sample run, then the MS filament would remain off for the rest of the run, and any further compounds eluting would be lost (see Figure 4.4 for an example of this; a typical chromatogram is shown in Figure 4.5 for comparison). This occurred for eight samples, mostly from the Elizabeth and Queens sampling sites. This problem was solved by reanalyzing a diluted aliquot. Each saturated sample was blown down to dryness, and 900 µL of methanol was added via glass volumetric syringe. The samples were mixed on the vortex mixing machine and allowed to sit for 24 hours. Half of the sample was then transferred to a fresh microvial and derivatized with PFBHA and BSTFA following the same method listed above, taking into account that in some cases, less PFBHA was needed than in the original derivatization since only half of the original mass was being derivatized. Samples were then re-run in the GC/MS with no further MS saturation problems. Four samples that did not have saturation problems also underwent this same redo process for comparison with their original chromatograms to check the validity of this method.

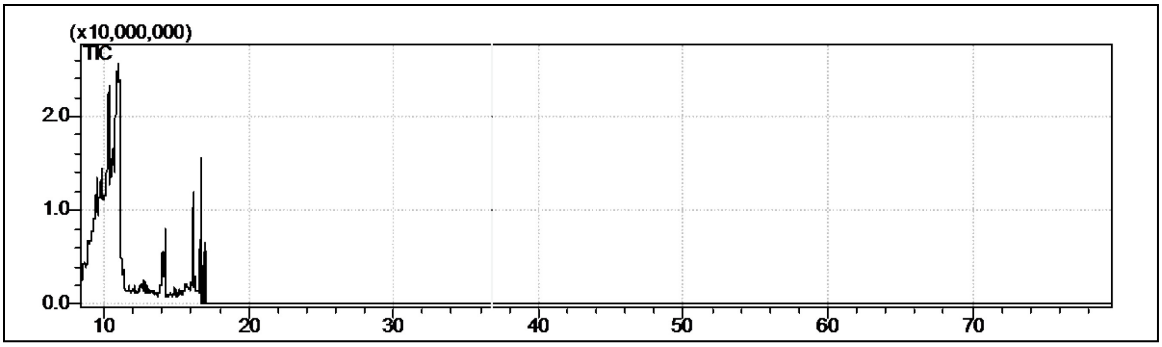

Figure 4.4. Chromatogram from saturated MS detector.

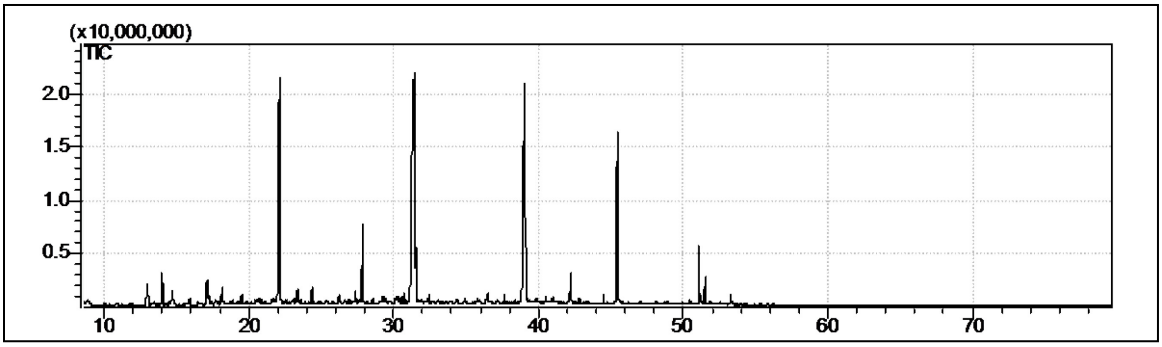

Figure 4.5. A typical chromatogram.

Additionally, the two field blank filters from the Chester, NJ site taken in the summer produced a complex chromatogram with many unresolved peaks, more similar in appearance to sample chromatograms than to other field blank chromatograms, despite the clean white appearance of the filters when extracted. The field notes written by the person who ran the sampler indicated one of the two filters had accidentally been subjected to two minutes of full air flow, rather than no air flow as is the usual procedure for field blanks. This made the Chester summer field blank unusable. Thus, to estimate the field blank levels for the summer Chester site, the peak areas from each compound from the other three Chester field blanks (fall, winter, and spring) were averaged and then used for this collection period.

4.6.2 Cloud water samples

The cloud water samples had far less OC per sample than did the $PM_{2.5}$ samples, so there were no problems with the MS detector flooding. One sample (#3065) was running in the GC/MS when the harddrive of the connected computer became completely full. The sample continued to elute through the GC/MS, but no data was recorded. There was no possible way to recover any data from that sample, and there was no extra volume left with which to attempt a replacement run, so the sample was excluded.

4.7 Preparation of laboratory standards

In order to correctly identify compounds in chromatograms, it was first necessary to create “lab standards”, or solutions of the target compounds in known concentrations. Initially, compounds were ordered from chemical companies, and for each individual compound, a solution of approximately 1000 ppm was prepared by dissolving 0.01 grams of the solid compound in 10 mL of methanol. The actual weight of the compound was usually slightly more or less than 0.01 g due to the difficulty of measuring out such a precise amount, but the exact weight was noted and figured into the concentration (for example, a weight of 0.0112 g dissolved in 10 mL of methanol makes a solution of 1120 ppm).

4.8 Creation of calibration curves

Initially, each standard was derivatized as necessary and run individually at a high concentration through the GC/MS to obtain its retention time. GC systems, by definition, separate compounds within a mixture. Thus, small, volatile compounds elute through the system quickly (for example, oxalic acid, one of the smallest targeted compounds, takes approximately 12 minutes to reach the end of the ~30 meter column inside the GC). Other heavier, less volatile compounds such as γ-keto pimelic acid take

approximately 45 minutes to cover the same distance. After each compound was run individually, all retention times were noted.

Once the retention times were known, solutions at five different concentration levels were prepared. By running five solutions of the same compound at five different concentrations in the GC/MS, it was possible to create a calibration curve, plotting the ratio of the area underneath the target compound peak to the area under the peak of the internal standard (x-axis). The y-axis had the ratio of the concentration of the compound, which was being solved for, to the concentration of the internal standard. Plotting these ratios for each of the five solution levels creates, ideally, a straight line, with the slope referred to as the relative response factor, or RRF. The RRF and the corresponding y-intercept of the plot can then be used to calculate the concentration of a compound which is not known beforehand, as in the case of the $PM_{2.5}$ and cloud water samples, in units of parts per million, as shown in Equation 4.1.

$$\frac{ppm_{target\ compound}}{ppm_{internal\ standard}} = (RRF\ x\ \frac{area\ under\ peak_{target\ compound}}{area\ under\ peak_{internal\ standard}}) + \text{y-intercept}$$

Equation 4.1. Calculation of concentration of a sample compound from peak area on chromatogram.

4.9 Problematic calibration curves

The calibration curves of four out of the nineteen target compounds had high R^2 values but negative y-intercepts, resulting in negative values when peak area was converted to concentration. Ideally, calibration curves should run through the origin, but in practice y-intercepts are usually slightly positive. Negative y-intercepts suggest a systematic bias in the GC/MS on the day the samples were run. Three of the cases of negative y-intercepts were among the keto-monoacids. To rectify, the y-intercepts were adjusted to be the same as the one keto-monoacid (glyoxylic acid) which did have a positive y-intercept. The other negative y-intercept came from the calibration curve for

glyoxal. It was adjusted to match the y-intercept from the other carbonyl target compound, glycolaldehyde. In the other classes of compounds (diacids and keto-diacids) where all y-intercepts were positive, good agreement was found among the y-intercepts of each compound class.

For one of the original target compounds in this study, pyruvic acid, a clear calibration curve with a reasonable R^2 value was never produced despite repeated careful attempts. Thus, concentration values and detection limits for this compound could not be determined, and it was excluded from further analysis.

4.10 Limit of detection calculations

Each compound has a threshold detection limit, below which the chromatogram shows a peak that is indistinguishable from background noise. Following the literature [*Lamanna and Goldstein*, 1999], a compound is considered "detected" if its peak on the chromatogram has an area at least three times larger than that of background noise peaks. Likewise, a compound is considered quantifiable if its area is at least ten times greater than the area of surrounding noise peaks. The February 2006 sample from the Pinnacle site was selected for detection limit calculations because of its clear signals and high HPOC concentrations. For each target compound, ten background noise peaks were integrated and averaged on the main quantifying m/z ion. This number was then multiplied by three, divided by the peak area of the internal standard, and converted to a value in ng m^{-3} as described in the previous section. The same procedure was followed to find each compound's limit of quantification, except that the background noise average was multiplied by ten instead of three. Tables of the limit of detection (LOD) and limit of quantification (LOQ) values for each compound are listed in Appendix B. In most cases, the LOD and LOQ are nearly indistinguishable for a given compound; the largest difference was for 5-oxohexanoic acid, which had an LOD that was 86% of

the LOQ. Most compounds had an LOD that was 95% or more of the LOQ, with many being far above 99%.

5 Overview of detected species

5.1 Summary of detected species

As noted previously, 73 PM samples (39 from SOAP 2002-2003 and 34 from SOAP-NY) and 68 cloud water samples were analyzed. A total of 19 compounds were searched for in the $PM_{2.5}$ and cloud water samples. Discussion will focus primarily on the compounds that are thought to be of the greatest significance in the climate system:

- cis-pinonic acid
- glyoxal
- glyoxylic acid
- oxalic acid

The structures of these four compounds are shown in below in Figure 5.1-Figure 5.4, as well as in Appendix A.

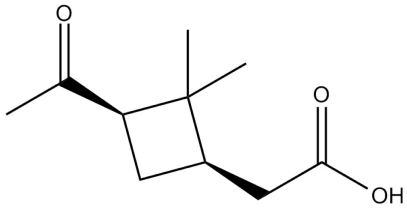

Figure 5.1. Cis-pinonic acid.

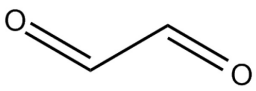

Figure 5.2. Glyoxal.

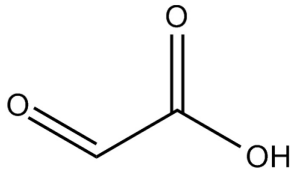

Figure 5.3. Glyoxylic acid.

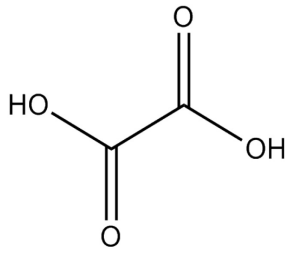

Figure 5.4. Oxalic acid.

Complete concentration data for all 19 identified HPOC can be found in Appendix E ($PM_{2.5}$ samples) and Appendix F (cloud water samples). Though each of the 19 target compounds was searched for in every $PM_{2.5}$ and cloud water sample, the compounds were not always unambiguously identified, due to interference from other compounds that eluted at the same time, a tendency to partition more into the gas phase than the liquid phase while eluting through the GC/MS, or simply not being present in measurable quantities in the first place. The four compounds listed above were found in the samples as described in Table 5.1.

Table 5.1. Identification rates of four HPOC in PM and cloud water samples.

	Times Quantified in PM (% of all samples)	Times Quantified in Cloud Water (% of all samples)
cis-pinonic acid	67 (92%)	18 (45%)
glyoxal	71 (97%)	16 (40%)
glyoxylic acid	64 (88%)	29 (73%)
oxalic acid	42 (58%)	16 (40%)

5.2 Molecular level QA/QC and blank data

As noted in Section 3.1, three types of blank filters were analyzed along with the sample filters in the SOAP project. Field blank filters traveled to each site and were

placed in a sampler for 24 hours with the vacuum pump off; this allowed for quantification of compounds that might land on the filter by chance rather than being forced into the filter by the vacuum.

Trip blanks were collected as well. Trip blanks were filters that were shipped out to the sampling sites along with the filters used for sampling and field blanks, but they were never unpacked or placed in the sampler. They were subsequently shipped back to Rutgers along with the used filters to help identify any contamination points from the transport of the filters from the lab to the sampling site and back.

Finally, a lab blank was analyzed. The lab blank was an extraction of a filter taken directly from the package and baked out at 500 °C for 8 hours; any HPOC found in the lab blank would have had to have come from the lab processing described in Section 4.2. Only one of the target compounds, succinic acid, was detected in the lab blank. This most likely came from the deuterated (i.e., deuterium atoms in place of hydrogen atoms) succinic acid that was added to the filters prior to extraction to serve as a recovery guide for the filters (Section 4.2); the chemical (Cambridge Isotope Laboratories, Inc., Andover, MA) was listed as only 98% pure. The remaining 2% of the succinic acid in the standard was likely only partially deuterated or not deuterated at all, and thus showed up in the lab blank chromatogram as regular, undeuterated succinic acid.

For the cloud water samples, a similar procedure was followed. Along with the regular cloud waters samples, a “rinse” and a blank were taken. The “rinse” sample was the collection of water used to clean the tube that connects the cloud water sampler to the collection bottles. The blank, meanwhile, consisted of ultrapure water from a Millipore system that was shipped to Rutgers in the same type of bottles as the samples. Succinic acid and glycolaldehyde were the only compounds detected in the rise and blank. Additionally, a lab blank was created by taking 20 mL of ultrapure water and then

following the same processing procedure described in Section 4.3. As with the filter lab blank, only succinic acid was detected. As with the PM filter blanks, the presence of succinic acid is almost certainly from impurities from the deuterated succinic acid that was added as an internal standard (Section 4.4).

6 $PM_{2.5}$ Results

6.1 HPOC concentration data

Initial analysis of the $PM_{2.5}$ samples from the two SOAP campaigns focused on differences in HPOC concentration among the six sites. Each compound is also normalized to organic carbon (OC) and elemental carbon (EC). Normalization to OC allows for clearer comparison across different sites, by removing the effects of organic precursor concentrations levels. Normalization to EC removes the effects of meteorology and the height of the boundary layer, since EC is a conservative tracer that does not undergo reactions with other compounds in the atmosphere. Thus, this section's results will consist of, for each of the four HPOC of interest, concentration data by itself and normalized to OC compared across the sampling sites, as well as discussion of concentration data normalized to EC compared across the seasons at an individual site. In the figures discussing concentration and OC normalization, the two rural sites, Chester and Pinnacle, are shown in green, while the other four sites, all urban, are shown in gray. Additionally, the width of the boxplots is correlated to the number of times that each compound was quantified (a wider box in the horizontal direction means the compound was quantified more frequently); this information is also listed in the captions. For brevity, EC normalization plots will only be presented for the Bronx and Pinnacle sites. In all boxplots, outliers are plotted as red plus signs. Outliers are those data points which are less than Q1 minus 1.5 times the interquartile range, or more than Q3 plus 1.5 times the interquartile range. Further discussion of the interrelationship of HPOC at each site and correlations of the compounds with sulfate and ozone concludes the chapter.

6.1.1 Cis-pinonic acid

Cis-pinonic acid is formed photochemically from the oxidation of α-pinene, a naturally-occurring gas phase compound emitted by trees [e.g. *Ma et al.*, 2008]. Thus, cis-pinonic acid concentrations would be expected to be higher in rural areas, which are closer to α-pinene emission sources, than in urban areas. However, concentration data from both of the SOAP campaigns does not fully support this, as seen in Figure 6.1 and Figure 6.2:

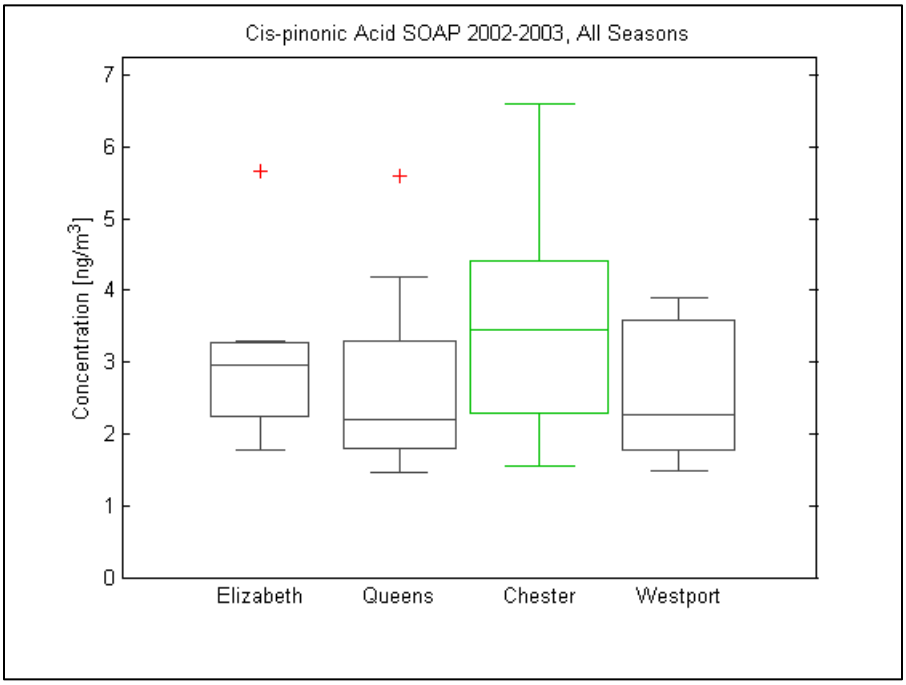

Figure 6.1. Cis-pinonic acid concentrations in SOAP 2002-2003 campaign. Cis-pinonic acid was quantified 7 times at Elizabeth, 8 times at Queens, 10 times at Chester, and 8 times at Westport, out of 9 samples at Westport and 10 at the other three sites.

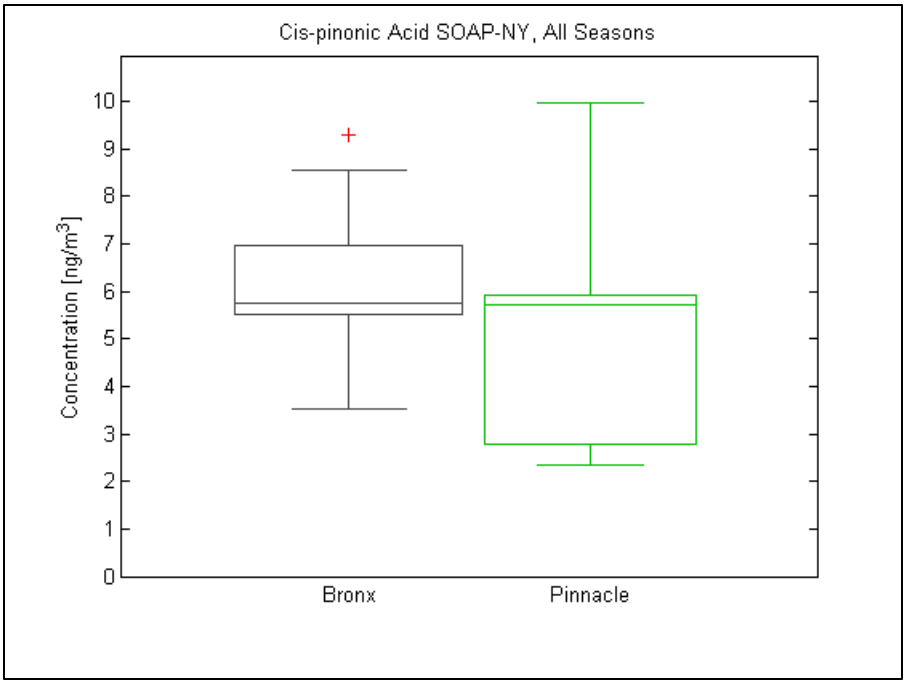

Figure 6.2. Cis-pinonic acid concentrations in SOAP-NY campaign. Cis-pinonic acid was quantified 16 times at the Bronx and 15 times at Pinnacle, out of 17 samples at each site.

Figure 6.1 shows only a slightly higher mean concentration of cis-pinonic acid over the course of the year in the rural site. In the SOAP-NY data (Figure 6.2) mean cis-pinonic acid concentrations are virtually identical between the two sites, with the Bronx site having a higher quartile ranges.

When normalized to OC, as shown in Figure 6.3, the overall differences among the SOAP 2002-2003 sites does not change much from what was seen in the concentration data alone.

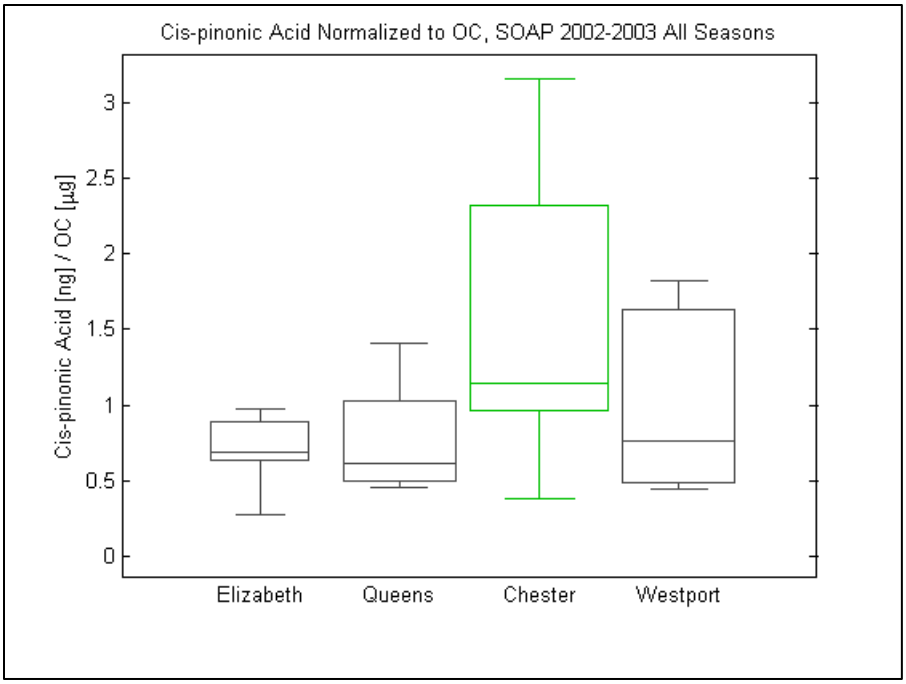

Figure 6.3. Cis-pinonic acid normalized to OC in SOAP 2002-2003 campaign.

Cis-pinonic acid makes up a higher portion of total organic carbon at the rural site, Chester, than it does at any of the other three sites, and it has a larger range at Chester as well. The trends otherwise match what was seen in the concentration data. Cis-pinonic acid is also a higher portion of OC at the rural site in the SOAP-NY campaign (Figure 6.4).

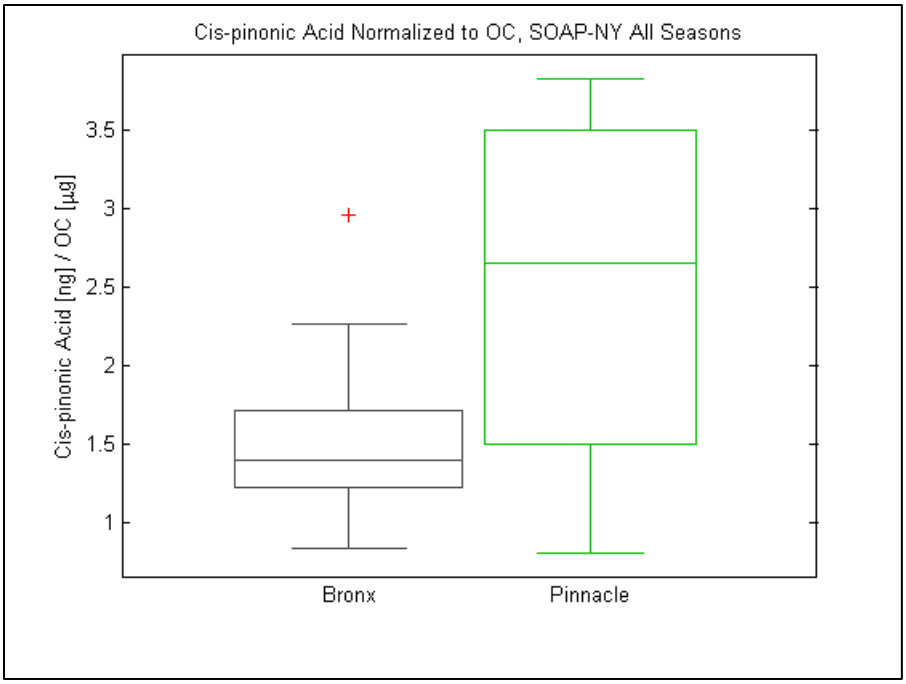

Figure 6.4. Cis-pinonic acid normalized to OC in SOAP-NY campaign.

As previously mentioned, normalizing to EC is particularly useful when comparing samples across seasons. The height of the boundary layer may vary dramatically at different times of year, which makes comparison of concentrations in units of mass per volume unreliable. Figure 6.5 shows cis-pinonic acid normalized to EC for the Bronx samples, while Figure 6.6 shows the same for the Pinnacle samples. The SOAP-NY campaign, which included the Bronx and Pinnacle sites, took place from October 2005 through February 2007. Each season contains three months' worth of data; for example, December, January, and February samples are combined for the winter plots. The first fall plot contains only two samples: October and November of 2005.

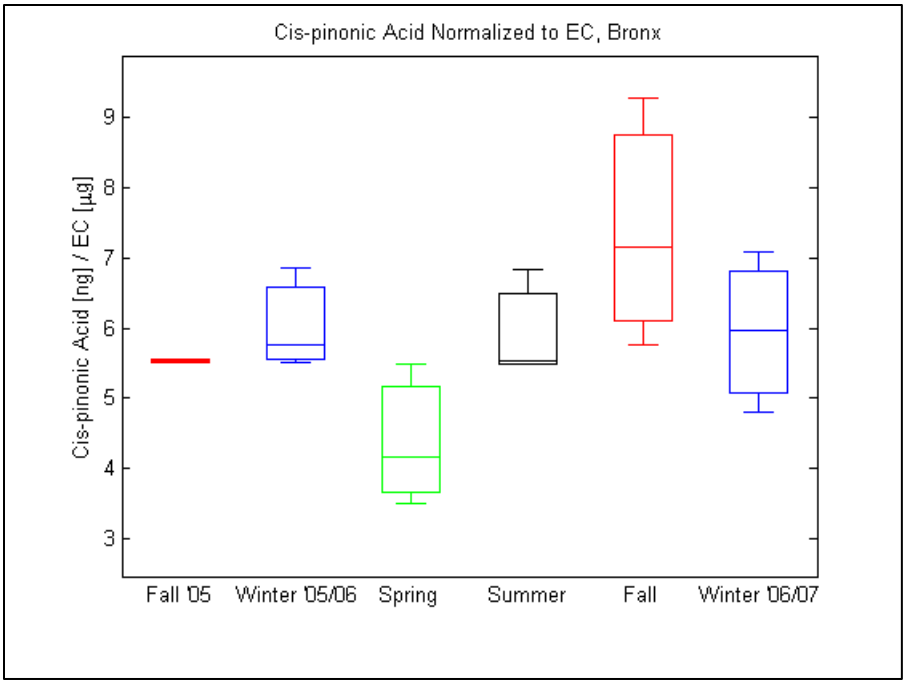

Figure 6.5. Cis-pinonic acid normalized to EC, Bronx.

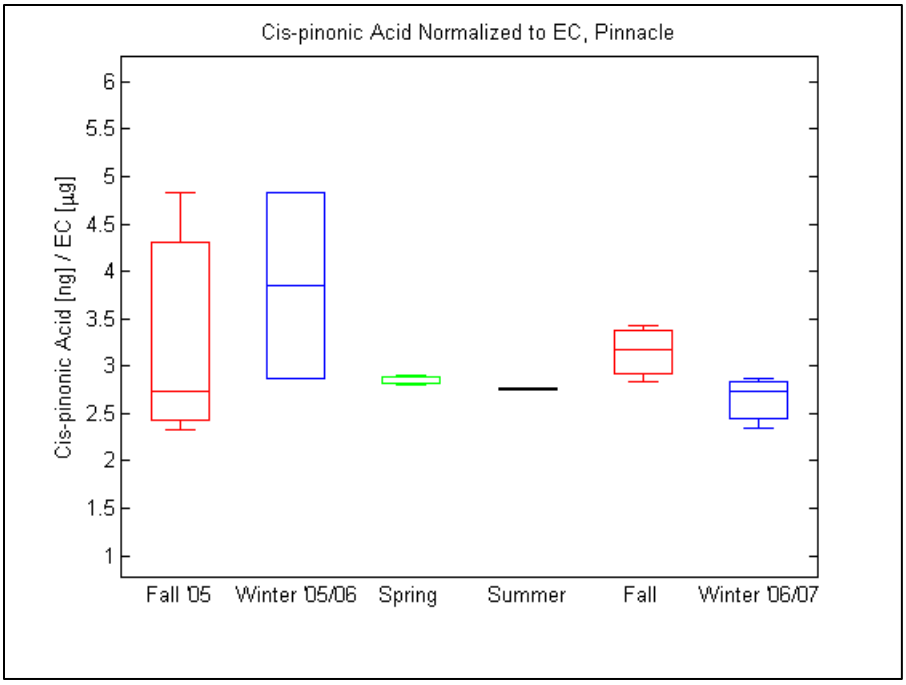

Figure 6.6. Cis-pinonic acid normalized to EC, Pinnacle.

The change in normalized cis-pinonic acid over the course of the sampling campaign is clearly different between the two sites. The Bronx site (Figure 6.5) shows a maximum amount of cis-pinonic acid in the second fall period and a minimum during the

spring. The first fall period shows only a very small range, and the two winter periods have similar means and distributions. Pinnacle, however, had its maximum concentration in the first winter period and minimum in the summer.

6.1.2 Glyoxal

Glyoxal is thought to be formed from cis-pinonic acid. Its concentrations at the SOAP-2002-2003 sites are shown in Figure 6.7:

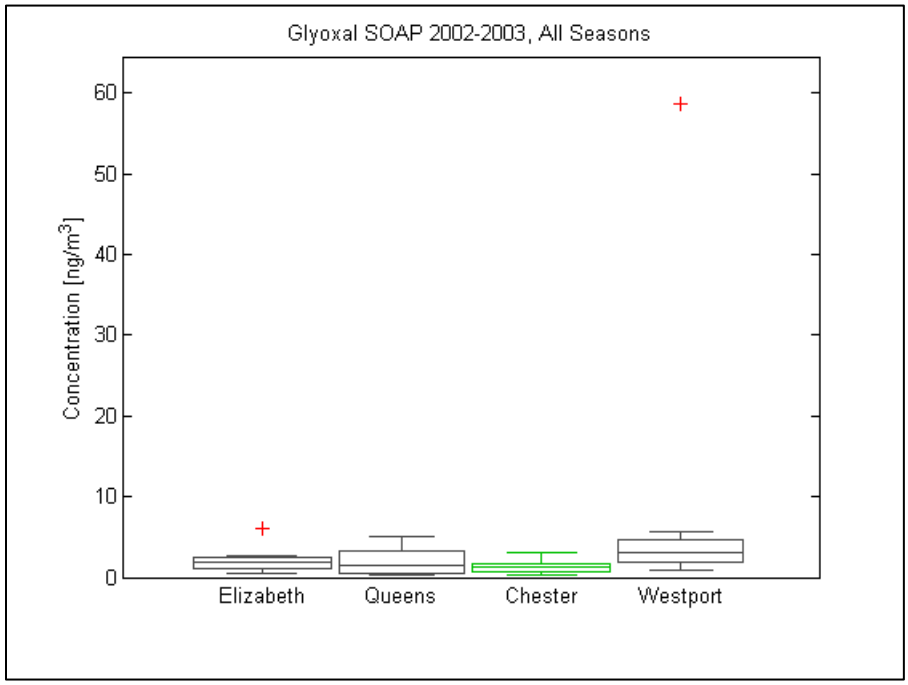

Figure 6.7. Glyoxal concentrations in SOAP 2002-2003 campaign. Glyoxal was quantified 10 times at Elizabeth, 9 times at Queens, 10 times at Chester, and 9 times at Westport, out of 9 samples at Westport and 10 at the other three sites.

Aside from the extreme outlier in the Westport data, the four sites show consistent concentrations of glyoxal. The concentrations are also similar to one another, and to the SOAP 2002-2003 sites, in the SOAP-NY sites (Figure 6.8), although the Bronx site also has a very high outlier:

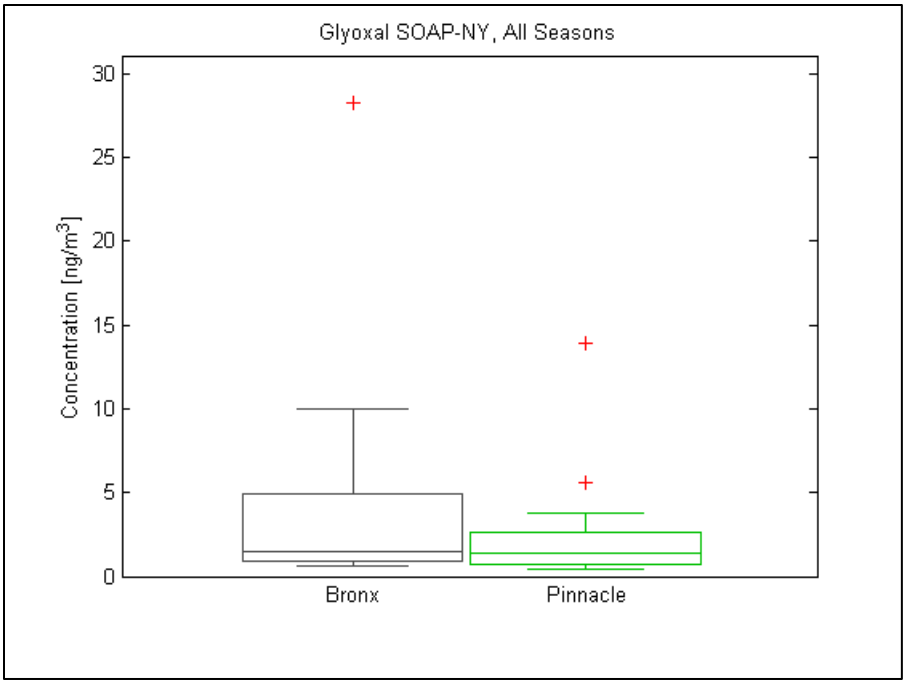

Figure 6.8. Glyoxal concentrations in SOAP-NY campaign. Glyoxal was quantified 16 times at the Bronx and 17 times at Pinnacle, out of 17 samples at each site.

When normalized to OC, glyoxal showed similar annual means and ranges in both of the SOAP-NY sites. However, some unexpected seasonal trends create this average. In summer, the means at each site are nearly identical (around 0.5 ng of glyoxal per 1000 µg of OC; Figure 6.9). However, the range of data is much larger at the Pinnacle sampling site.

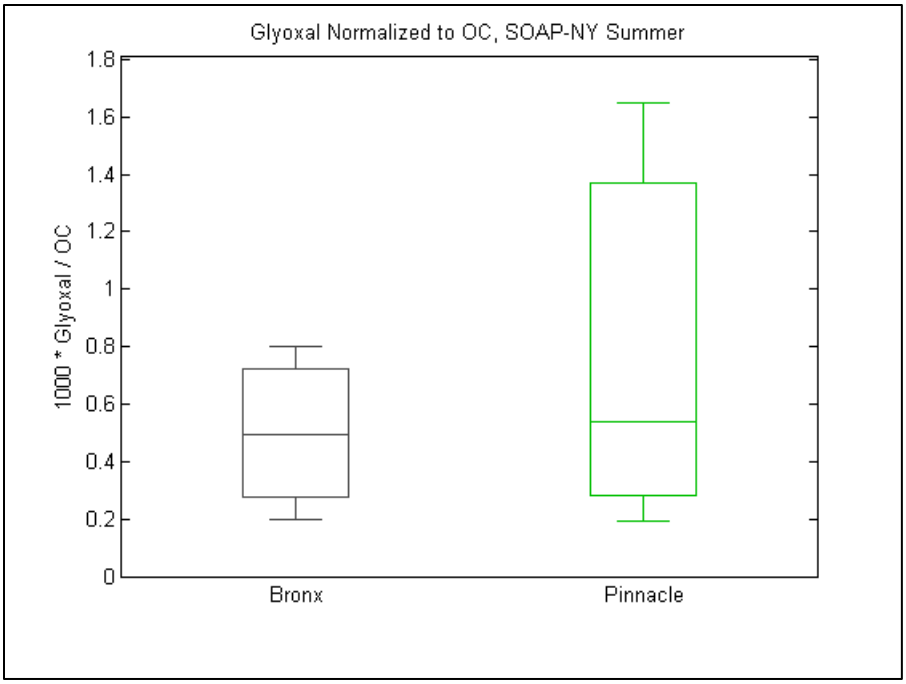

Figure 6.9. Glyoxal normalized to OC, summer months. There are 3 data points for each site.

The fall data show the opposite, with the range being much wider in the Bronx site (Figure 6.10):

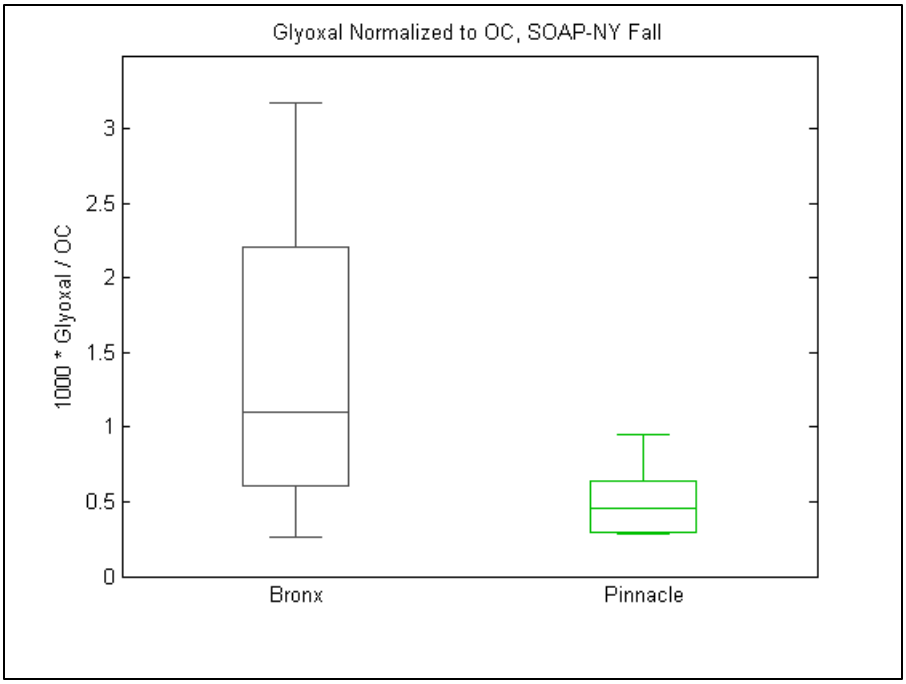

Figure 6.10. Glyoxal normalized to OC, fall months. There are 5 data points for each site.

For the spring months, the SOAP 2002-2003 and SOAP-NY data show similar characteristics. In both campaigns, the glyoxal/OC ratio has a lower mean and smaller range in the urban areas (Elizabeth, Queens, and Bronx), and higher means and larger ranges in the rural (Chester and Pinnacle) and downwind (Westport) sites (Figure 6.11; Figure 6.12).

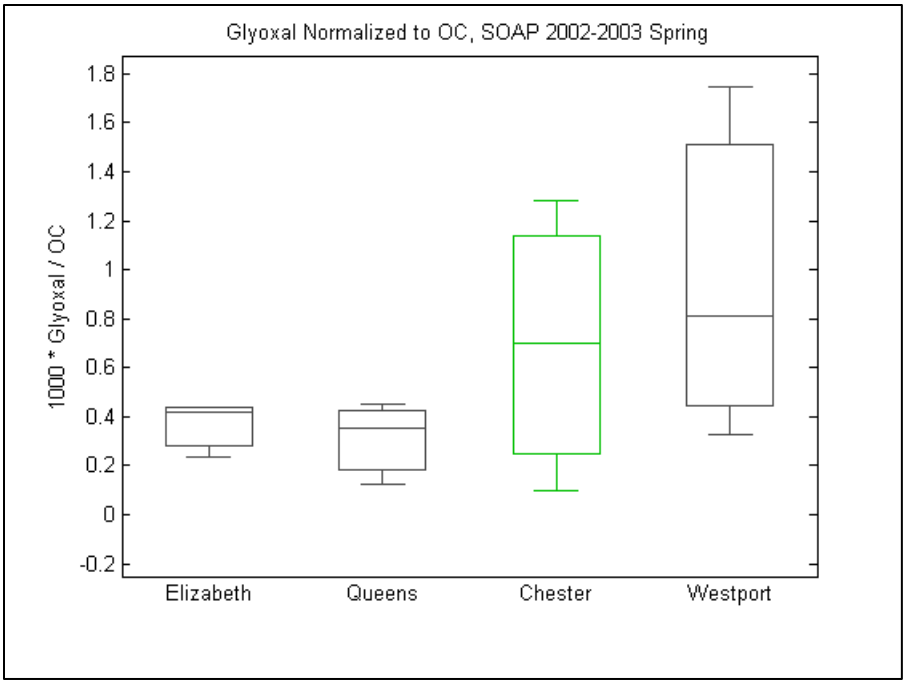

Figure 6.11. Glyoxal normalized to OC, SOAP 2002-2003 spring. There are 3 data points for each site.

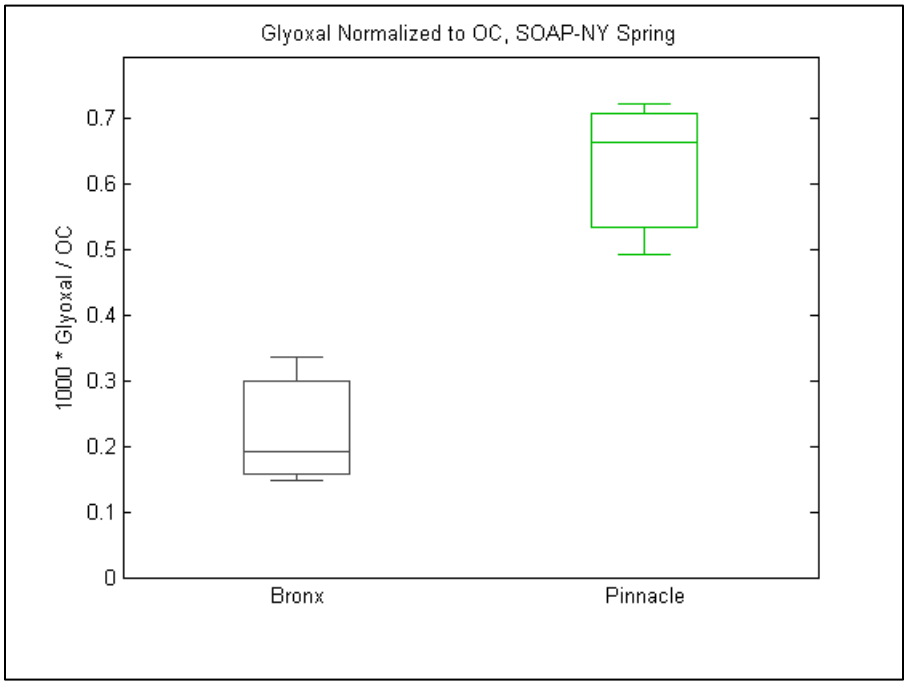

Figure 6.12. Glyoxal normalized to OC, SOAP-NY spring months. There are 3 data points for each site.

According to the literature, glyoxal is thought to be formed photochemically from isoprene, which is emitted by trees. Thus, we would expect to see the highest glyoxal

values in the two rural sites (Chester in SOAP 2002-2003, and Pinnacle in SOAP-NY), and less at the urban and downwind sites as the glyoxal would be converted to other compounds along the way. However, this doesn't appear to be the case in these measurements, and normalizing to OC makes virtually no difference in the mean or range of glyoxal at any of the sites (compare Figure 6.13 below, showing concentration of glyoxal in the spring months with Figure 6.11 showing glyoxal concentrations normalized to OC in spring). The same similarities are seen for all of the seasons in SOAP 2002-2003.

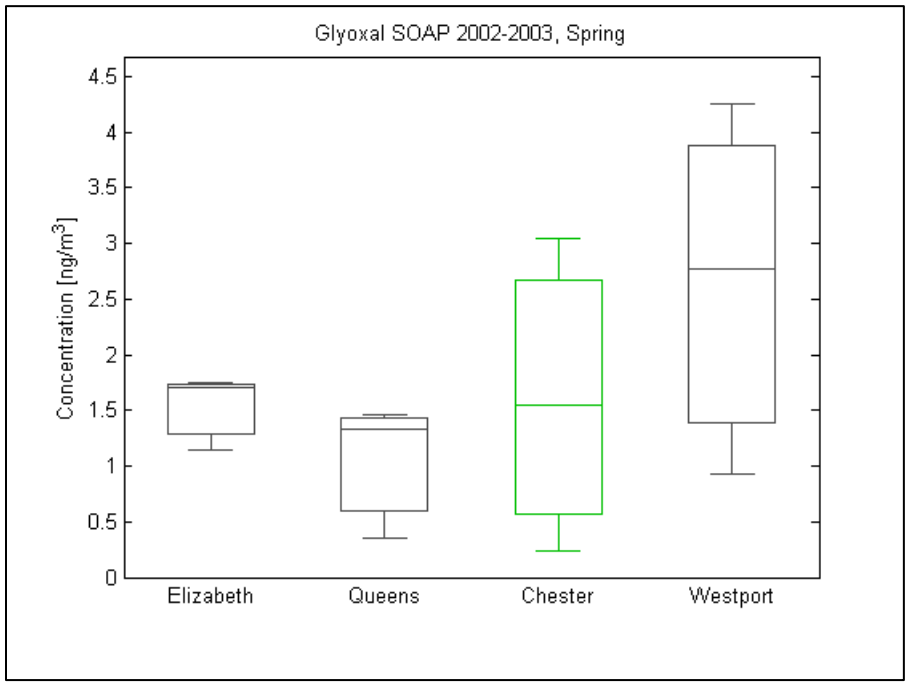

Figure 6.13. Glyoxal concentrations, ng m^{-3}, in SOAP 2002-2003 in spring. There are 3 data points for each site.

Normalized to EC, glyoxal in the Bronx (Figure 6.14) shows the same trends that were seen with cis-pinonic acid (Figure 6.15). The highest mean value of glyoxal was seen in the second fall of the study period, while concentrations were lowest in the beginning of the study period, with spring the lowest of all.

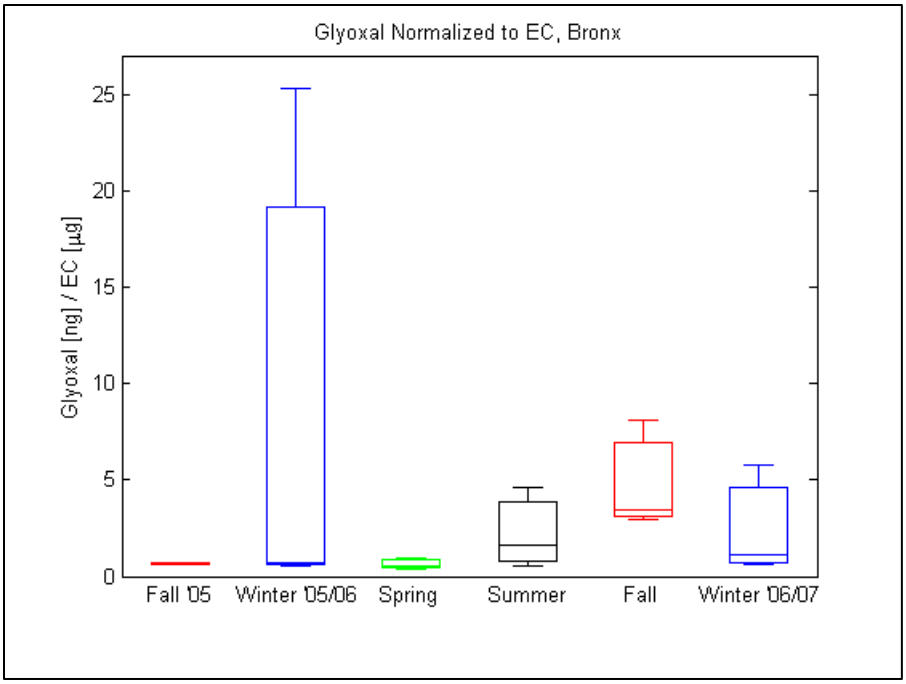

Figure 6.14. Glyoxal normalized to EC, Bronx.

At Pinnacle, the highest value of glyoxal is found in the first winter, with concentrations steady in the seasons following that.

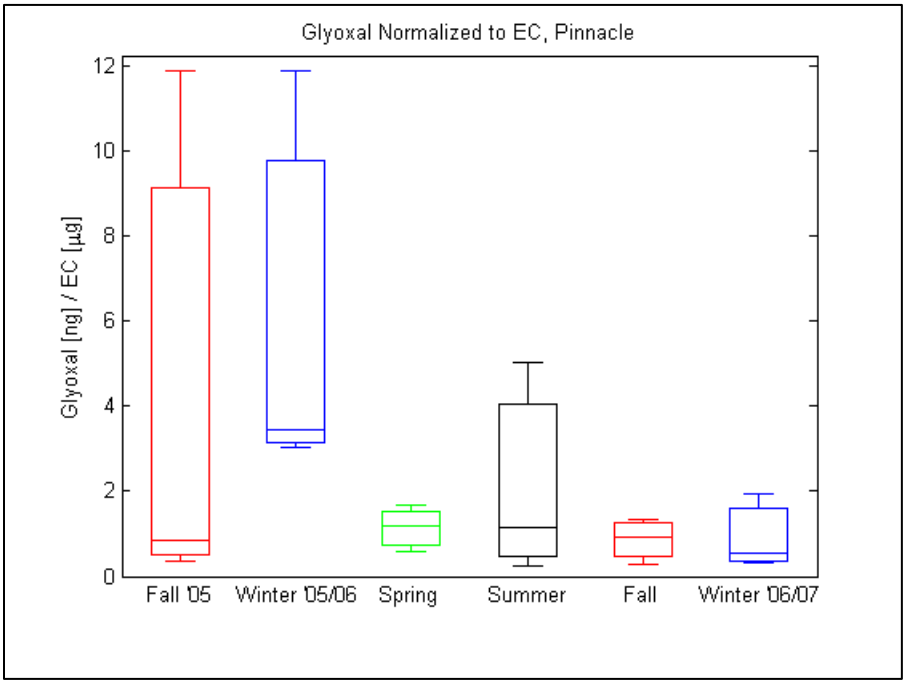

Figure 6.15. Glyoxal normalized to EC, Pinnacle.

6.1.3 Glyoxylic acid

Glyoxylic acid was identified in the chromatograms in nearly all samples. Its annual average concentrations are shown below for SOAP 2002-2003 (Figure 6.16) and SOAP-NY (Figure 6.17).

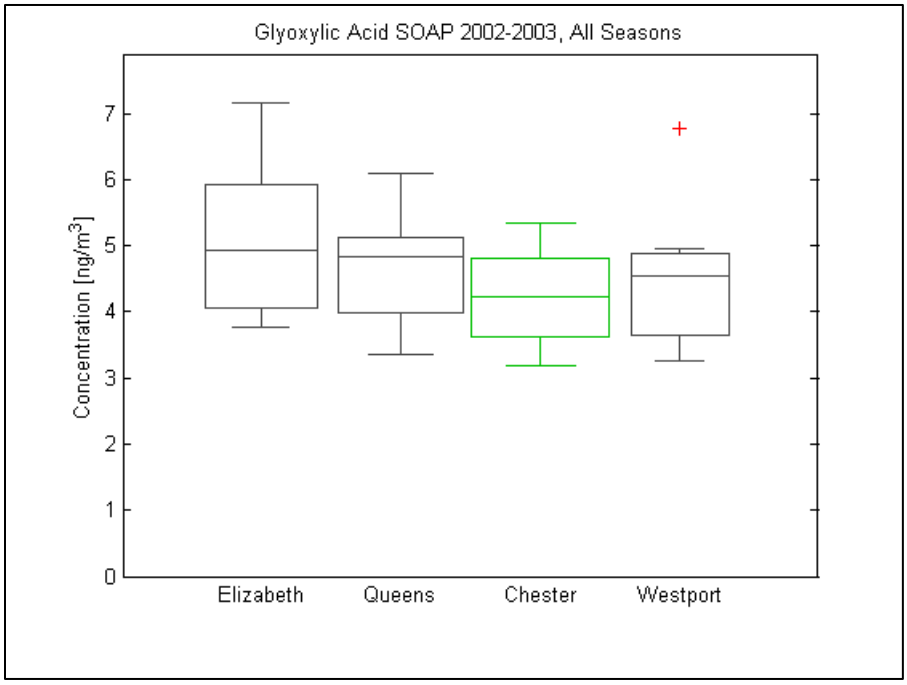

Figure 6.16. Glyoxylic acid concentrations in SOAP 2002-2003 campaign. Glyoxylic acid was quantified 8 times at Elizabeth, 9 times at Queens, 10 times at Chester, and 7 times at Westport, out of 9 samples at Westport and 10 at the other three sites.

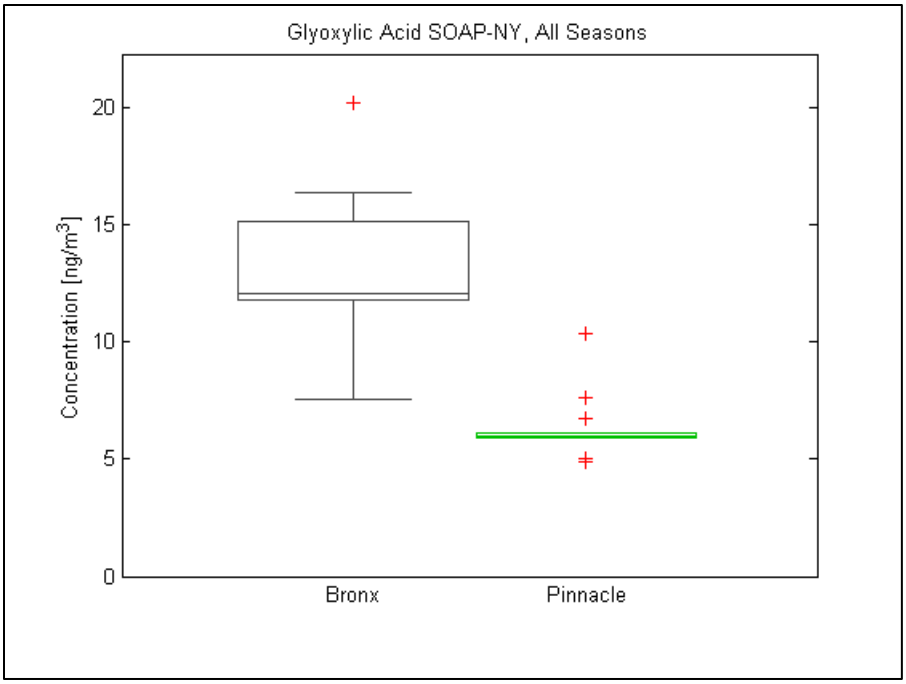

Figure 6.17. Glyoxylic acid concentrations in SOAP-NY campaign. Glyoxylic acid was quantified 17 times at the Bronx and 16 times at Pinnacle, out of 17 samples at each site.

In SOAP 2002-2003, there is not much difference among the sites. The highest average value and largest range are found at the Elizabeth site, but the other three sites are fairly similar in their median values and range. However, there is a much more striking difference in the SOAP-NY sites (Figure 6.17). The Bronx site clearly shows much higher annual average glyoxylic acid than does Pinnacle, with the lowest data point higher than all but one of the Pinnacle values. The Bronx site values are also much higher than those seen in the SOAP 2002-2003 campaign (Figure 6.16), while the Pinnacle average is similar to (though slightly higher) than those seen in the older SOAP campaign. Additionally, the range of concentration values is clearly much smaller at Pinnacle than at the Bronx.

When normalized to OC, glyoxylic acid shows the same trends as glyoxal. Figure 6.18 shows that glyoxylic acid makes up a slightly larger portion of OC at Chester than at the other three sites, although the difference is not large.

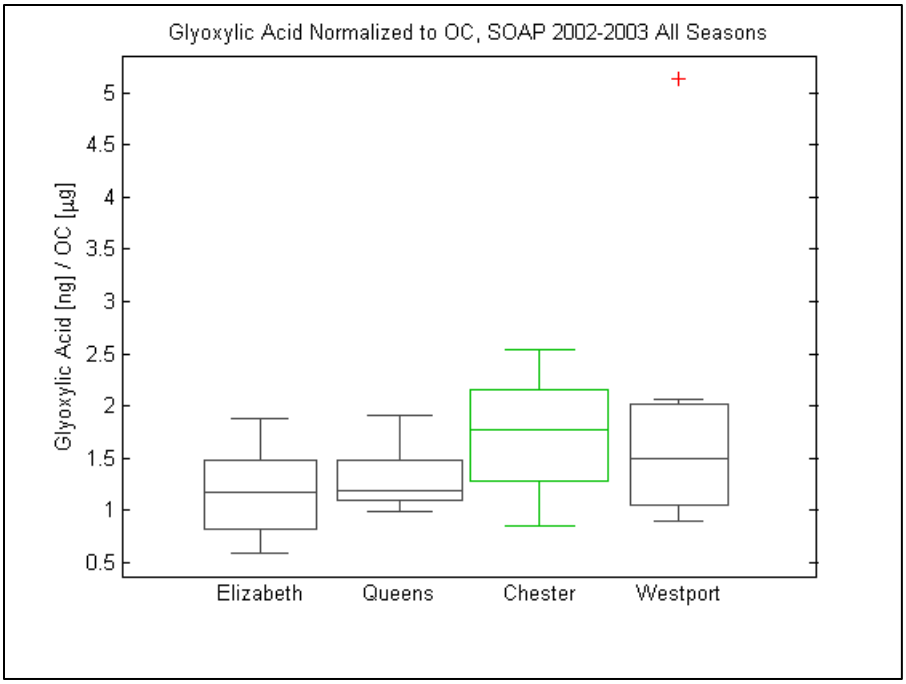

Figure 6.18. Glyoxylic acid normalized to OC in SOAP 2002-2003 campaign.

However, there is no discernible difference between the means in the SOAP-NY data (Figure 6.19); glyoxylic acid appears to make up a nearly identical fraction of OC at the two sites.

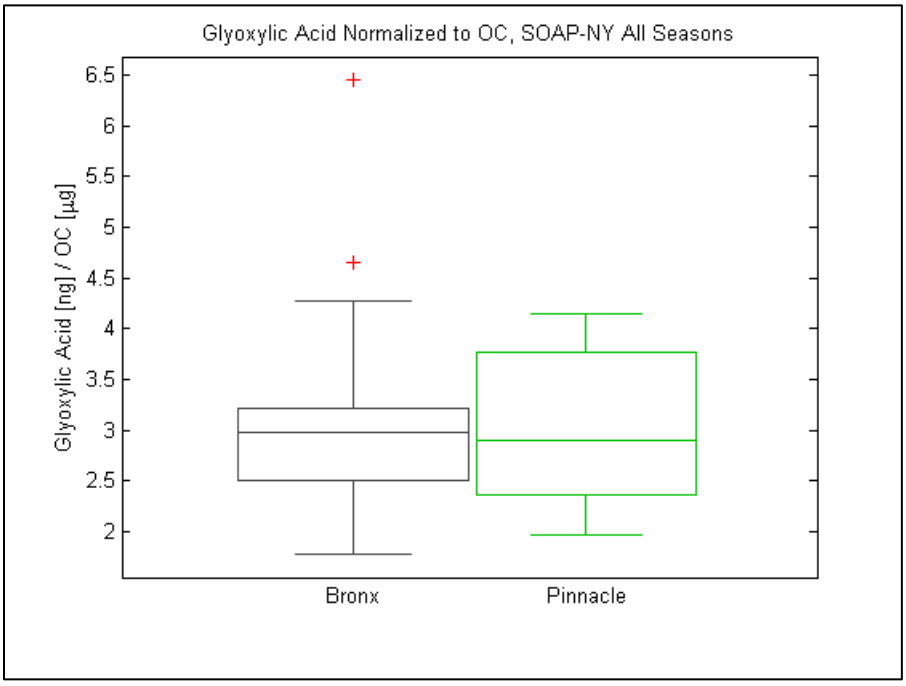

Figure 6.19. Glyoxylic acid normalized to OC in SOAP-NY campaign.

The pattern of glyoxylic acid concentrations after normalization to EC for the Bronx (shown in Figure 6.20) looks similar to the previous two HPOC at the Bronx, suggesting that the EC concentration values themselves may be driving the differences among the seasons more than changes in concentration of glyoxylic acid. Even if that is the case, the consistency of the ratios of cis-pinonic acid (Figure 6.5), glyoxal (Figure 6.14), and glyoxylic acid (below) throughout the year is still intriguing and will be discussed more later. The same similarities are seen among glyoxylic acid at Pinnacle (Figure 6.21) and the previous plots showing HPOC normalized to EC.

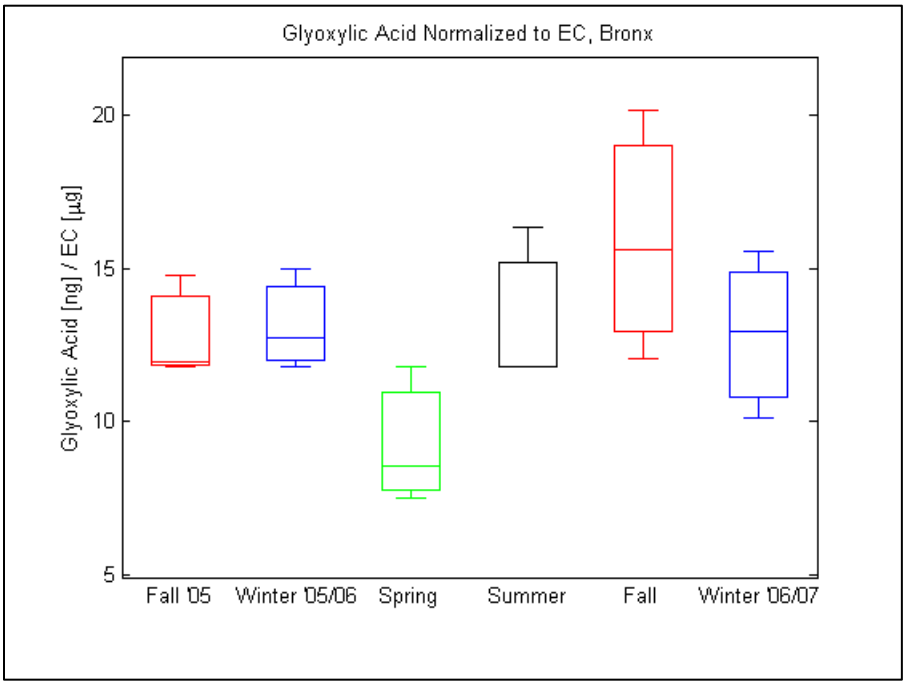

Figure 6.20. Glyoxylic acid normalized to EC, Bronx.

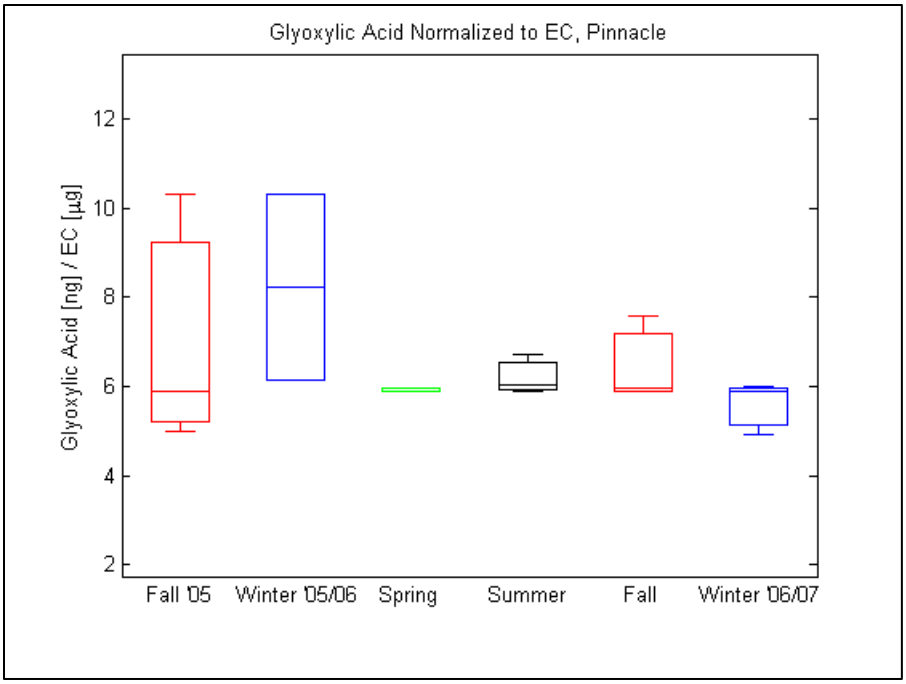

Figure 6.21. Glyoxylic acid normalized to EC, Pinnacle.

6.1.4 Oxalic acid

Oxalic acid was one of the most difficult compounds to quantify out of the 19 target compounds in this study, and by far the most difficult of the four HPOC discussed here. It was particularly hard to find oxalic acid in the Westport samples, where it was only positively identified in one of the nine samples for that site.

Figure 6.22 shows the concentration of oxalic acid at each site in the SOAP 2002-2003 campaign through the full sampling period. The mean concentration at each site shows little difference among the four sites, although with only one value at Westport makes it difficult to state any firm findings for that site.

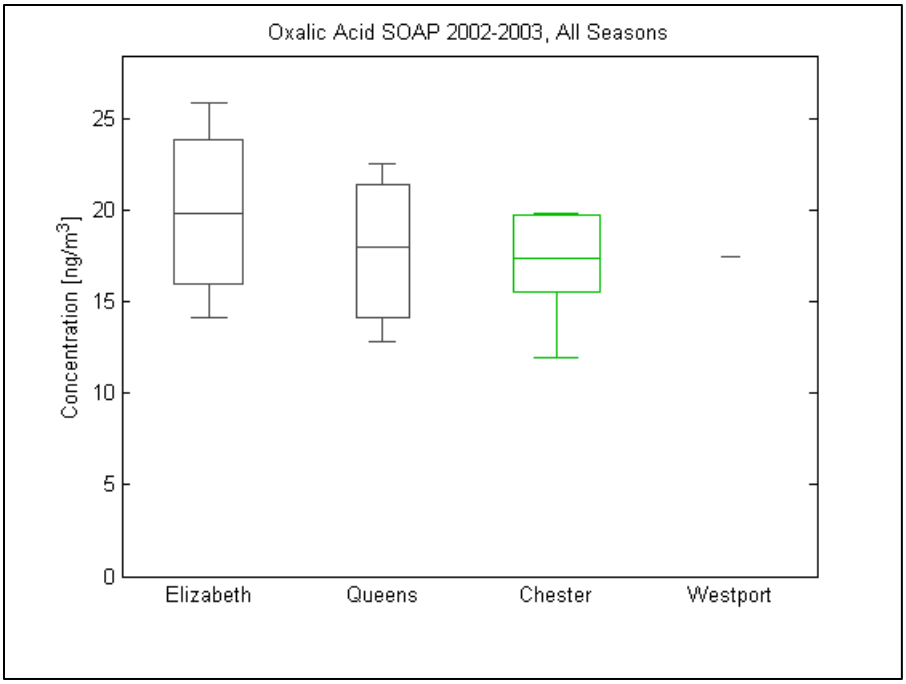

Figure 6.22. Oxalic acid concentrations in SOAP 2002-2003 campaign. Oxalic acid was quantified 4 times at Elizabeth, 3 times at Queens, 5 times at Chester, and 1 time at Westport, out of 9 samples at Westport and 10 at the other three sites.

However, the oxalic acid distribution is quite different at the SOAP-NY sites (Figure 6.23). As with glyoxylic acid (Figure 6.17), the mean concentration is clearly much higher at Bronx than at Pinnacle, and the range of concentrations at Pinnacle is very small.

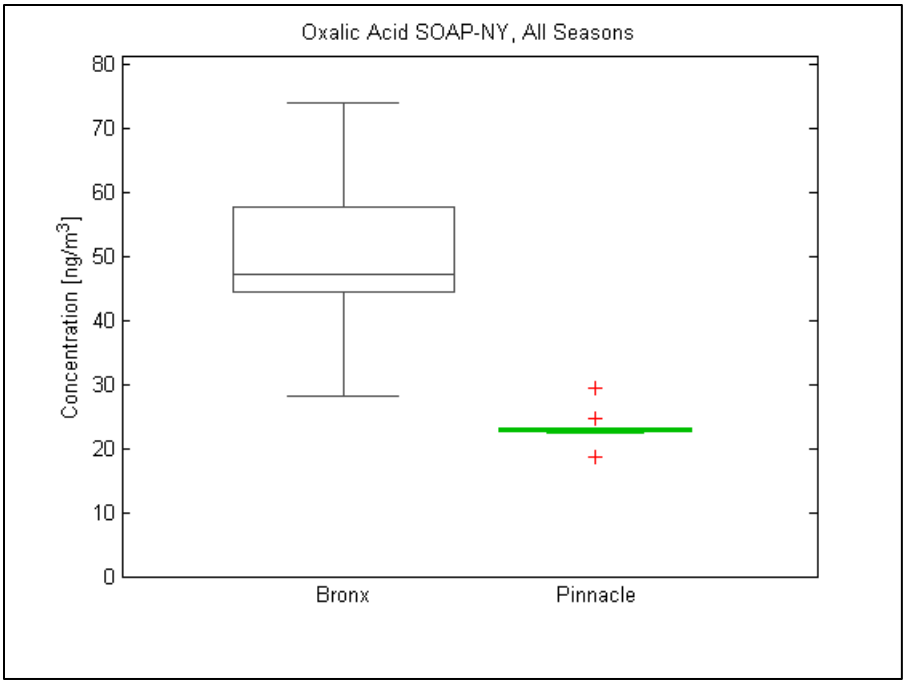

Figure 6.23. Oxalic acid concentrations in SOAP-NY campaign. Oxalic acid was quantified 15 times at the Bronx and 13 times at Pinnacle, out of 17 samples at each site.

When normalized to OC, a different pattern emerges (Figure 6.24):

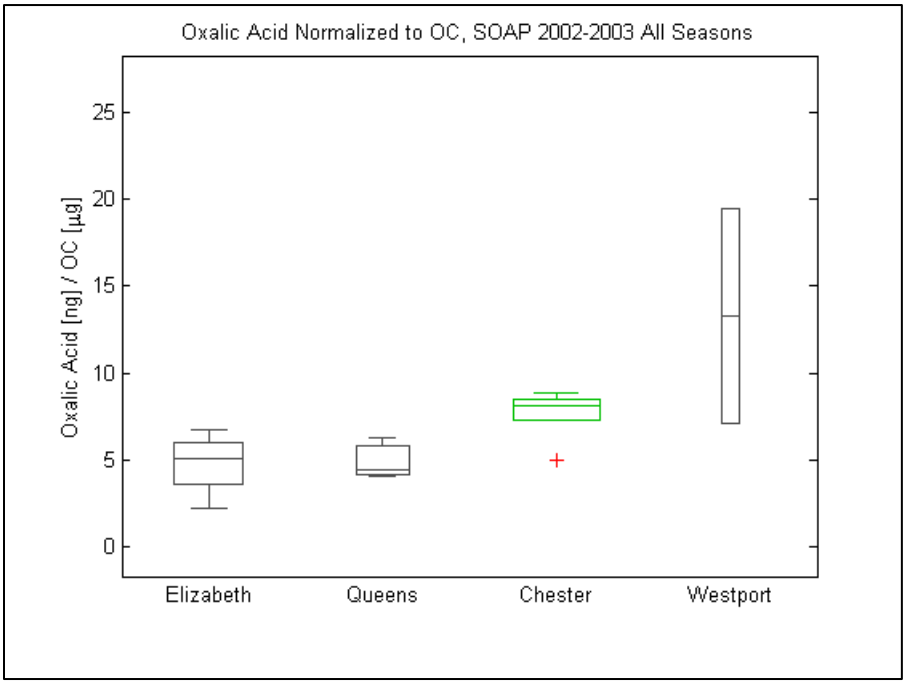

Figure 6.24. Oxalic acid normalized to OC in SOAP 2002-2003 campaign.

Unlike the concentration data (Figure 6.22), one site clearly has the highest mean. Oxalic acid makes up a larger portion of the organic carbon at Westport than it does at the other three sites. However, the rural site in SOAP-NY (Pinnacle) shows the same proportion of oxalic acid as does the urban site, the Bronx (Figure 6.25):

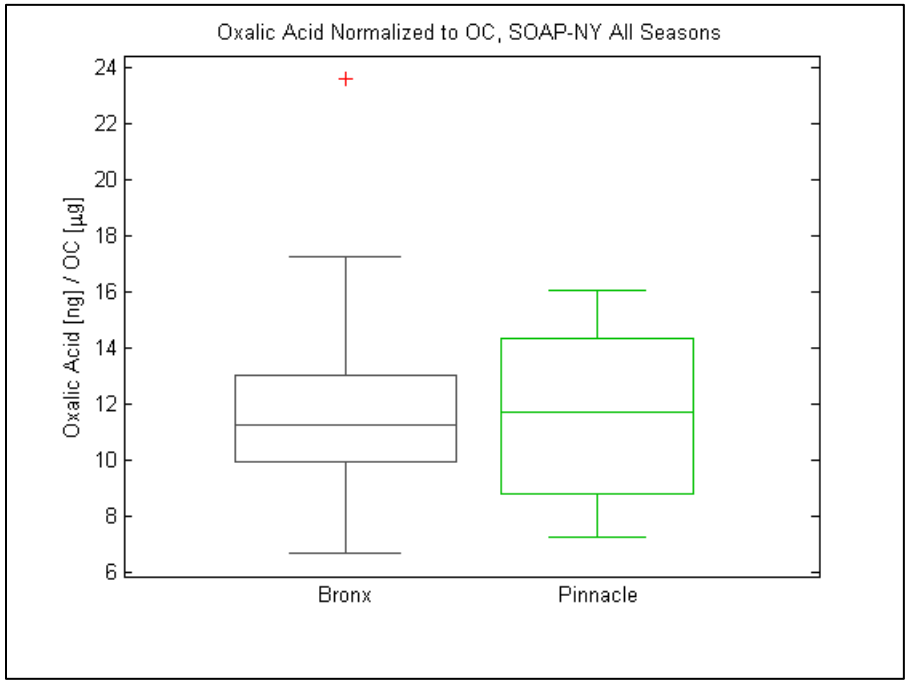

Figure 6.25. Oxalic acid normalized to OC in SOAP-NY campaign.

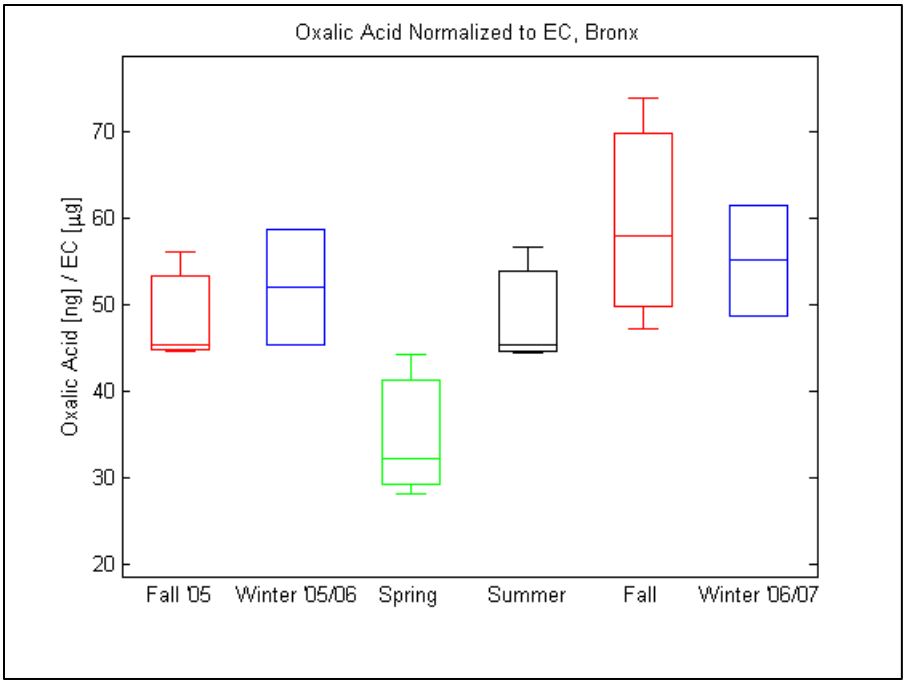

Figure 6.26. Oxalic acid normalized to EC, Bronx.

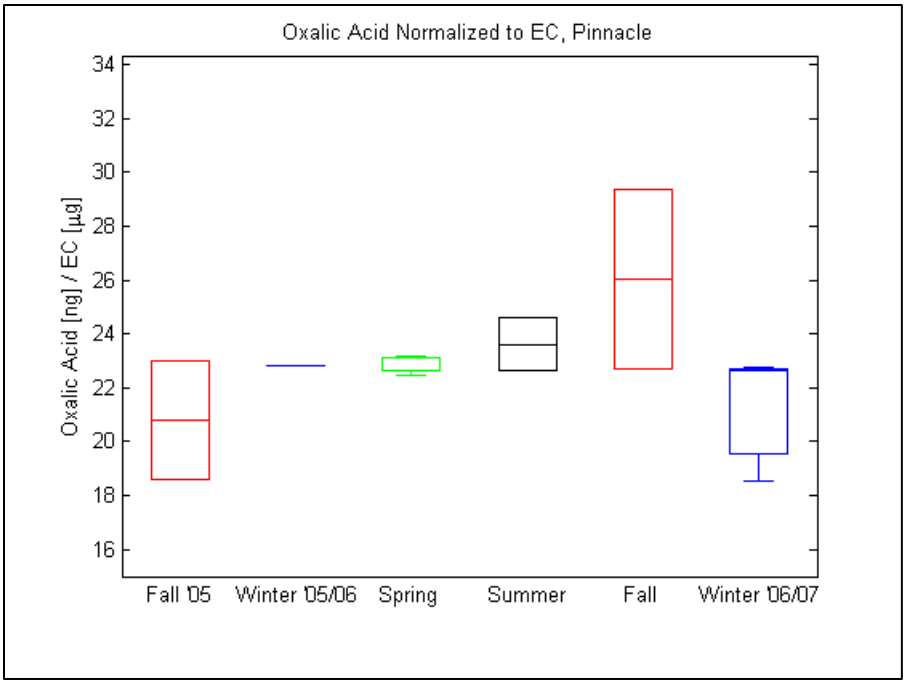

Figure 6.27. Oxalic acid normalized to EC, Pinnacle.

Oxalic acid patterns look different from those of the other three HPOC when normalized to EC. Instead of the first winter maximum and summer minimum, the

overall distribution looks more similar to what has been seen at the Bronx site (Figure 6.26, and Bronx plots for other HPOC).

6.2 Interrelationship of major HPOC

As discussed previously, a common sequence of processing leads cis-pinonic acid to glyoxal, glyoxylic acid, and finally oxalic acid. The ratios of these compounds are presented for each of the six SOAP sites.

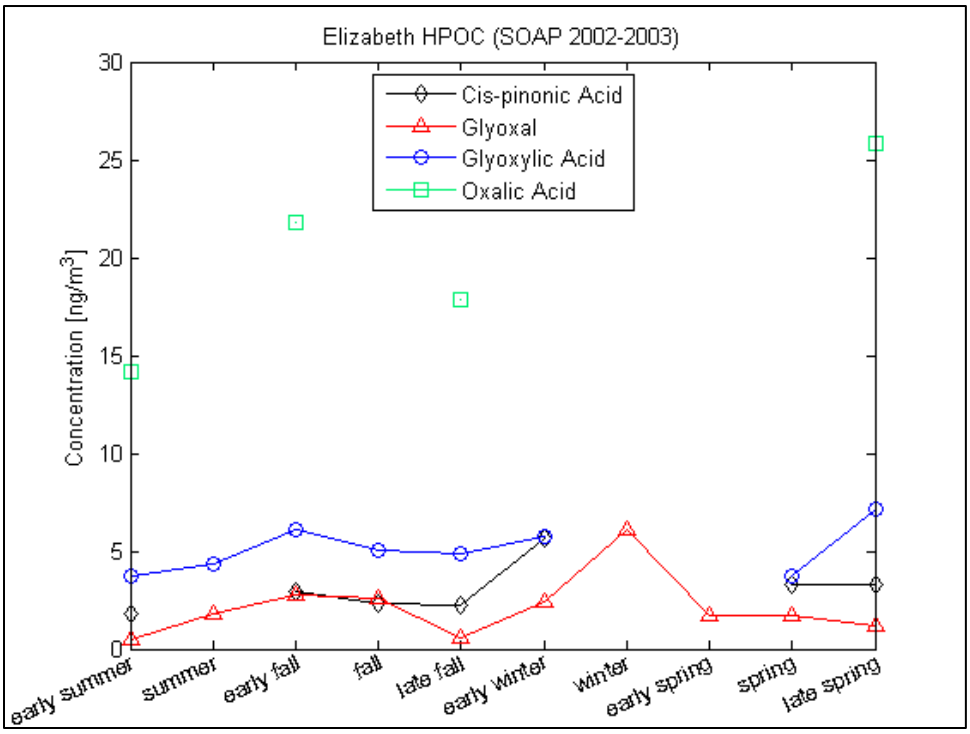

Figure 6.28. Selected HPOC at Elizabeth.

At Elizabeth (Figure 6.28), as with many of the SOAP 2002-2003 sites, oxalic acid was detected only intermittently. This may have been a consequence of its volatility; it is possible that the samples for which it was detected had a high enough concentration to overcome the loss of part of the concentration. The other three compounds of interest were detected more regularly and tend to stay in approximately the same ratios throughout the sampling period; glyoxal has the lowest concentration,

while glyoxylic acid has the highest, and cis-pinonic acid falls in between. The other urban site from SOAP 2002-2003, Queens, sees largely the same patterns and same general concentrations (Figure 6.29). However, the ratios are different at Chester and Westport. At Chester, the upwind rural site, the relative amounts of glyoxal and glyoxylic acid remain constant in all seasons (glyoxylic acid approximately twice as high as glyoxal in concentration). However, cis-pinonic acid varies more throughout the year in relation to glyoxal and glyoxylic acid. Since cis-pinonic acid is produced from α-pinene, which is emitted by trees year-round, we would expect to see higher concentrations at Chester than at the urban sites, which are not as strongly influenced by vegetation. Additionally, α-pinene and other terpenes are emitted in greater quantities at higher temperatures, so the concentration of cis-pinonic acid should likewise be greater in the warmer months.

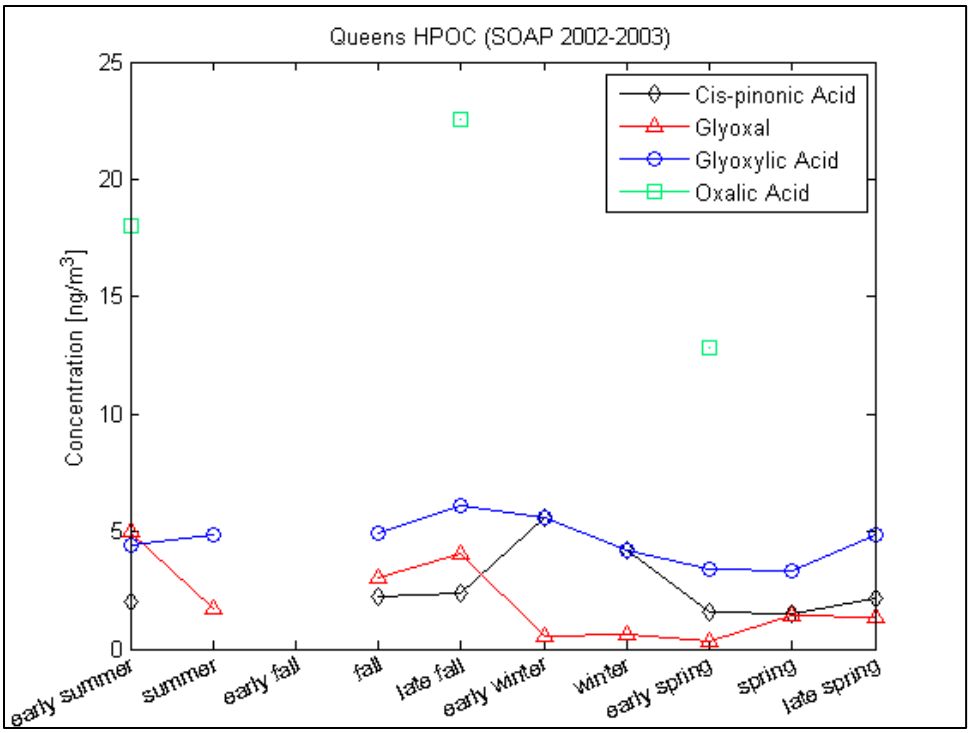

Figure 6.29. Selected HPOC at Queens.

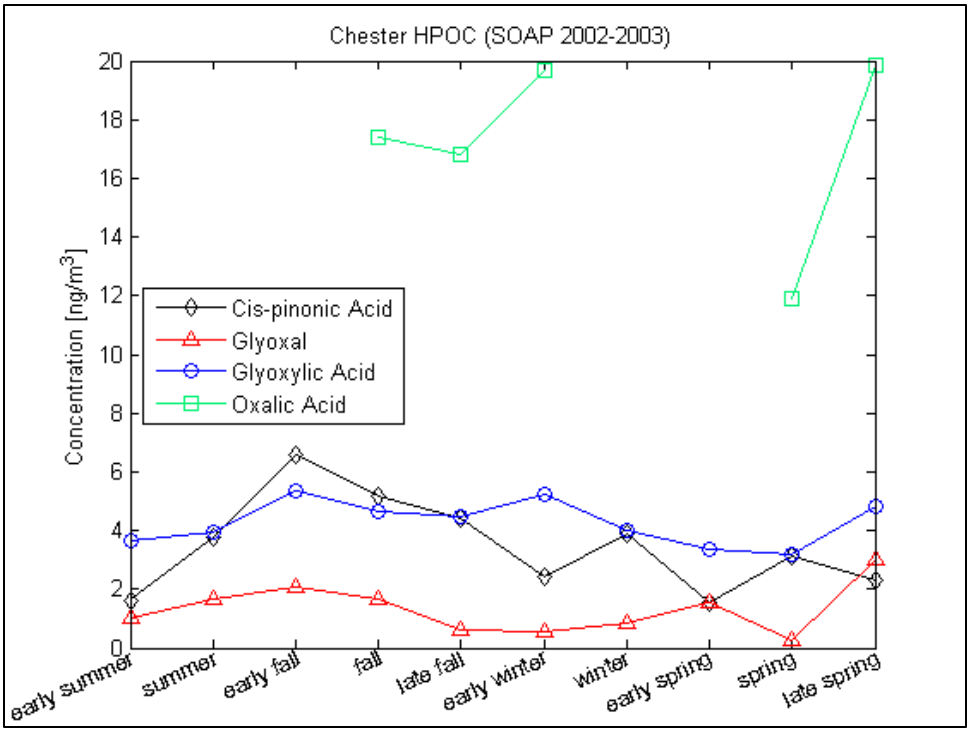

Figure 6.30. Selected HPOC at Chester.

Westport (Figure 6.31) shows additional characteristics that are not seen in the other three SOAP 2002-2003 sites. The clearly-defined interrelationship of glyoxal, glyoxylic acid, and cis-pinonic acid seen in the other three sites is not evident at Westport; the three compounds are seen at very similar concentrations and are random in their relationship to one another. Additionally, oxalic acid was only quantified once, in the late spring sample, and only glyoxal was seen in the late fall sample, and at an anomalously high concentration. That data point is likely untrustworthy, especially given that none of the other three compounds were seen in that sample.

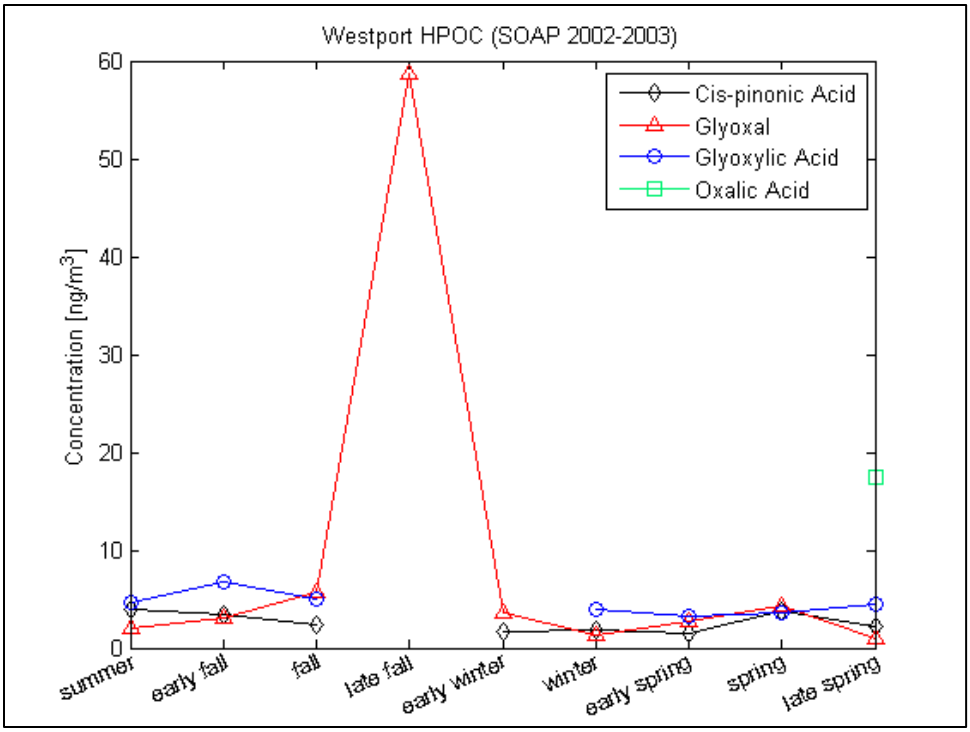

Figure 6.31. Selected HPOC at Westport.

The SOAP-NY sites tend to follow the same trend as the first three SOAP 2002-2003 sites. Figure 6.32 shows the HPOC in approximately the same ratios as the other sites. Oxalic acid was more readily quantified in the Bronx and Pinnacle samples than in the SOAP 2002-2003 samples, allowing for more detail in the annual trends of that compound.

In the Bronx data, a trend becomes apparent that was not seen in the previous samples. Oxalic acid tends to track the other three compounds, rising and falling in the same months as they do. However, the magnitude of the changes across the months is much larger for oxalic acid than for the other three compounds. Furthermore, cis-pinonic acid has the most constant concentrations of the four HPOC on the plot. Glyoxal and glyoxylic acid show the same up and down trends as cis-pinonic acid, but to a larger extent, and oxalic acid's trends are larger still. This is particularly evident from Oct. 2005 to January 2006 and May to November 2006 on Figure 6.32.

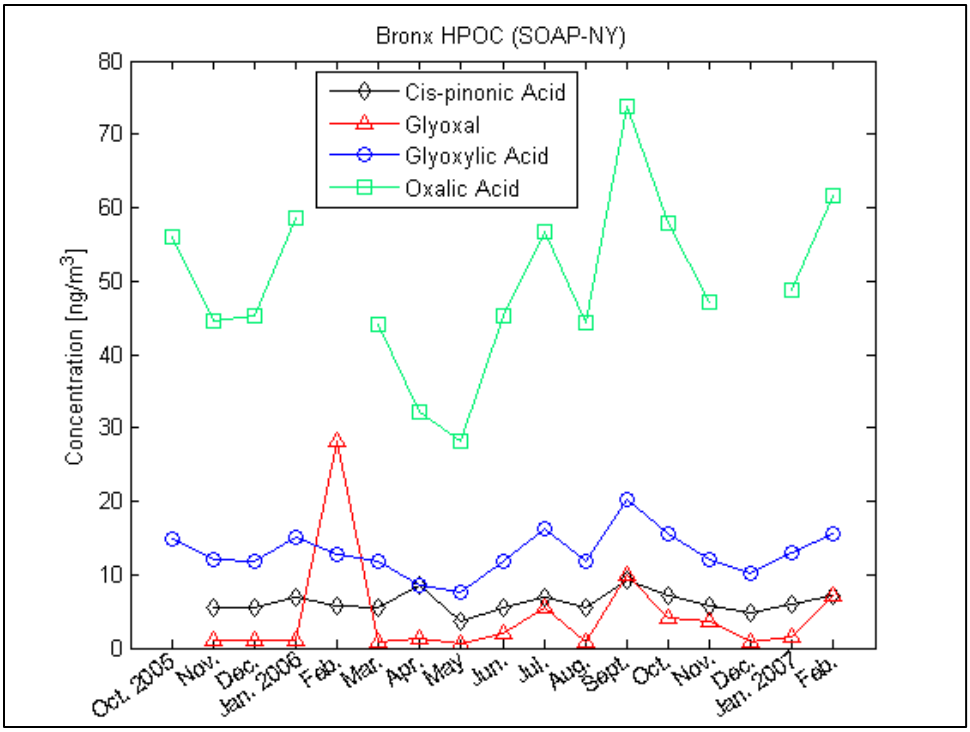

Figure 6.32. Selected HPOC at Bronx.

Finally, the Pinnacle samples (Figure 6.33) show some unique results as well. The most notable feature is that the cis-pinonic acid concentrations, shown as black diamonds, are frequently at or very near the same concentration level as glyoxylic acid, shown as blue circles. This suggests a slower rate of degradation of cis-pinonic acid, or a higher concentration to begin with, or possibly both. The concentration of oxalic acid appears much more constant at Pinnacle than it was at the Bronx site, and the average concentration of oxalic acid is only about half that of the Bronx site (around 17 to 30 ng m^{-3} at Pinnacle compared to 30 to 75 ng m^{-3} at the Bronx). Oxalic acid concentrations also do not appear to be as well-correlated with the concentrations of the other HPOC at Pinnacle as was seen at the Bronx site, suggesting that some other, more constant formation mechanism for oxalic acid may be contributing to concentration levels.

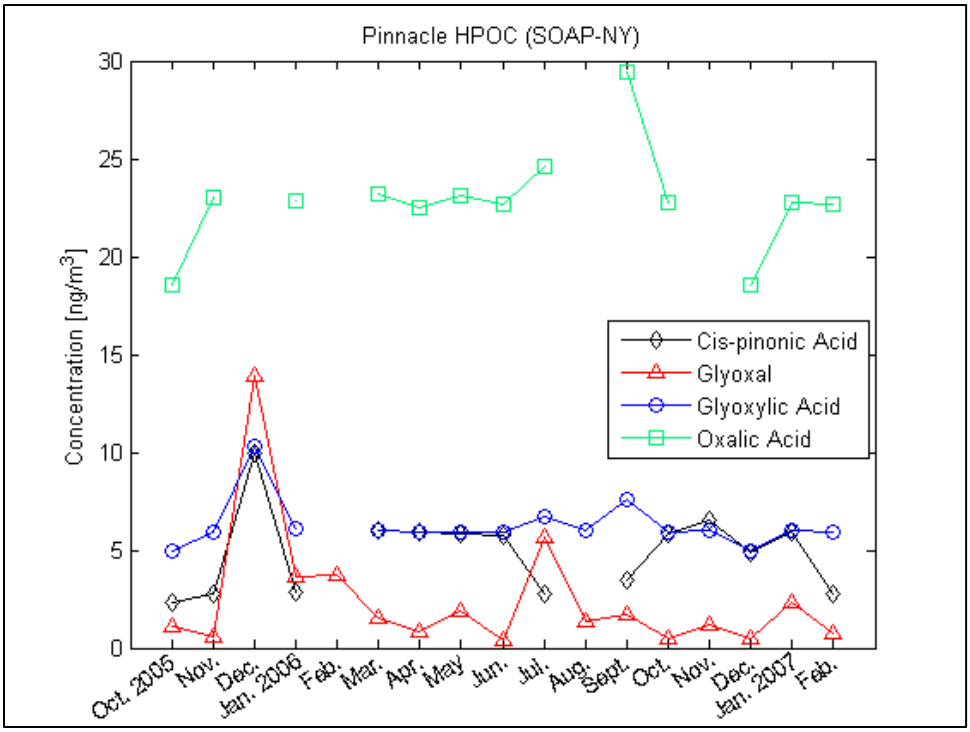

Figure 6.33. Selected HPOC at Pinnacle.

6.3 Correlations with other species

Understanding the relationship between a compound's concentration as a fraction of all organic carbon (OC), and in relationship to elemental carbon (EC), can help determine the level of formation of that particular compound and determine the level of processing. Additionally, plotting target compounds against secondary markers (for example, sulfate in the particle phase, and ozone in the gas phase) can help determine whether the target compounds are themselves secondary.

6.3.1 Organic carbon

Organic carbon (OC) includes carbon atoms in many different molecular configurations, including highly-oxygenated compounds. The expected processing from cis-pinonic acid to glyoxal, glyoxylic acid, and finally oxalic acid should be reflected in the correlation plots. R-values are listed in Table 6.1 on page 73.

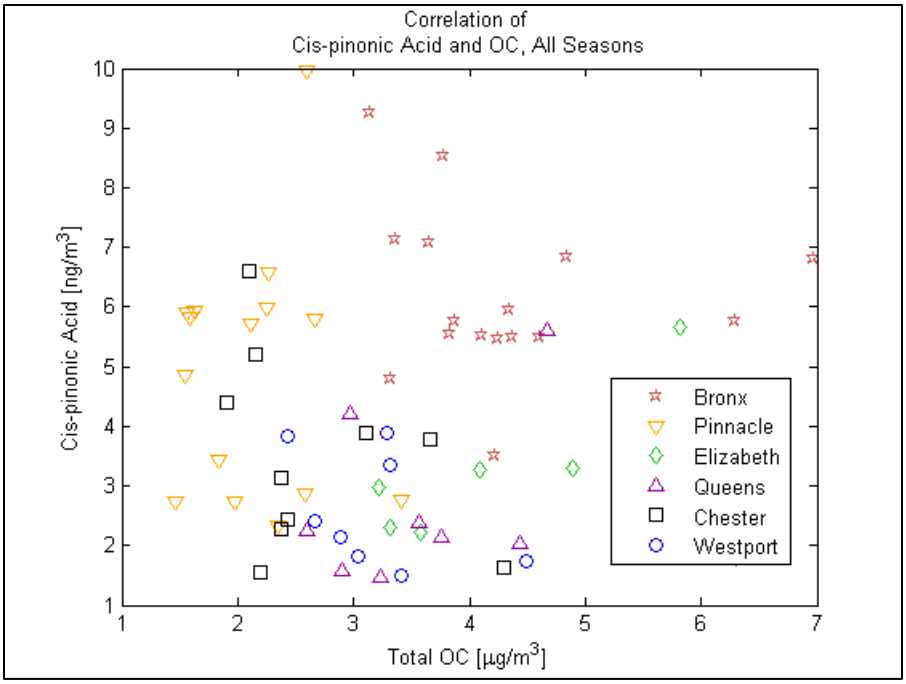

Figure 6.34. Correlation of cis-pinonic acid and OC in $PM_{2.5}$ samples.

Figure 6.34 above shows cis-pinonic acid plotted against organic carbon. No clear correlation is seen for any site. The same is true for glyoxal, shown in Figure 6.35. An anomalously high reading at the Westport site (~58 ng m^{-3}) was removed.

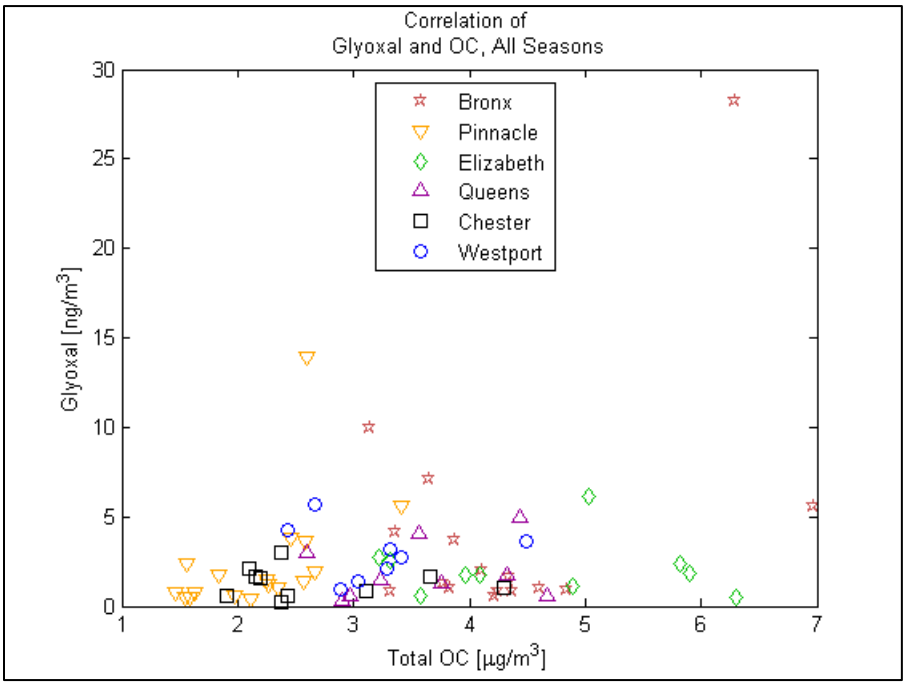

Figure 6.35. Correlation of glyoxal and OC in $PM_{2.5}$ samples.

The correlation of glyoxylic acid found in each $PM_{2.5}$ sample with the total organic carbon found in that sample is shown in Figure 6.36:

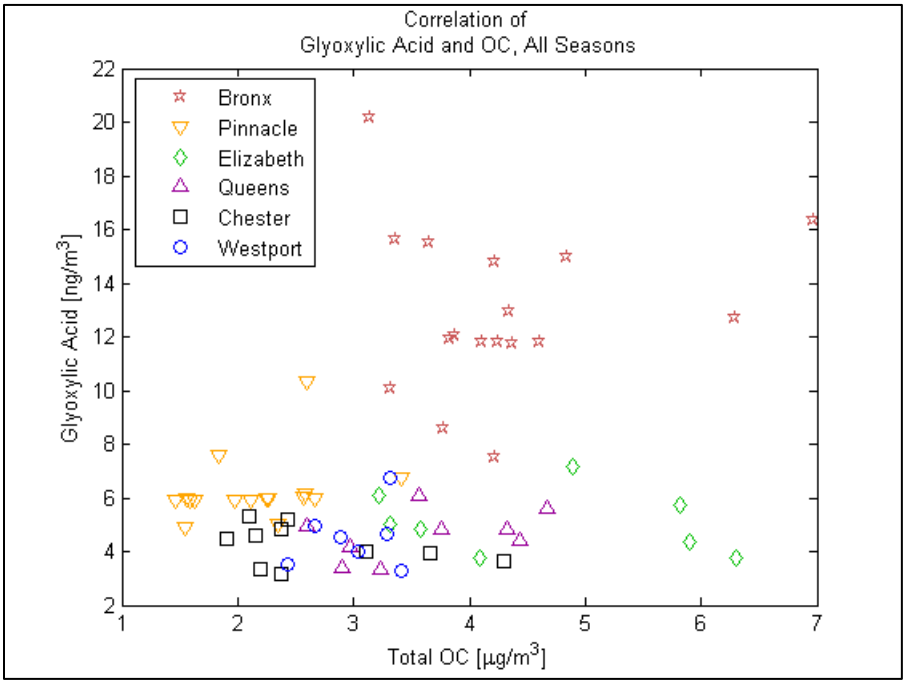

Figure 6.36. Correlation of glyoxylic acid with OC in $PM_{2.5}$ samples.

Glyoxylic acid is most prevalent at the Bronx sampling site, with little difference in concentrations among the other five sites. The most organic carbon, meanwhile, is found in Elizabeth and the two New York City sites. The correlation coefficients are not strong for any of the six sites, as shown in Table 6.1.

The correlation of oxalic acid with organic carbon is similar to that of glyoxylic acid (Figure 6.37):

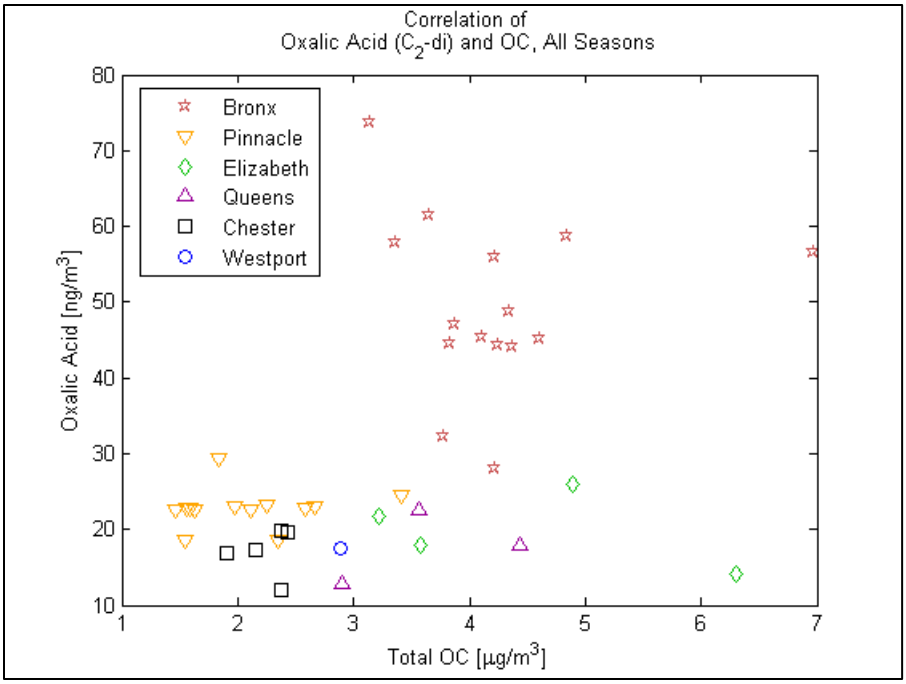

Figure 6.37. Correlation of oxalic acid with OC in $PM_{2.5}$ samples.

As with glyoxylic acid, oxalic acid shows the highest concentrations at the Bronx site and not much difference among the other sites. Oxalic acid was one of the more difficult compounds to quantify by GC/MS (Table 5.1), so there are not as many data points to consider in the SOAP 2002-2003 samples.

The R-values for the preceding plots are listed below:

Table 6.1. R-values for HPOC correlations with OC in $PM_{2.5}$ samples.

	Cis-pinonic acid	Glyoxal	Glyoxylic Acid	Oxalic Acid
	R-value	R-value	R-value	R-value
Elizabeth	0.31	0.05	-0.21	-0.40
Queens	0.43	0.18	0.42	0.46
Chester	-0.38	-0.10	-0.39	0.07
Westport	-0.41	-0.26	0.25	n/a
Bronx	-0.15	0.44	0.06	-0.04
Pinnacle	-0.02	0.50	0.31	0.13

6.3.2 Sulfate

Sulfate (SO_4^{2-}) makes up a large fraction of particulate matter mass: as much as one quarter to one half. It is formed from the oxidation of SO_2, which is emitted from factories and the combustion of coal that contains sulfur impurities. This oxidation typically occurs in the particle phase after the uptake of SO_2 by a hydrated particle or cloud droplet [Finlayson and Finlayson-Pitts, 1999]. The pathway from SO_2 to sulfate is irreversible; sulfate does not move back to SO_2. Thus, a compound that is highly correlated with sulfate may indicate that that compound follows a similar production mechanism, possibly even with the same oxidant.

Correlation coefficients for the following plots are listed in Table 6.2 on page 77.

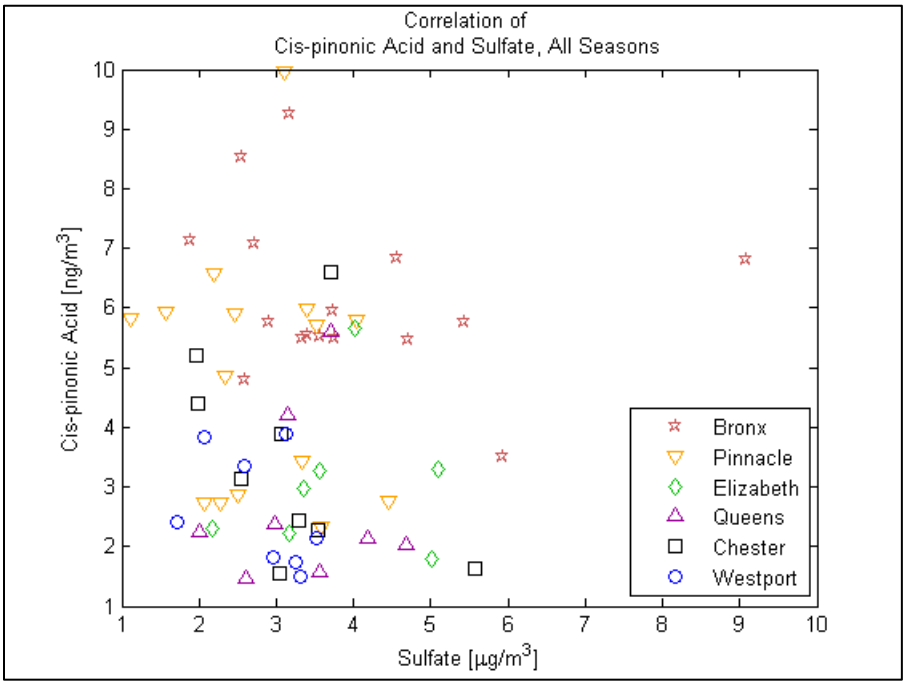

Figure 6.38. Correlation of cis-pinonic acid with sulfate in $PM_{2.5}$ samples.

Cis-pinonic acid and sulfate concentrations both vary widely among the six sites, with no noticeable correlation seen.

Glyoxal correlations with sulfate are not particularly strong in the $PM_{2.5}$ sample either. Figure 6.39 shows the correlations. An anomalously high glyoxal reading of 58

ng m^{-3} was removed from the Westport data prior to plotting. The removal of that point actually results in a strong negative correlation between glyoxal and sulfate at the Westport site, with an R-value of -0.82. This R-value is the largest absolute value correlation of any point in the PM sample data.

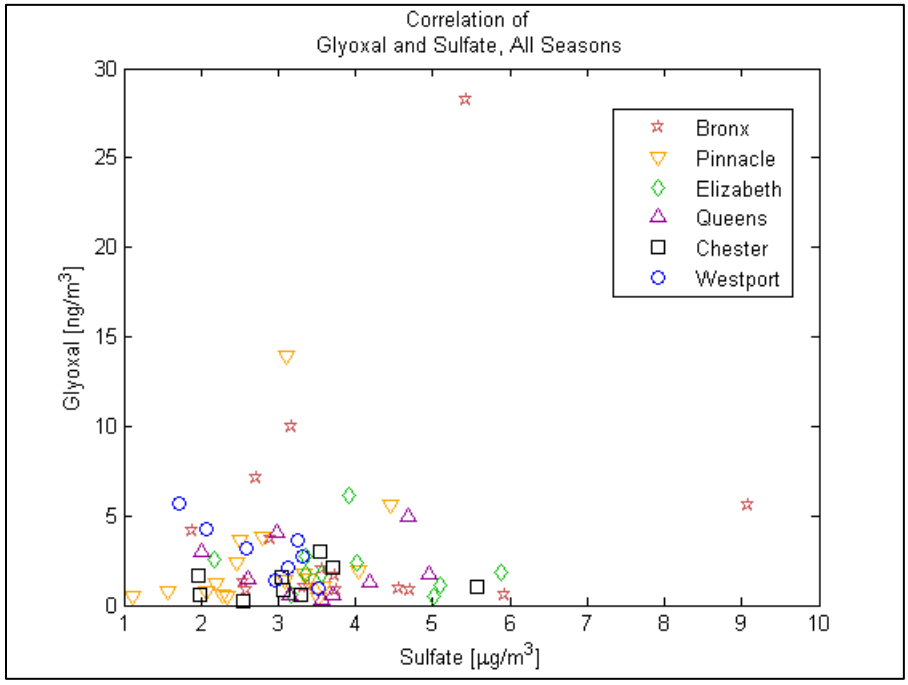

Figure 6.39. Correlation of glyoxal with sulfate in $PM_{2.5}$ samples.

Glyoxylic acid and sulfate are plotted in Figure 6.40. Again, no strong correlations are seen, as glyoxylic acid concentrations tend to remain steady throughout the year in different samples.

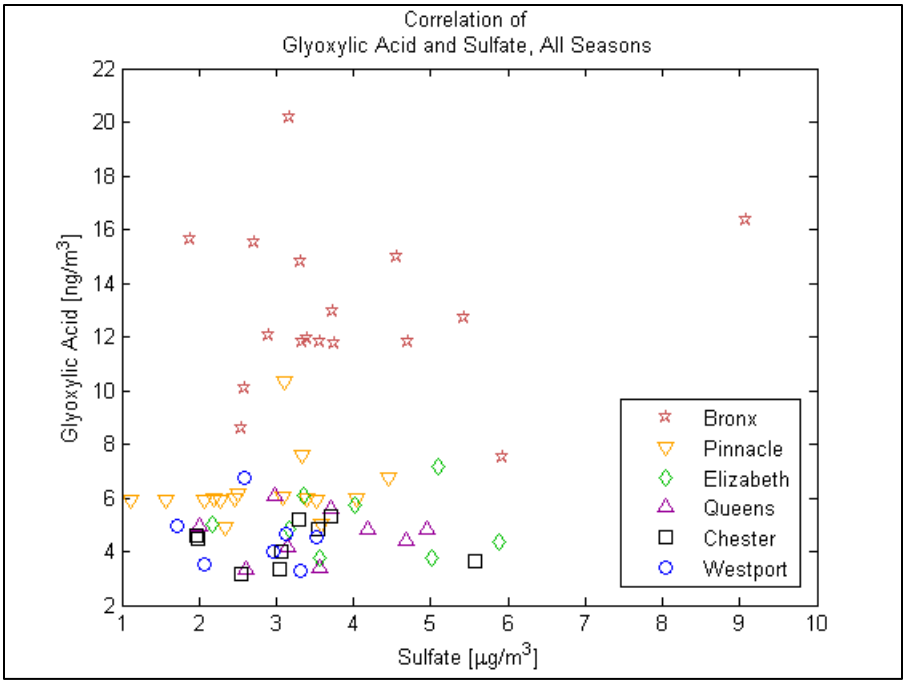

Figure 6.40. Correlation of glyoxylic acid with sulfate in $PM_{2.5}$ samples.

Finally, oxalic acid is plotted against sulfate in Figure 6.41. There is no obvious correlation among any of the six sites. Only Chester and Pinnacle show any hint of a relationship, but the r-values for those two sites are 0.39 and 0.20, respectively.

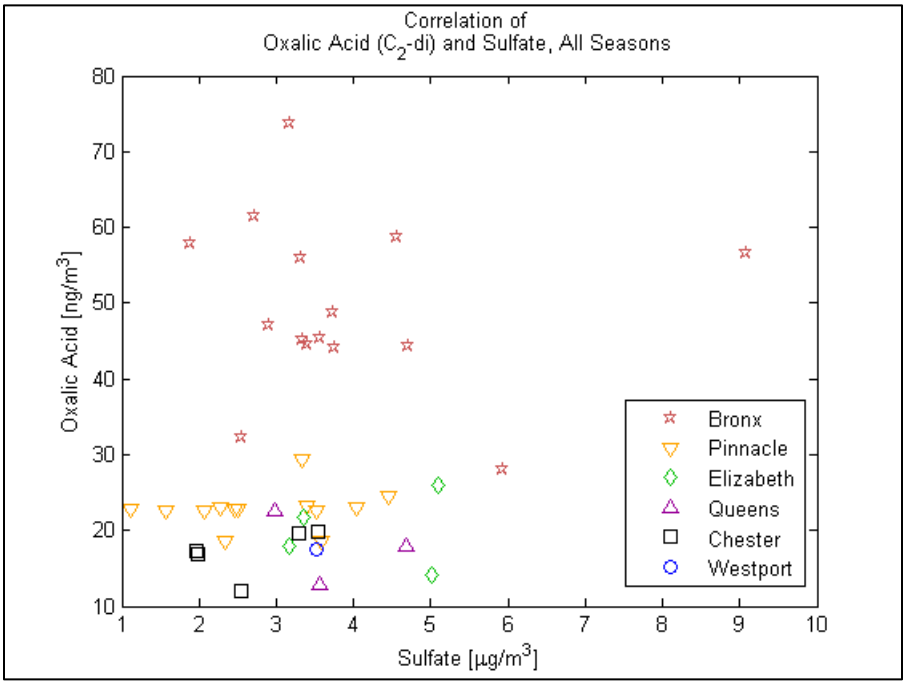

Figure 6.41. Correlation of oxalic acid with sulfate in $PM_{2.5}$ samples.

The R-values for the preceding tables are listed below.

Table 6.2. R-values for HPOC correlations with sulfate in $PM_{2.5}$ samples.

	Cis-pinonic acid	Glyoxal	Glyoxylic Acid	Oxalic Acid
	R-value	R-value	R-value	R-value
Elizabeth	0.14	-0.20	-0.02	0.08
Queens	0.09	0.05	0.05	-0.31
Chester	-0.40	0.16	-0.08	0.49
Westport	-0.43	-0.82	-0.19	n/a
Bronx	-0.22	0.21	0.05	-0.09
Pinnacle	-0.12	0.29	0.20	0.20

6.3.3 Ozone

Ozone is formed photochemically, so a compound that shows a strong correlation with ozone may also be formed photochemically, though this is not necessarily the only mechanism by which it could form. The ozone measurements used here are 8-hour maximum values per day as recorded by EPA AQS monitors. The values from the same days that the SOAP samples were collected were averaged to create a matching "ozone composite" for each SOAP composite. Measurements were not available for Elizabeth, NJ, so no points appear on the figures for that site. Additionally, the Westport ozone sampling site only recorded data between April and September. Since the first SOAP campaign ran from May 2002 to May 2003, only the summer and late spring composites were able to be matched up with ozone measurements. R-values for each plot are listed at the end of this section in Table 6.3 on page 81.

Cis-pinonic acid is plotted against ozone in Figure 6.42:

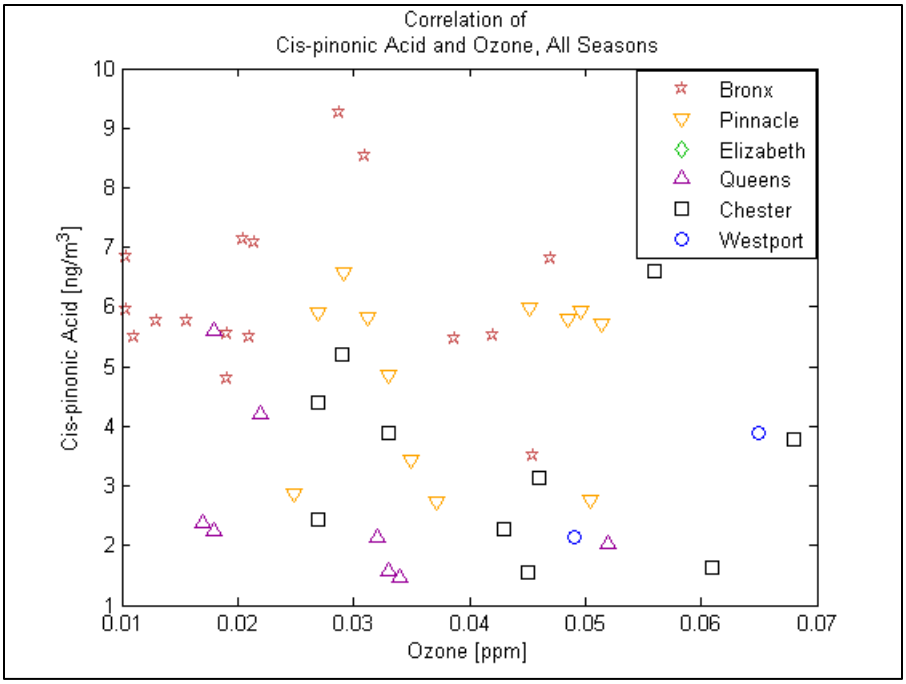

Figure 6.42. Correlation of cis-pinonic acid and ozone in $PM_{2.5}$ samples.

There is no clear correlation between cis-pinonic acid and ozone at any of the sites except for Westport. However, given that Westport only has two samples which were able to be matched up with ozone readings, the real relationship cannot be determined.

Glyoxal also shows no correlation (Figure 6.43). This is partly driven by, as discussed before, the fact that glyoxal concentrations tend to be very consistent across samples at a site, particularly at Pinnacle. As with the sulfate correlation plot, a very high glyoxal reading from Westport has been removed.

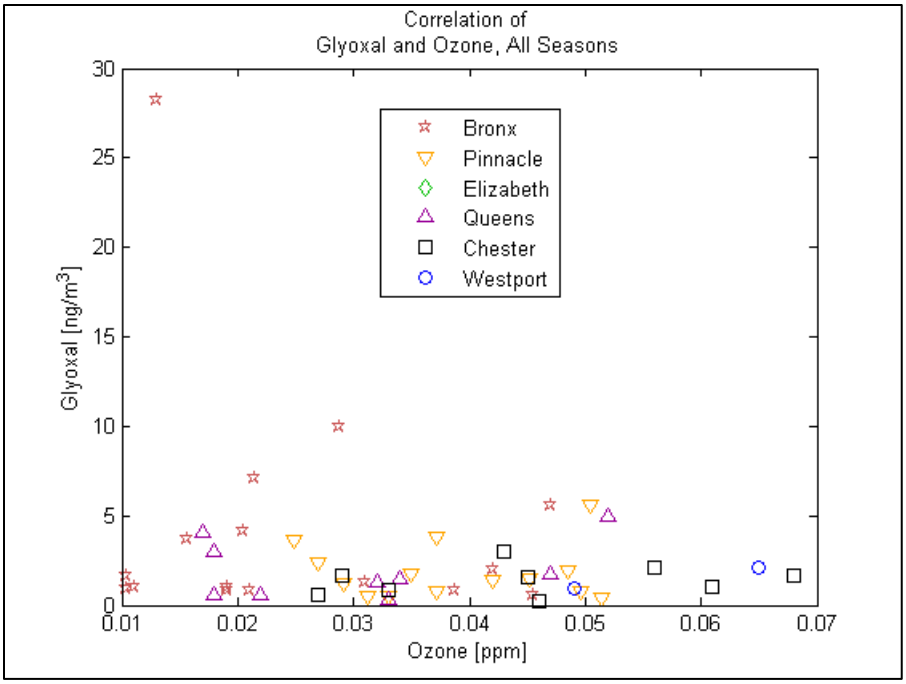

Figure 6.43. Correlation of glyoxal and ozone in $PM_{2.5}$ samples.

The correlation of glyoxylic acid with ozone is as follows:

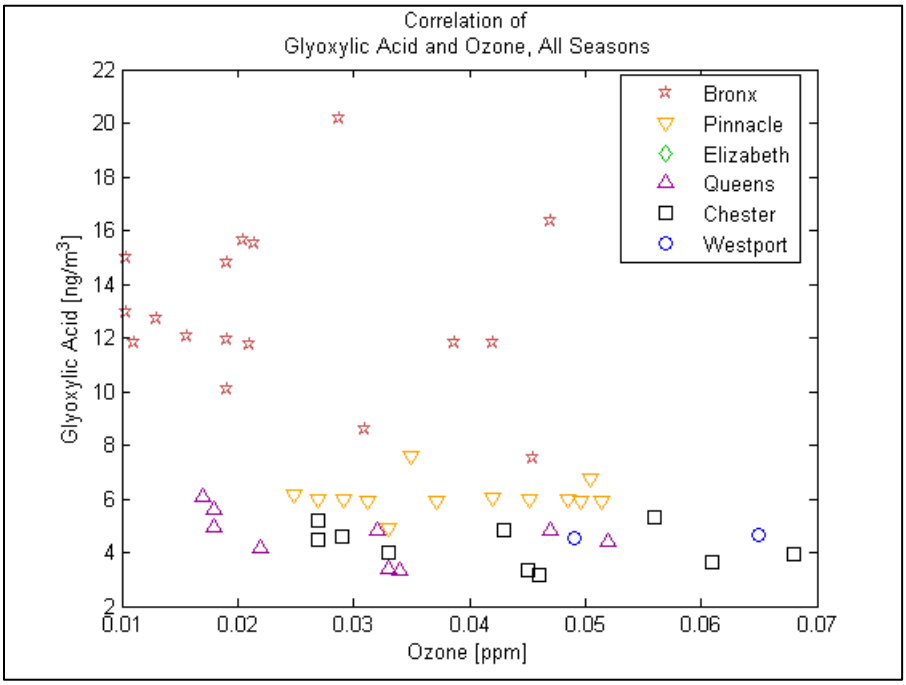

Figure 6.44. Correlation of glyoxylic acid with ozone in all seasons. Note that no ozone data were available for the Elizabeth site, so it is not represented on this chart.

Little correlation is seen at any site, even though the ozone concentrations vary throughout the year due to increased production in the summer months. Though the Bronx site shows no overall correlation, a possible bimodal distribution is apparent, with a possible correlation within each mode. When the Bronx data are isolated from the other sites and broken down by season, some intriguing features become apparent, as shown in Figure 6.45:

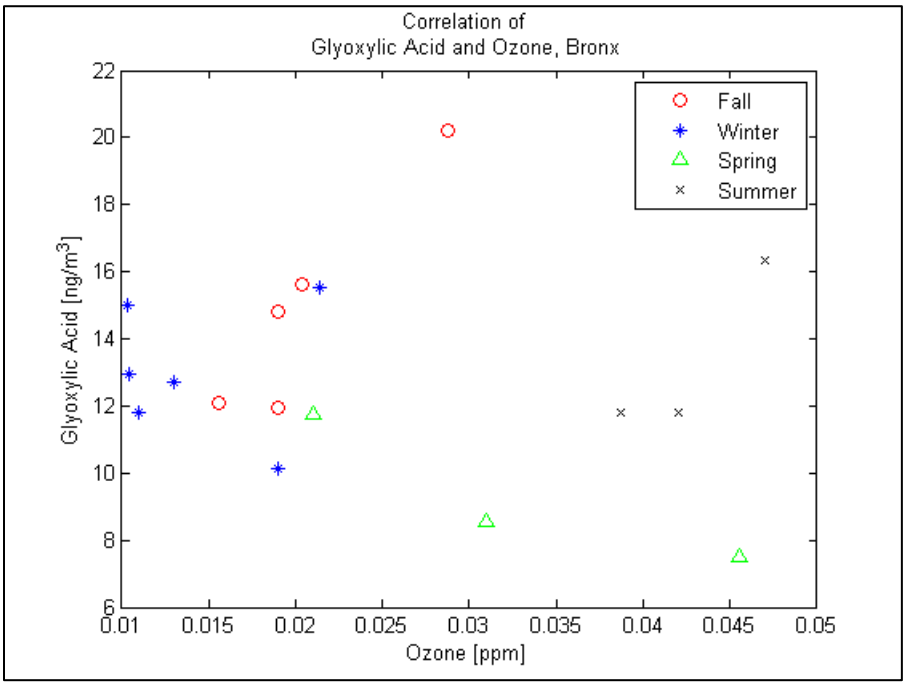

Figure 6.45. Seasonal correlation of glyoxylic acid and ozone for the Bronx.

The fall samples, shown as red circles, do appear to be positively correlated with ozone. The summer samples, shown as black x's, may also be positively correlated, although it is impossible to reach a clear conclusion with only three points. The winter samples show no correlations, and the spring samples, if anything, appear to be negatively correlated with ozone (although, again, only three points exist).

Finally, oxalic acid and ozone are plotted in Figure 6.46:

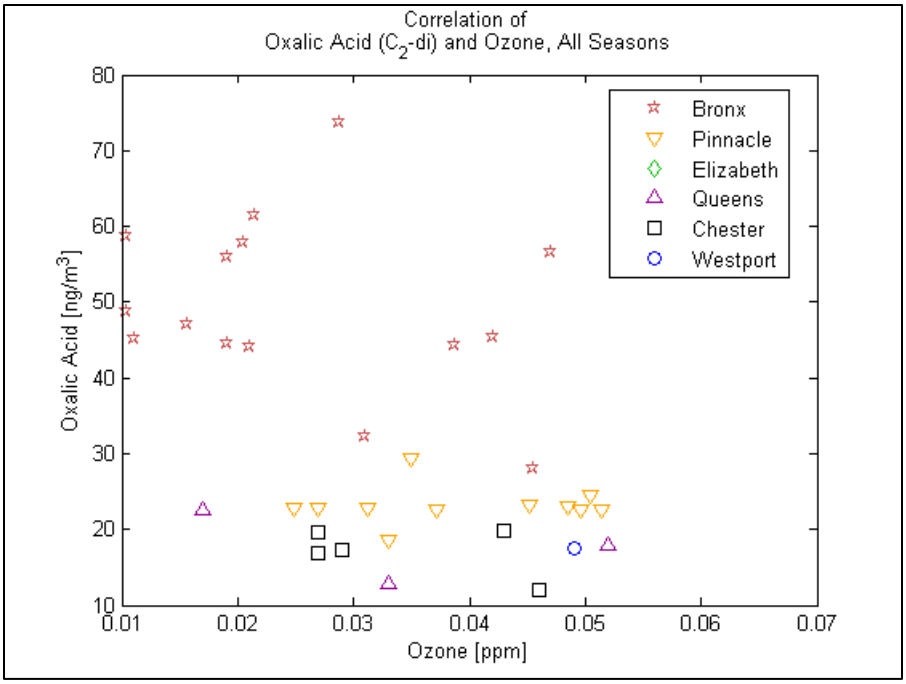

Figure 6.46. Correlation of oxalic acid and ozone in $PM_{2.5}$ samples.

Oxalic acid's correlation with ozone is fairly similar to glyoxylic acid's, which is not surprising since the two are so closely correlated themselves.

The R-values for HPOC with ozone are listed in the following table.

Table 6.3. R-values for HPOC correlations with ozone in $PM_{2.5}$ samples.

	Cis-pinonic acid	Glyoxal	Glyoxylic Acid	Oxalic Acid
	R-value	R-value	R-value	R-value
Elizabeth	n/a	n/a	n/a	n/a
Queens	-0.51	0.25	-0.43	-0.43
Chester	-0.07	0.03	-0.32	-0.46
Westport	n/a	n/a	n/a	n/a
Bronx	-0.06	-0.18	-0.13	-0.27
Pinnacle	0.09	0.02	0.08	0.08

7 Cloud Water Results

As noted, the cloud water samples were taken in the summer of 2010. A total of 68 samples were provided to Rutgers. Of these 68, 20 were replicates that were filtered through a 0.7 μm Millipore filter to remove small suspended particles. No significant difference was observed in the species seen, or their concentrations, between the filtered and unfiltered sample pairs, suggesting that the compounds of interest in this study were primarily dissolved in the water. This is to be expected since polar compounds were targeted. Thus, this discussion will focus only on the unfiltered samples. Additionally, eight unfiltered samples were derivatized and run in the GC/MS but failed to produce acceptable chromatograms as described previously in Section 4.6.2. The results presented here encompass the 40 samples for which satisfactory chromatograms were obtained.

7.1 TOC overview

Cloud water samples have many variables that affect the concentrations of species, such as liquid water content of the cloud. Normalizing to total organic carbon (TOC) provides common ground for comparison among samples taken at different points during the summer. Additionally, the cloud water samples were taken at one-hour intervals when the four sampling conditions discussed in Section 3.2 were met. Thus, unlike the $PM_{2.5}$ samples, the cloud water samples were taken sporadically throughout the summer. Some of the samples were taken consecutively, but there were large gaps between others. The 40 valid samples included twelve instances or “sets” of samples taken consecutively or nearly consecutively. Two sets of these consecutive samples were discarded because of a wind direction change of greater than 45 degrees between samples. Such a large change could indicate sampling of a different air mass, where the meteorological and HPOC characteristics would likely be different, defeating the purpose

of studying changes within an event. Thus, this analysis will focus on ten cloud water "events": groups of two or more samples that are consecutive, with little change in the wind direction during the event. The events are numbered and listed in Table 7.1.

Table 7.1. Cloud water events. All samples were taken in 2010, and all times are EDT.

Event #	# of samples	Date	First Sample Time	Last Sample Time
1	2	6/14	12:00	15:00
2	2	7/1	0:00	3:00
3	2	7/20	3:00	7:00
4	2	7/22	9:00	12:00
5	3	7/25	9:00	15:00
6	2	7/26	4:00	6:00
7	3	8/2	3:00	9:00
8	5	8/3	0:00	12:00
9	2	8/4	3:00	6:00
10	2	9/8	21:00	0:00 (9/9)

Before looking at HPOC within these events, it is important to see if TOC concentrations tend to increase or decrease within the events. Figure 7.1 shows TOC concentration for each sample within each event. Of the seven events composed of just two samples, four showed an increase in TOC concentration from the first sample to the last, two showed a decrease, and one (Event 10) showed a very slight increase. Additionally, all of the events consisting of three or more samples showed both increases and decreases in TOC concentration over the course of the event; none showed only an increase or only a decrease. Given this apparent randomness in changes in TOC concentration during the events, any study of HPOC concentrations within the events must include normalization to TOC.

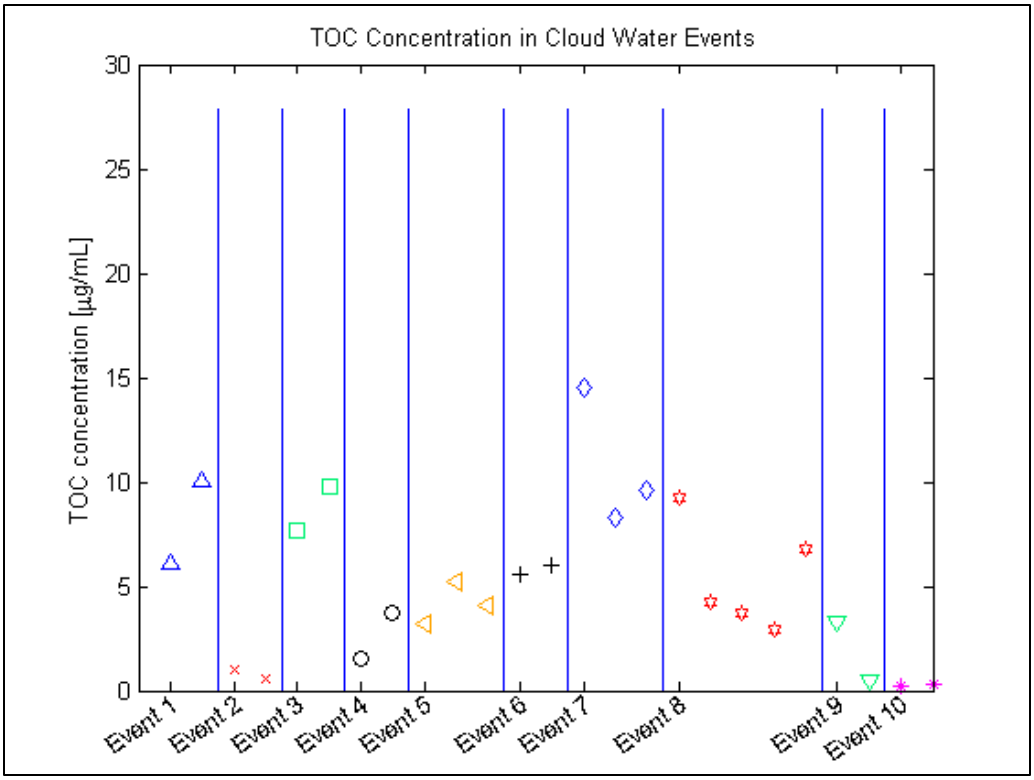

Figure 7.1. TOC values in the ten cloud water events. The events are separated by blue lines and plotted with different colors and symbols.

7.2 Evolution of HPOC within cloud water events

One way to approach the question of in-cloud processing is to examine how the amount of HPOC changes within an "event". Cloud water samples taken consecutively can be assumed to have come from the same air mass; thus, we might expect a higher level of processing (more highly oxidized compounds) in samples that came at a later point within the same event. Figure 7.2 shows the HPOC concentrations normalized to TOC during each event:

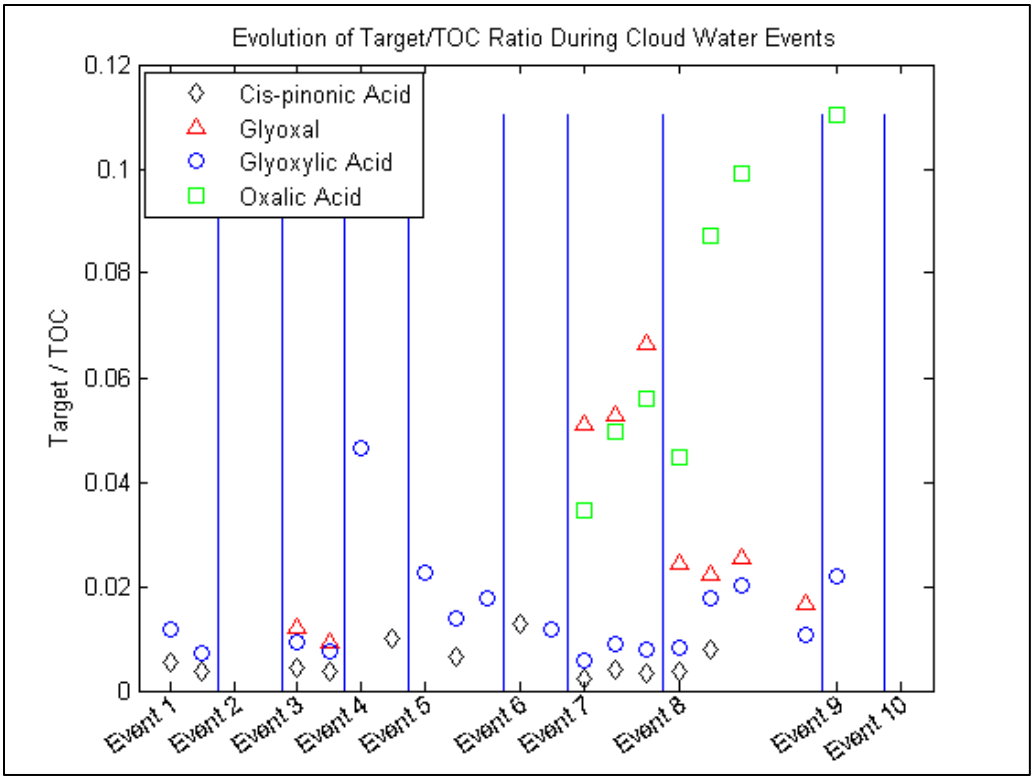

Figure 7.2. Evolution of HPOC during cloud water events. Events are separated by blue lines.

None of the four HPOC were quantified in the samples in events 2 and 10, and events 4, 6, and 9 did not have enough quantified to yield any useful information.

Event 7, which encompasses three consecutive samples, was the only one in which all four compounds were found in all of the samples in the event. Cis-pinonic acid and glyoxylic acid stay relatively constant throughout the event, while glyoxal and oxalic acid both increase during the event. In event 8, oxalic acid increases for the first three samples in the event but is not detected in the fourth one. Glyoxylic acid shows the same pattern, while glyoxal decreases, increases, then decreases again, and cis-pinonic acid increases between the first two samples, but is not detected after that.

7.3 Correlation of HPOC with sulfate

As with the $PM_{2.5}$ samples, the HPOC of interest were checked for correlation with sulfate, a secondary compound. The sulfate concentrations were provided by

ALSC from their own search for inorganic ions. Rather than focusing on the events designated above, all available samples over the course of the summer were included.

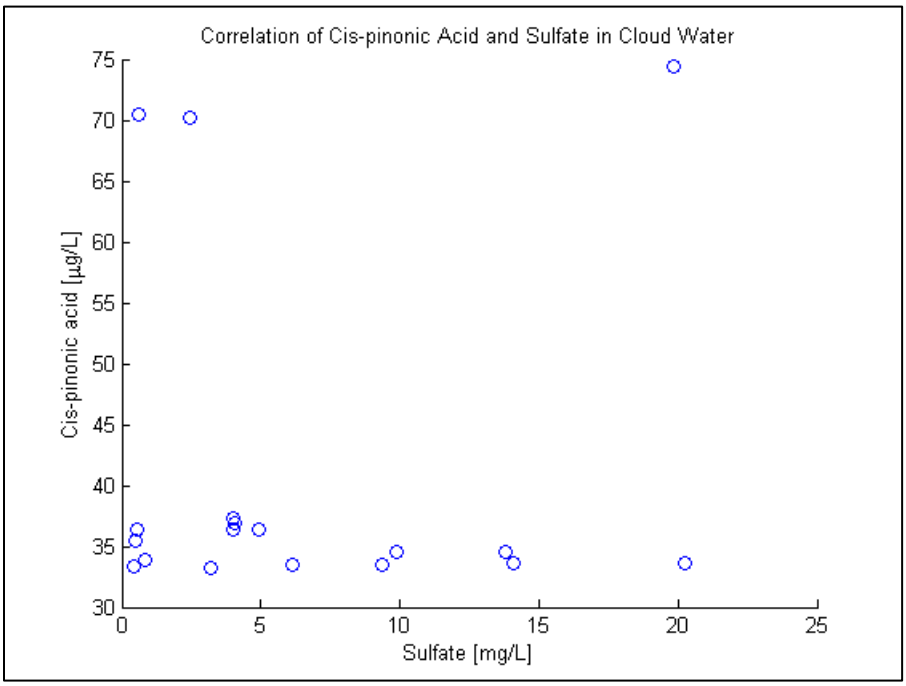

Figure 7.3. Correlation of cis-pinonic acid with sulfate in cloud water.

Cis-pinonic acid shows no correlation with sulfate (Figure 7.3). In the cloud water samples, cis-pinonic acid concentrations were very stable at around 30 to 40 ppb (or µg L^{-1}) throughout the sampling period, with only three samples outside of this range.

Glyoxal and glyoxylic acid show more of a positive correlation with sulfate than does cis-pinonic acid (Figure 7.4 and Figure 7.5, respectively):

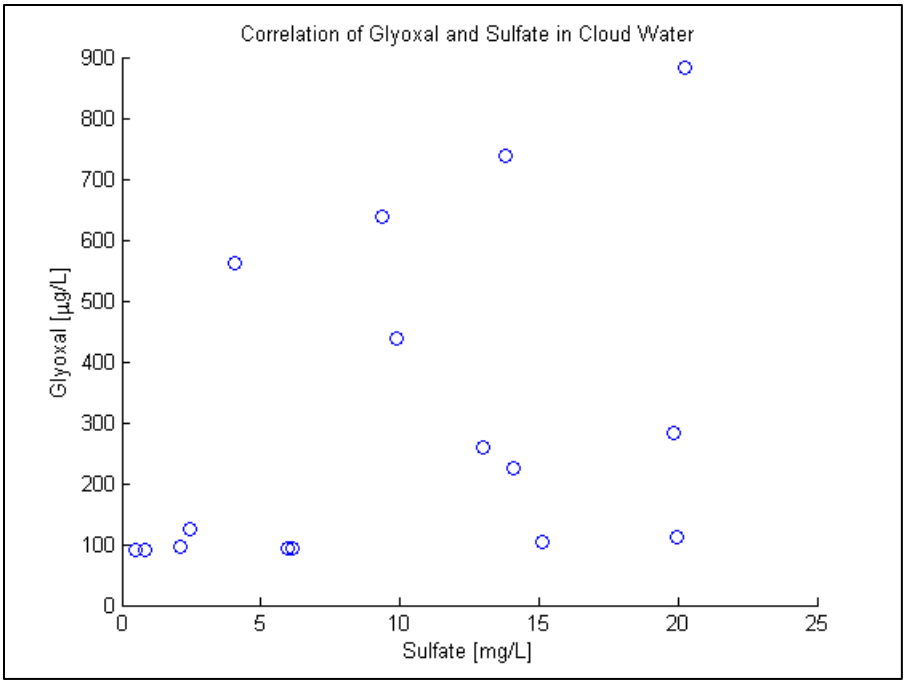

Figure 7.4. Correlation of glyoxal and sulfate in cloud water.

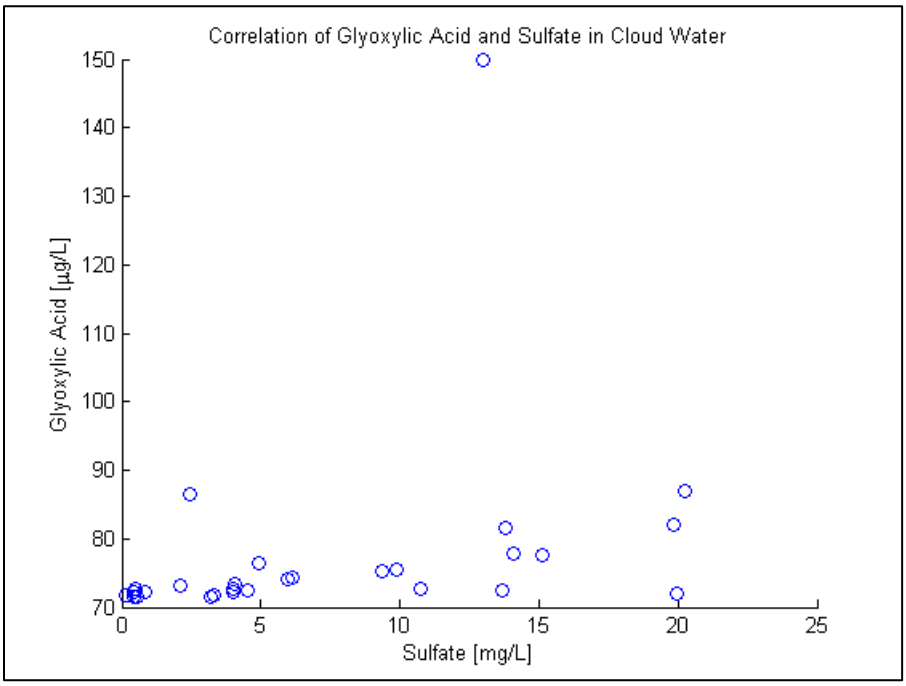

Figure 7.5. Correlation of glyoxylic acid and sulfate in cloud water.

Oxalic acid has the highest correlation with sulfate of the four HPOC (Figure 7.6):

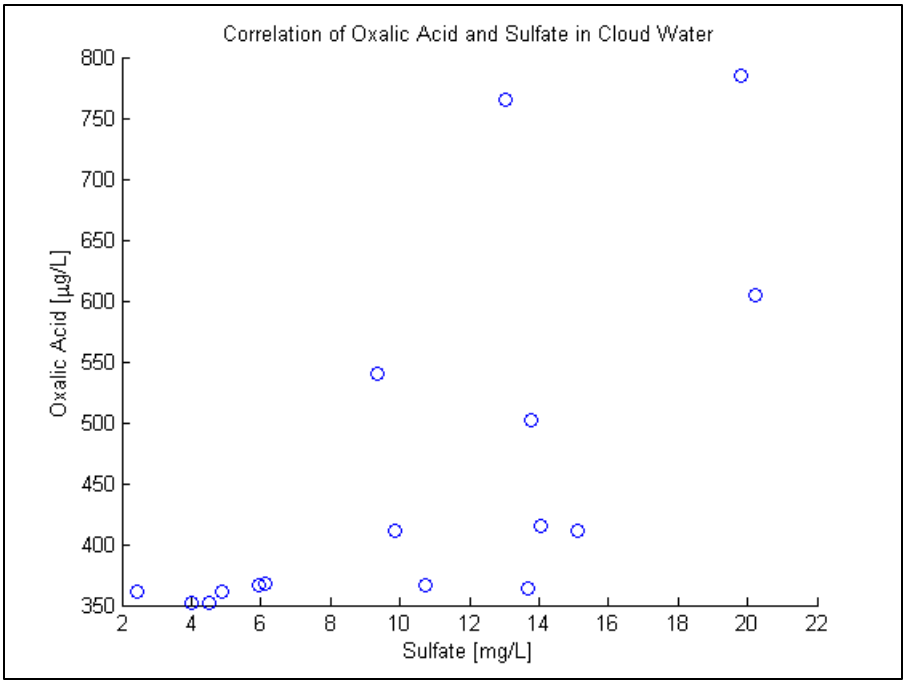

Figure 7.6. Correlation of oxalic acid and sulfate in cloud water.

The correlation coefficients for the four figures just shown are listed in Table 7.2. If the high outlier in the glyoxylic acid plot (~150 µg L^{-1} in Figure 7.5) is removed, the R value for glyoxylic acid increases to 0.54.

Table 7.2. Correlation coefficients for HPOC with sulfate in cloud water.

	R-value
cis-pinonic acid	0.08
glyoxal	0.39
glyoxylic acid	0.32
oxalic acid	0.68

8 Comparison of summer $PM_{2.5}$ and cloud water

HPOC concentrations in the SOAP $PM_{2.5}$ samples were calculated as nanograms of compound per cubic meter of air, while concentrations in the cloud water samples were calculated as ppb, or micrograms of compound per liter of water. The characteristics of HPOC can be compared between the two media by normalizing to another species. For the cloud water samples, only total organic carbon (TOC, which includes carbon species that are dissolved in the water as well as those that remain in particles within the water) is available. For the following comparisons, the HPOC are divided by OC (for the $PM_{2.5}$ samples) and TOC (for the cloud water samples) and multiplied by a conversion factor to make the ratio dimensionless. Additionally, cloud water samples were taken only in the summer months (Appendix D), so only $PM_{2.5}$ summer samples are included in the comparison.

Figure 8.1 and Figure 8.2 show the four HPOC of main interest in the summer SOAP samples and in the cloud water, respectively:

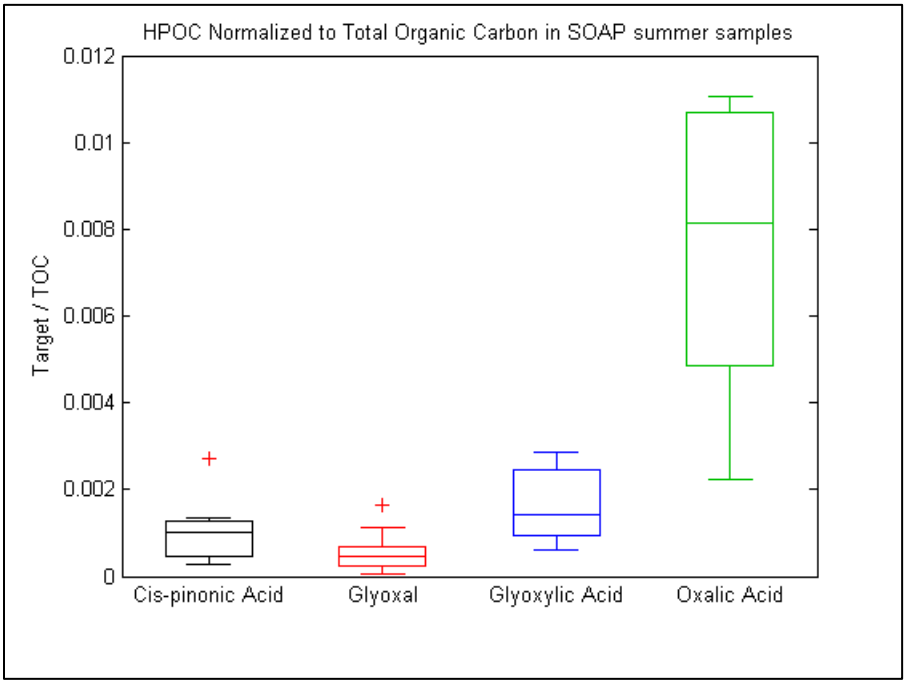

Figure 8.1. HPOC normalized to OC in summer $PM_{2.5}$ samples.

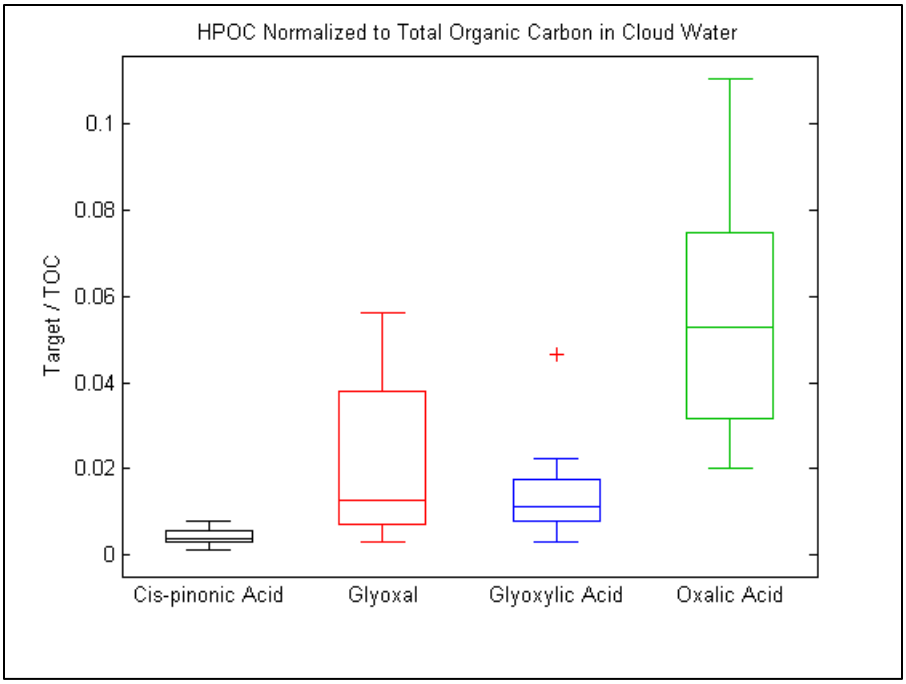

Figure 8.2. HPOC normalized to TOC in cloud water samples.

The first noticeable difference is the order of magnitude. In the cloud water samples, the HPOC make up a much greater fraction (approximately a factor of ten) of the organic carbon than they do in the $PM_{2.5}$ samples. However, the relationship among the four compounds is quite similar between the two media. In both cases, the median values of cis-pinonic acid, glyoxal, and glyoxylic acid are nearly the same, while the median value for oxalic acid is much higher. Clearly oxalic acid's concentration is higher than the others as a result of its place at the end of multiple lines of reactions, including others not studied here. The fact that both media have the four compounds in similar proportions of their organic carbon content suggests that either the same formation mechanisms are present and working at equal rates in both media, or the ratio is more coincidental as different mechanisms dominate between the two media.

As previously discussed, several studies (e.g. Yu et al. [2005], Sorooshian et al. [2006]) have concluded that in-cloud processing is the major formation pathway for oxalic acid. For the two sample sets studied here, the correlation of oxalic acid and

sulfate was noticeably stronger in the cloud water (Table 7.2) than in the PM samples (Table 6.2), lending support to the theory of in-cloud processing as a major production mechanism. Glyoxylic acid was also much more strongly correlated in the cloud water, which suggests that it too may be formed primarily in cloud water.

The strong differences in the correlations with sulfate between the PM samples and the cloud water support the second possibility suggested at the end of the previous section: that the fact that the ratios of the four HPOC are similar between the cloud water and PM is a coincidence.

9 Implications of Findings

9.1 Final thoughts on key scientific questions

The first question to be addressed in this study, as listed in Section 1.4, was:

1. **Which HPOC are present in ambient air samples and cloud water?** Do the two media differ in composition and relative abundance of individual HPOC?

This question forms the basis for the entire study. Full concentration data is listed in Appendix E and Appendix F. A suite of 19 HPOC were identified in both the $PM_{2.5}$ samples and the cloud water samples. Not every compound was found in every sample, whether due to never being present in the sample at all, or simply being unidentifiable or unquantifiable in the chromatograms. In some cases, such as with oxalic acid, it is safe to assume that the compound was indeed present in the sample based on consistent detection in published studies, but for some reason was not detected in this study. For other lesser-studied compounds such as the keto-diacids, it is not as obvious whether the compound was really not present in samples, or whether it was simply difficult to detect.

However, the same compounds were generally present in both media; no major differences were found. The cloud water samples tended to be “spottier” and less consistent than the $PM_{2.5}$ samples, probably as a result of the lower organic carbon content per sample. Had the cloud water samples been pooled in the same manner that the $PM_{2.5}$ samples were, the presence of the compounds seen would likely have been more consistent.

2. **Are HPOC concentrations correlated with EC (elemental carbon), OC (organic carbon), and secondary gas and PM species (ozone and**

sulfate)? Can these correlations, if they exist, be used to estimate HPOC concentrations in samples for which full organic speciation data are not available?

Question 2 asked whether the HPOC are correlated with other bulk species within their sample period. The answer to this question for the samples seems to be generally no. Regarding organic carbon, though the HPOC studied take up a larger fraction of organic carbon in the cloud water than they do in the PM samples, the correlations between the individual compounds and OC on a sample-by-sample basis are unconvincing. Sulfate correlations are only convincing for two of the HPOC in the cloud water, and not convincing at all in the $PM_{2.5}$ samples. Corresponding ozone readings were not available for the cloud water samples.

Additionally, it is important to remember that each $PM_{2.5}$ sample consisted of five or more filters pooled together. The corresponding sulfate and ozone readings for those days were averaged together to create a matching data point. Comparing two data points that are each themselves an average is not the most ideal method of determining correlation, since it could smooth out the effects of higher or lower day-to-day measurements. Unfortunately, there was no other option for studying correlations for the $PM_{2.5}$ filters.

The final question asked about spatial and temporal differences among the $PM_{2.5}$ samples:

3. **Do HPOC concentrations in particulate matter vary significantly by season and site (urban vs. rural)?** If so, can their sources be established, and concentrations predicted?

The answer is a qualified yes. There are definitely differences throughout the year in the concentrations of the compounds studied, but no clear season trends were apparent. From this, it appears that either (a) meteorological factors have more of an influence on concentrations that was previously assumed, or (b) the formation mechanisms for these HPOC are more complicated than previously thought. If neither of these were case, we would expect to see an increase in concentrations of the four target HPOC when normalized to OC in the summer months due to increased photochemical production (the increase would likely not be apparent in concentration data alone, since the increased boundary layer height in the summer would tend to decrease concentrations measured in mass per volume). But since this was not seen, there must be additional factors that are influencing the production of these compounds.

9.2 Air quality, climate change, and public policy

As previously noted, PM is one of the least-understood components of Earth's radiative balance [*IPCC* 2007], and organic compounds are the most complicated part of PM. More work on understanding how the presence of compounds, or classes of compounds in particles affects overall hygroscopicity is necessary to understand how organics in PM may contribute in turn to climate change. Any influence from climate change on the classes of compounds or their concentrations seen in the $PM_{2.5}$ and cloud water samples in this work would not be evident due to the short timescale of a few years (and, in the case of the cloud water, only one summer). Likewise, it is doubtful that any changes in chemical composition over this timescale, even if very pronounced, could be found to cause a change in the radiation balance in the study area, thus influencing climate. It is possible that long-term, high temporal resolution monitoring could help clarify the influence of HPOC on climate and climate change, as well as the role of climate change on HPOC concentrations and speciation.

Furthermore, a greater understanding of the sources of primary PM and the precursors of secondary PM could help lead to regulations on emissions. Though this study focused on quantifying compounds rather than establishing sources, knowing the chemical makeup of PM is a necessary first step to determining how the compounds got there. Research on atmospheric processing of primary organic species, both gas-phase and aqueous phase, is being carried out in both modeling and lab bench studies. If a convincing link is found between the presence of secondary PM and aspects of climate change, particularly undesirable aspects of climate change, such a link could help drive legislation to limit the amount of primary emissions and/or emissions of precursors of secondary PM. Additionally, though beyond the scope of this work, any further research that finds negative impacts of PM on human health, or the health of animals and ecosystems, might inspire such legislation.

9.3 Recommendations for future work

The cloud water project in particular is far from finished. For this study, only one summer's worth of samples was analyzed. This is clearly too short of a time period to identify any long-term trends, so it is highly recommended that samples continue to be collected over future summers so that an overall picture of organics in cloud water may emerge. Samples were also collected in the summer of 2011, which included several samples taken as the remnants of Hurricane Irene passed through upstate New York. There are also many more compounds that could be identified and quantified in cloud water; this study represents only a tiny fraction of those which are present. Additionally, studies on organic compounds in cloud water are few and far between, so there are interesting questions to be answered by comparing HPOC in cloud water from different continents, as well as from different types of sampling sites (mountaintop, aircraft measurements over oceans, etc.).

The filters used in the SOAP project analysis have been consumed, so no further lab work can be performed. However, the project has resulted in a dataset that is atypical among organic samples. Many campaigns focus on short-duration (days to weeks) sampling, with short time intervals between samples as well. However, the long duration of the SOAP campaign captured seasonal cycles at six different sites. This data may be useful to research groups that model particle-phase atmospheric chemistry, as observational data is not readily available in many areas.

Four filters do remain from the SOAP project: these are from July 7, 2002 and were omitted from the composition scheme because the filters from those days picked up many particles produced from wildfires in Quebec. These samples were thus not representative of a “normal” day at any of the four sites and were excluded. The filters themselves look strikingly different from the others used in the SOAP project; while the filters received in this study ranged in color from light gray to solid black, the particles picked up by the filters influenced by the wildfires are brown in appearance. However, the filters could provide valuable information on the organic compounds formed as a result of biomass burning. Three-quarters of each of these filters was previously extracted in an acetone:DCM mixture, but additional compounds might emerge from an extraction cycle in a more polar solvent such as methanol.

Aside from these two specific sample sets, it would be helpful to see more long-term monitoring of organic species in PM samples. Though the laboratory analysis used in this project is time- and labor-intensive, the use of newer technologies such as AMS instruments could assist in getting results more quickly. Since AMS instruments provide fast results, they are frequently used in short-term sampling campaigns, but they would be well-suited to longer-term campaigns as well. Deployment of such instruments simultaneously in and around large megacities would allow for near real-time characterization of organics at a given location and would eliminate the need for

compositing samples, as was necessary with the filters in the SOAP campaign. This would also provide more opportunities to study organic compounds concurrently with meteorological conditions, allowing for robust study of correlations of HPOC compounds with atmospheric variables such as solar radiation, wind direction (important for specific sources), and relative humidity.

10 References

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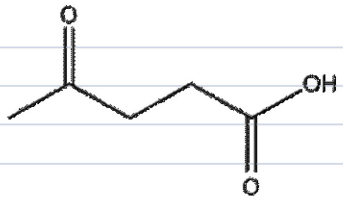
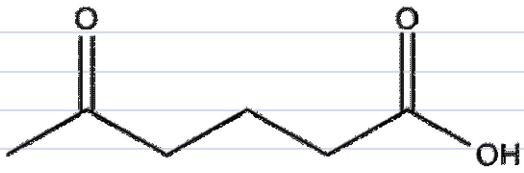
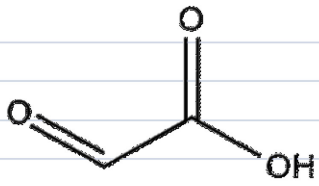
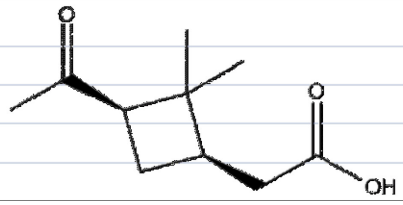
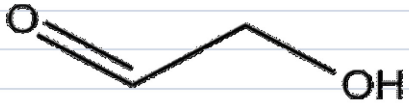
Appendix A Molecular Structures of Target Compounds

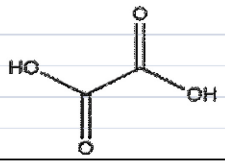
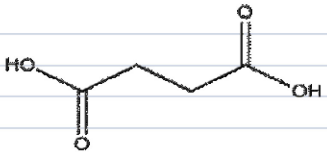
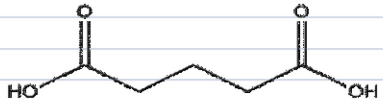
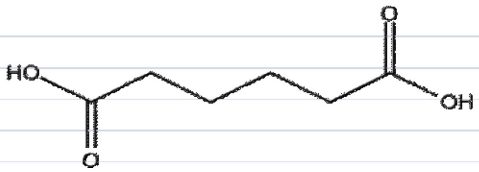
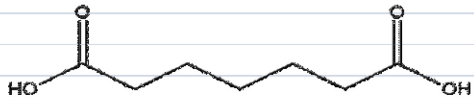
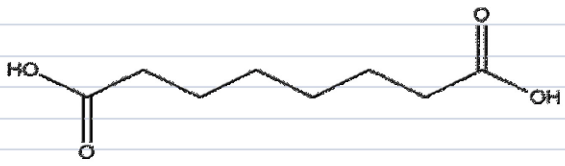
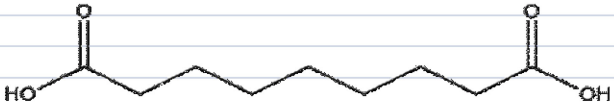
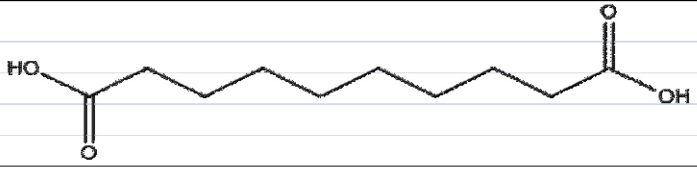
Ketomonoacids

Compound	Formula	Structure
4-oxopentanoic acid	$C_5H_8O_3$	
5-oxohexanoic acid	$C_6H_{10}O_3$	
Glyoxylic acid	$C_4H_6O_4$	
Cis-pinonic acid	$C_{10}H_{16}O_3$	

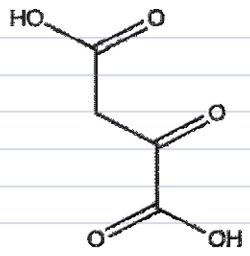
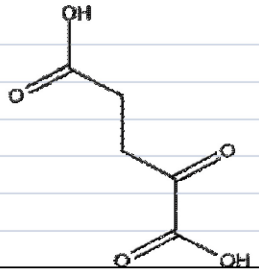
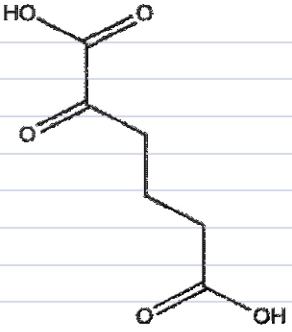
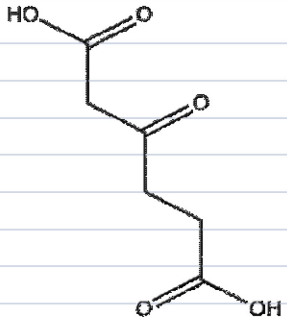
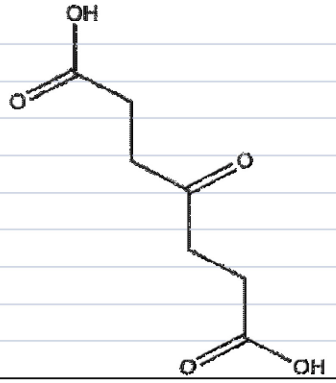
Carbonyls

Compound	Formula	Structure
Glycolaldehyde	$C_2H_4O_2$	
Glyoxal	$C_2H_2O_2$	

Diacids

Compound	Formula	Structure
Oxalic Acid	$C_2H_2O_4$	
Malonic Acid	$C_3H_4O_4$	
Succinic Acid	$C_4H_6O_4$	
Glutaric Acid	$C_5H_8O_4$	
Adipic Acid	$C_6H_{10}O_4$	
Pimelic Acid	$C_7H_{12}O_4$	
Suberic Acid	$C_8H_{14}O_4$	
Azelaic Acid	$C_9H_{16}O_4$	
Sebacic Acid	$C_{10}H_{18}O_4$	

Ketodiacids

Compound	Formula	Structure
α-keto succinic acid	$C_4H_4O_5$	
α-keto glutaric acid	$C_5H_6O_5$	
α-keto adipic acid	$C_6H_8O_5$	
β-keto adipic acid	$C_6H_8O_5$	
γ-keto pimelic acid	$C_7H_{10}O_5$	

Appendix B Limits of Detection and Quantification

Oxo-monoacids	**LOD [ng m^{-3}]**	**LOQ [ng m^{-3}]**
4-oxo pentanoic acid	0.31	0.34
5-oxohexanoic acid	0.31	0.36
glyoxylic acid	0.31	0.34
cis-pinonic acid	0.31	0.35
Diacids (straight-chain)		
oxalic acid	18.4	18.4
malonic acid	25.1	25.1
succinic acid	0.235	0.236
glutaric acid	1.11	1.12
adipic acid	1.20	1.21
pimelic acid	1.29	1.30
suberic acid	1.13	1.14
azelaic acid	1.26	1.26
sebacic acid	1.45	1.46
Oxodiacids		
α-keto succinic acid	2.20	2.22
α-keto glutaric acid	3.87	3.95
α-keto adipic acid	7.51	7.95
β-keto adipic acid	8.68	9.08
γ-keto pimelic acid	2.04	2.12
Diacids (with -OH group(s))		
malic acid	0.00	0.00
Carbonyls (non-acidic)		
glycolaldehyde	2.22	2.22
glyoxal	2.22	2.23

Appendix C Composite Scheme for SOAP filters

	Elz, Qns, Chs	Wpt
early summer	5/26/02	n/a*
	6/1/02	
	6/4/02	
	6/7/02	
	6/10/02	
	7/10/02	
	7/13/02	
	7/16/02	
	7/19/02	

	all sites
summer	7/25/02
	7/28/02
	8/12/02
	8/15/02
	8/18/02
	8/21/02
	8/24/02
	8/27/02

	Elz, Qns, Chs	Wpt
early fall	9/2/02	9/5/02
	9/5/02	9/8/02
	9/8/02	9/14/02
	9/11/02	9/29/02
	9/20/02	11/10/02
	10/5/02	

	all sites
fall	9/26/02
	10/17/02
	10/20/02
	10/23/02
	10/26/02
	10/29/02
	11/13/02

	all sites
late fall	11/1/02
	11/4/02
	11/16/02
	11/19/02
	11/22/02
	11/28/02

	Elz, Qns, Chs	Wpt
early winter	12/4/02	12/4/02
	12/7/02	12/7/02
	12/13/02	12/10/02
	12/19/02	12/13/02
	1/12/03	12/19/02
	2/2/03	1/3/03
		1/6/03
		2/5/03
		2/20/03

	all sites
winter	1/9/03
	1/24/03
	1/30/03
	2/8/03
	2/11/03
	2/14/03
	2/17/03
	2/26/03

	all sites
early spring	3/1/03
	3/4/03
	3/10/03
	3/16/03
	3/19/03
	3/22/03
	3/25/03
	4/6/03
	4/9/03
	4/12/03

	all sites
spring	4/15/03
	4/18/03
	4/24/03
	4/27/03
	4/30/03
	5/3/03
	5/6/03
	5/9/03
	5/12/03
	5/15/03

	12/1/02	
	Qns, Chs, Wpt	Elz
late spring	3/28/03	3/13/03
	3/31/03	5/21/03
	4/3/03	5/24/03
	5/18/03	5/27/03
	5/21/03	5/30/03
	5/24/03	
	5/30/03	

*Problems with the sampler at the Westport resulted in no early spring composite for that site.

The SOAP-NY composite scheme is as follows. There was no difference in sampling days between the Bronx and Pinnacle sites.

Oct. 2005	10/1/05	Mar. 2006	3/6/06	Aug. 2006	8/3/06	Jan. 2007	1/6/07
	10/705		3/12/06		8/9/06		1/12/07
	10/13/05		3/18/06		8/15/06		1/18/07
	10/19/05		3/24/06		8/21/06		1/24/07
	10/25/05		3/30/06		8/27/06		1/30/07
	10/31/05	Apr. 2006	4/5/06	Sept. 2006	9/2/06	Feb. 2007	2/5/07
Nov. 2005	11/6/05		4/11/06		9/8/06		2/11/07
	11/12/05		4/17/06		9/14/06		2/17/07
	11/18/05		4/23/06		9/20/06		2/23/07
	11/24/05		4/29/06		9/26/06		3/1/07
	11/30/05	May 2006	5/5/06	Oct. 2006	10/2/06		
Dec. 2005	12/6/05		5/11/06		10/8/06		
	12/12/05		5/17/06		10/14/06		
	12/18/05		5/23/06		10/20/06		
	12/24/05		5/29/06		10/26/06		
	12/30/05	Jun. 2006	6/4/06	Nov. 2006	11/1/06		
Jan. 2006	1/5/06		6/10/06		11/7/06		
	1/11/06		6/16/06		11/13/06		
	1/17/06		6/22/06		11/19/06		
	1/23/06		6/28/06		11/25/06		
	1/29/06	Jul. 2006	7/4/06	Dec. 2006	12/1/06		
Feb. 2006	2/4/06		7/10/06		12/7/06		
	2/10/06		7/16/06		12/13/06		
	2/16/06		7/22/06		12/19/06		
	2/22/06		7/28/06		12/25/06		
	2/28/06				12/31/06		

Appendix D Cloud Water Sampling Dates and Times

Sample ID	Date Collected	Time Collected (local)	Notes
3001	6/3/2010	3:00 PM	
3009	6/6/2010	12:00 PM	
3010		3:00 PM	
3011		6:00 PM	
3034	6/14/2010	12:00 PM	
3035		3:00 PM	
3039	6/16/2010	3:00 PM	
3046	6/17/2010	12:00 PM	
3065*	6/23/2010	12:00 PM	
3115	7/1/2010	12:00 AM	
3116		3:00 AM	freezing
3121	7/6/2010	12:00 AM	
3123		6:00 AM	
3125	7/8/2010	3:00 AM	
3128		10:00 PM	
3130	7/9/2010	3:00 AM	
3131		8:00 AM	
3171	7/20/2010	10:00 AM	
3172		12:00 PM	
3173		3:00 PM	
3174		6:00 PM	
3177		3:00 AM	
3178		7:00 AM	
3182	7/22/2010	9:00 AM	
3183		12:00 PM	
3202	7/26/2010	9:00 AM	
3203		12:00 PM	
3204		3:00 PM	
3206		4:00 AM	
3207		6:00 AM	
3217	8/2/2010	3:00 AM	
3218		6:00 AM	
3219	8/3/2010	9:00 AM	
3220		12:00 AM	
3221		3:00 AM	
3222		6:00 AM	

3223		9:00 AM	
3224		12:00 PM	
3228	8/4/2010	6:00 AM	
3241	9/8/2010	10:15 AM	rinse
3242		10:20 AM	blank
3343		9:00 PM	
3344		12:00 AM	
3358*	9/13/2010	9:00 PM	
3359*		12:00 AM	
3360*		3:00 AM	
3361*		6:00 AM	
3362*	9/14/2010	9:00 AM	
3368*		3:00 AM	
3369*		6:00 AM	

* Not included in analysis due to unsatisfactory chromatograms.

Appendix E $PM_{2.5}$ Concentration Data

Concentration data for the two SOAP campaigns is given below. Unless otherwise stated, all data is in ng m^{-3}.

	Elz 21 early summer	Elz 24 summer	Elz 28 early fall	Elz 32 fall	Elz 36 late fall
Keto-monoacids					
4-oxo pentanoic acid	2.2	0.8	3.2	1.9	1.8
5-oxohexanoic acid (b)	1.6	0.0	2.4	1.9	1.9
glyoxylic acid	3.8	4.4	6.1	5.0	4.8
cis-pinonic acid (b)	1.8	0.0	3.0	2.3	2.2
Diacids					
oxalic acid	14.2	0.0	21.8	0.0	17.8
malonic acid	0.0	0.0	7.3	0.0	0.0
succinic acid	0.4	0.2	0.8	0.3	0.3
glutaric acid	0.8	0.8	1.2	1.0	0.9
adipic acid	0.8	0.9	1.2	1.0	1.0
pimelic acid	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	0.0	0.0	0.9	0.0
azelaic acid	0.8	0.9	1.3	1.0	1.0
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	5.9	6.5	9.0	7.4	7.1
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	6.6	13.2	0.0
gamma-keto pimelic acid	1.5	2.6	0.0	2.4	0.0
Carbonyls					
glycolaldehyde	3.2	3.5	4.9	4.2	4.0
glyoxal	0.5	1.8	2.7	2.6	0.6
OC total [ug/m3]*	6.3	5.9	3.2	3.3	3.6
EC total [ug/m3]*	1.5	1.8	1.3	1.4	0.9
PM2.5 [ug/m3]*	17.9	20.2	11.4	10.5	15.4
sulfate [ug/m3]*	5.0	5.9	3.4	2.2	3.2
ozone [ppm]*	n/a	n/a	n/a	n/a	n/a

	Elz 41 early winter	Elz 45 winter	Elz 49 early spring	Elz 53 spring	Elz 57 late spring
Keto-monoacids					
4-oxo pentanoic acid	1.9	0.0	0.7	1.3	2.8
5-oxohexanoic acid (b)	2.2	0.0	0.7	1.3	2.8
glyoxylic acid	5.7	0.0	0.0	3.8	7.2
cis-pinonic acid (b)	5.7	0.0	0.0	3.3	3.3
Diacids					
oxalic acid	0.0	0.0	0.0	0.0	25.9
malonic acid	0.0	0.0	0.0	0.0	0.0
succinic acid	0.3	0.0	0.1	0.1	1.0
glutaric acid	1.1	0.0	0.6	0.6	1.4
adipic acid	1.2	0.0	0.7	0.7	1.4
pimelic acid	0.0	0.0	0.0	0.0	0.0
suberic acid	1.1	0.0	0.0	0.0	0.0
azelaic acid	1.2	0.0	0.7	0.7	1.5
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	20.0	6.5	5.0	12.1	10.1
alpha keto adipic acid	7.7	0.0	4.7	0.0	0.0
beta keto adipic acid	5.8	0.0	8.6	3.6	0.0
gamma-keto pimelic acid	2.0	0.0	1.3	1.4	2.5
Carbonyls					
glycolaldehyde	4.5	3.8	2.8	2.8	5.9
glyoxal	2.4	6.1	1.7	1.7	1.1
OC total [ug/m3]*	5.8	5.0	4.0	4.1	4.9
EC total [ug/m3]*	1.5	1.0	0.9	1.2	1.4
PM2.5 [ug/m3]*	20.4	22.3	14.1	16.7	20.4
sulfate [ug/m3]*	4.0	3.9	3.3	3.6	5.1
ozone [ppm]*	n/a	n/a	n/a	n/a	n/a

	Qns 22 early summer	Qns 25 summer	Qns 29 early fall	Qns 33 fall	Qns 37 late fall
Keto-monoacids					
4-oxo pentanoic acid	4.0	1.6	0.0	2.2	2.6
5-oxohexanoic acid (b)	1.9	0.0	0.0	1.0	2.0
glyoxylic acid	4.4	4.8	0.0	5.0	6.1
cis-pinonic acid (b)	2.0	0.0	0.0	2.3	2.4
Diacids					
oxalic acid	18.0	0.0	0.0	0.0	22.6
malonic acid	0.0	0.0	0.0	0.0	0.0
succinic acid	1.1	0.2	0.0	0.5	0.6
glutaric acid	1.0	0.8	0.0	0.0	1.0
adipic acid	0.9	0.9	0.0	1.0	1.0
pimelic acid	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	0.8	0.0	0.0	0.0
azelaic acid	0.9	0.9	0.0	0.0	1.1
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	7.2	0.0	0.0	7.7	8.2
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	5.1	2.5	0.0	0.0	1.8
Carbonyls					
glycolaldehyde	6.1	3.4	0.0	4.2	5.4
glyoxal	5.0	1.7	0.0	3.0	4.1
OC total [ug/m3]*	4.4	4.3	3.1	2.6	3.6
EC total [ug/m3]*	0.6	0.6	0.6	0.6	0.7
PM2.5 [ug/m3]*	15.7	14.7	12.8	7.0	12.7
sulfate [ug/m3]*	4.7	5.0	2.7	2.0	3.0
ozone [ppm]*	0.1	0.0	0.0	0.0	0.0

	Qns 42 early winter	Qns 46 winter	Qns 50 early spring	Qns 54 spring	Qns 58 late spring
Keto-monoacids					
4-oxo pentanoic acid	2.3	1.6	1.4	1.1	1.2
5-oxohexanoic acid (b)	2.3	1.7	1.4	0.7	0.9
glyoxylic acid	5.6	4.2	3.4	3.4	4.8
cis-pinonic acid (b)	5.6	4.2	1.6	1.5	2.1
Diacids					
oxalic acid	0.0	0.0	12.8	0.0	0.0
malonic acid	0.0	0.0	0.0	0.0	0.0
succinic acid	0.5	0.0	0.4	0.2	0.2
glutaric acid	1.2	0.8	0.7	0.0	0.8
adipic acid	1.2	0.9	0.7	0.6	0.9
pimelic acid	0.0	0.0	0.0	0.0	0.0
suberic acid	1.1	0.8	0.6	0.0	0.0
azelaic acid	1.3	0.9	0.7	0.7	1.0
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	8.3	6.3	5.0	11.6	0.0
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	3.3	11.8
gamma-keto pimelic acid	0.0	1.5	1.2	1.1	2.9
Carbonyls					
glycolaldehyde	4.8	3.6	2.7	2.7	3.5
glyoxal	0.5	0.6	0.4	1.5	1.3
OC total [ug/m3]*	4.7	3.0	2.9	3.2	3.8
EC total [ug/m3]*	1.0	0.5	0.5	0.6	0.6
PM2.5 [ug/m3]*	17.4	13.6	11.9	9.5	12.6
sulfate [ug/m3]*	3.7	3.1	3.6	2.6	4.2
ozone [ppm]*	0.0	0.0	0.0	0.0	0.0

	Chs 23 early summer	Chs 27 summer	Chs 31 early fall	Chs 35 fall	Chs 39 late fall
Keto-monoacids					
4-oxo pentanoic acid	1.3	1.4	4.0	3.5	1.7
5-oxohexanoic acid (b)	0.7	0.0	2.6	2.1	1.8
glyoxylic acid	3.6	3.9	5.3	4.6	4.5
cis-pinonic acid (b)	1.6	3.8	6.6	5.2	4.4
Diacids					
oxalic acid	0.0	0.0	0.0	17.4	16.8
malonic acid	4.6	0.0	0.0	0.0	0.0
succinic acid	0.2	0.0	1.6	1.0	0.3
glutaric acid	0.0	0.0	1.6	1.1	0.9
adipic acid	0.0	0.8	1.4	1.1	0.9
pimelic acid	0.0	0.0	1.3	1.0	1.0
suberic acid	0.0	0.0	1.1	1.0	0.0
azelaic acid	0.0	0.0	1.4	1.2	1.0
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	5.4	6.1	8.2	6.9	6.7
alpha keto adipic acid	0.0	0.0	11.1	9.5	0.0
beta keto adipic acid	3.8	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	1.3	0.0	10.9	3.5	1.6
Carbonyls					
glycolaldehyde	3.1	3.7	5.5	5.2	3.8
glyoxal	1.0	1.7	2.1	1.7	0.6
OC total [ug/m3]*	4.3	3.7	2.1	2.2	1.9
EC total [ug/m3]*	0.2	0.2	0.1	0.2	0.2
PM2.5 [ug/m3]*	8.7	x	10.0	6.1	6.3
sulfate [ug/m3]*	5.6	x	3.7	2.0	2.0
ozone [ppm]*	0.1	0.1	0.1	0.0	0.0

	Chs 44 early winter	Chs 48 winter	Chs 52 early spring	Chs 56 spring	Chs 60 late spring
Keto-monoacids					
4-oxo pentanoic acid	1.9	1.4	1.5	1.2	2.0
5-oxohexanoic acid (b)	2.1	1.6	1.3	1.3	1.9
glyoxylic acid	5.2	4.0	3.4	3.2	4.8
cis-pinonic acid (b)	2.4	3.9	1.5	3.1	2.3
Diacids					
oxalic acid	19.7	0.0	0.0	11.9	19.8
malonic acid	0.0	5.0	4.1	0.0	5.9
succinic acid	0.3	0.2	0.2	0.3	0.4
glutaric acid	1.0	0.8	0.6	0.6	1.0
adipic acid	1.1	0.8	0.7	0.7	1.0
pimelic acid	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	0.0	0.6	0.0	0.0
azelaic acid	0.0	0.9	0.7	0.7	1.0
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	7.8	5.9	11.4	4.7	16.9
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	4.2	8.5	0.0	12.2
gamma-keto pimelic acid	1.8	1.4	1.4	1.1	6.3
Carbonyls					
glycolaldehyde	4.2	3.2	2.6	2.6	3.7
glyoxal	0.5	0.8	1.5	0.2	3.0
OC total [ug/m3]*	2.4	3.1	2.2	2.4	2.4
EC total [ug/m3]*	0.3	0.6	0.2	0.2	0.1
PM2.5 [ug/m3]*	11.6	7.4	9.4	9.5	11.5
sulfate [ug/m3]*	3.3	3.1	3.0	2.5	3.5
ozone [ppm]*	0.0	0.0	0.0	0.0	0.0

	Wpt 26 summer	Wpt 30 early fall	Wpt 34 fall	Wpt 38 late fall	Wpt 43 early winter
Keto-monoacids					
4-oxo pentanoic acid	1.7	3.6	2.9	0.0	0.7
5-oxohexanoic acid (b)	1.6	2.7	2.0	0.0	0.0
glyoxylic acid	4.6	6.8	5.0	0.0	0.0
cis-pinonic acid (b)	3.9	3.4	2.4	0.0	1.7
Diacids					
oxalic acid	0.0	0.0	0.0	0.0	0.0
malonic acid	5.1	0.0	0.0	0.0	0.0
succinic acid	0.3	0.8	0.5	0.0	0.0
glutaric acid	0.8	1.4	1.0	0.0	0.0
adipic acid	0.8	1.4	1.0	0.0	0.0
pimelic acid	0.0	1.4	0.0	0.0	0.0
suberic acid	0.0	0.0	0.9	0.0	0.0
azelaic acid	0.9	1.4	1.1	0.0	0.0
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	0.0	0.0	0.0	0.0
alpha keto glutaric acid	14.5	10.4	6.9	0.0	5.2
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	10.3	0.0	13.1	0.0	0.0
gamma-keto pimelic acid	3.0	2.9	2.7	0.0	0.0
Carbonyls					
glycolaldehyde	3.1	5.9	4.8	0.0	3.0
glyoxal	2.1	3.1	5.7	58.6	3.6
OC total [ug/m3]*	3.3	3.3	2.7	2.7	4.5
EC total [ug/m3]*	0.4	0.4	0.4	0.4	0.7
PM2.5 [ug/m3]*	10.6	9.6	6.9	9.8	13.0
sulfate [ug/m3]*	3.1	2.6	1.7	2.6	3.3
ozone [ppm]*	0.1	NaN	NaN	NaN	NaN

	Wpt 47 winter	Wpt 51 early spring	Wpt 55 spring	Wpt 59 late spring
Keto-monoacids				
4-oxo pentanoic acid	1.4	1.4	1.3	1.8
5-oxohexanoic acid (b)	1.6	1.3	1.3	1.8
glyoxylic acid	4.0	3.3	3.5	4.6
cis-pinonic acid (b)	1.8	1.5	3.8	2.1
Diacids				
oxalic acid	0.0	0.0	0.0	17.5
malonic acid	0.0	0.0	4.0	0.0
succinic acid	0.2	0.3	0.2	0.4
glutaric acid	0.7	0.6	0.6	0.9
adipic acid	0.8	0.7	0.7	0.9
pimelic acid	0.0	0.0	0.0	0.0
suberic acid	0.0	0.0	0.6	0.0
azelaic acid	0.8	0.0	0.7	1.0
sebacic acid	0.0	0.0	0.0	0.0
Keto-diacids				
alpha keto succinic acid	0.0	0.0	0.0	0.0
alpha keto glutaric acid	5.9	4.8	5.0	6.8
alpha keto adipic acid	0.0	0.0	0.0	0.0
beta keto adipic acid	9.9	0.0	9.0	0.0
gamma-keto pimelic acid	1.4	1.1	2.0	1.7
Carbonyls				
glycolaldehyde	3.2	4.4	2.7	3.9
glyoxal	1.4	2.8	4.3	0.9
OC total [ug/m3]*	3.0	3.4	2.4	2.9
EC total [ug/m3]*	0.3	0.3	0.3	0.4
PM2.5 [ug/m3]*	12.1	10.1	7.1	10.4
sulfate [ug/m3]*	3.0	3.3	2.1	3.5
ozone [ppm]*	NaN	NaN	NaN	0.0

*Data provided by state agencies and Sunset Labs.

Appendix F Cloud Water Concentration Data

Cloud water sample names are listed at the top of each column; the corresponding date and time of collection can be found in Appendix D. Units are ppb, or μg L^{-1}.

	3001	3009	3010	3011	3034	3035
Keto-monoacids						
4-oxopentanoic acid	14.3	14.3	0.0	0.0	24.2	25.0
5-oxohexanoic acid	15.2	0.0	0.0	0.0	0.0	0.0
glyoxylic acid	73.0	0.0	0.0	0.0	71.6	72.3
cis-pinonic acid	0.0	0.0	0.0	0.0	33.3	37.3
Diacids						
oxalic acid	0.0	0.0	0.0	0.0	0.0	0.0
malonic acid	0.0	0.0	0.0	0.0	0.0	0.0
succinic acid	32.0	16.5	1.9	1.2	4.1	3.5
glutaric acid	15.2	13.4	0.0	0.0	13.7	13.9
adipic acid	15.2	14.6	12.0	0.0	13.0	0.0
pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
suberic acid	12.6	0.0	0.0	0.0	0.0	0.0
azelaic acid	14.5	13.1	0.0	0.0	0.0	0.0
sebacic acid	0.0	0.0	0.0	0.0	0.0	0.0
Keto-diacids						
alpha keto succinic acid	33.1	0.0	0.0	0.0	27.6	31.0
alpha keto glutaric acid	0.0	0.0	0.0	0.0	0.0	0.0
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
Carbonyls						
glycolaldehyde	70.0	71.7	26.6	27.2	26.6	70.1
glyoxal	95.4	0.0	0.0	0.0	0.0	0.0

	3039	3046	3065	3115	3116	3121
Keto-monoacids						
4-oxopentanoic acid	24.3	28.0	n/a	0.0	0.0	24.3
5-oxohexanoic acid	0.0	0.0	n/a	0.0	0.0	0.0
glyoxylic acid	73.4	86.6	n/a	0.0	0.0	72.5
cis-pinonic acid	36.9	70.2	n/a	0.0	0.0	0.0
Diacids						
oxalic acid	0.0	361.0	n/a	0.0	0.0	364.3
malonic acid	0.0	0.0	n/a	0.0	0.0	0.0
succinic acid	5.5	23.5	n/a	1.3	0.0	6.1
glutaric acid	12.5	19.1	n/a	0.0	0.0	16.3
adipic acid	0.0	38.4	n/a	12.5	0.0	15.6
pimelic acid	0.0	0.0	n/a	13.1	0.0	0.0
suberic acid	0.0	20.9	n/a	0.0	0.0	0.0
azelaic acid	0.0	23.4	n/a	0.0	0.0	15.8
sebacic acid	0.0	0.0	n/a	0.0	0.0	0.0
Keto-diacids						
alpha keto succinic acid	31.9	82.1	n/a	0.0	0.0	32.0
alpha keto glutaric acid	0.0	0.0	n/a	0.0	0.0	0.0
alpha keto adipic acid	0.0	0.0	n/a	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	n/a	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	n/a	0.0	0.0	0.0
Carbonyls						
glycolaldehyde	70.3	71.3	n/a	26.7	0.0	70.1
glyoxal	561.9	125.0	n/a	0.0	0.0	0.0

	3123	3125	3128	3130	3131	3171U
Keto-monoacids						
4-oxopentanoic acid	24.6	29.7	31.5	29.8	49.0	24.1
5-oxohexanoic acid	0.0	0.0	0.0	0.0	0.0	0.0
glyoxylic acid	76.5	82.0	77.5	86.9	149.8	72.6
cis-pinonic acid	36.3	74.4	0.0	33.6	0.0	36.4
Diacids						
oxalic acid	360.9	784.3	411.4	604.6	765.4	351.3
malonic acid	0.0	0.0	0.0	0.0	0.0	0.0
succinic acid	6.2	8.8	14.0	23.8	10.3	10.2
glutaric acid	17.9	21.6	17.2	18.3	25.2	13.9
adipic acid	41.5	16.3	20.4	26.3	26.7	18.6
pimelic acid	16.0	0.0	0.0	0.0	0.0	13.1
suberic acid	27.6	0.0	0.0	0.0	0.0	12.9
azelaic acid	33.3	19.6	21.6	28.7	31.2	15.3
sebacic acid	17.1	0.0	0.0	0.0	0.0	0.0
Keto-diacids						
alpha keto succinic acid	36.3	44.7	53.4	68.4	68.7	29.5
alpha keto glutaric acid	0.0	0.0	159.9	182.0	313.3	0.0
alpha keto adipic acid	0.0	155.1	0.0	156.1	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
Carbonyls						
glycolaldehyde	26.6	71.1	70.4	71.1	141.4	26.6
glyoxal	0.0	281.9	104.9	883.4	260.3	0.0

	3172U	3173 U	3174U	3177U	3178U	3182U
Keto-monoacids						
4-oxopentanoic acid	14.5	0.0	23.9	25.1	24.5	0.0
5-oxohexanoic acid	0.0	0.0	0.0	0.0	0.0	0.0
glyoxylic acid	72.5	0.0	71.9	72.1	72.6	71.7
cis-pinonic acid	0.0	0.0	0.0	33.8	35.5	0.0
Diacids						
oxalic acid	352.2	0.0	0.0	0.0	0.0	0.0
malonic acid	0.0	0.0	0.0	0.0	0.0	0.0
succinic acid	4.9	0.0	5.4	2.8	3.4	0.9
glutaric acid	12.7	0.0	12.1	12.0	16.3	0.0
adipic acid	14.0	0.0	12.4	12.0	30.4	11.5
pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	0.0	0.0	0.0	0.0	0.0
azelaic acid	14.1	0.0	13.1	14.2	0.0	16.1
sebacic acid	0.0	0.0	0.0	0.0	0.0	0.0
Keto-diacids						
alpha keto succinic acid	29.7	0.0	28.3	30.6	36.1	27.9
alpha keto glutaric acid	0.0	0.0	0.0	0.0	0.0	0.0
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
Carbonyls						
glycolaldehyde	26.6	0.0	26.6	70.2	70.3	70.1
glyoxal	0.0	0.0	0.0	91.5	90.7	0.0

	3183U	3202U	3203U	3204U	3206U	3207U
Keto-monoacids						
4-oxopentanoic acid	0.0	14.4	0.0	24.7	0.0	0.0
5-oxohexanoic acid	0.0	0.0	0.0	15.8	0.0	0.0
glyoxylic acid	0.0	71.5	71.5	72.3	0.0	71.5
cis-pinonic acid	36.3	0.0	33.4	0.0	70.4	0.0
Diacids						
oxalic acid	0.0	0.0	0.0	0.0	0.0	0.0
malonic acid	0.0	0.0	0.0	0.0	0.0	0.0
succinic acid	1.7	1.3	2.1	1.8	2.3	2.3
glutaric acid	11.0	11.0	14.2	13.7	11.7	11.2
adipic acid	0.0	11.9	14.2	13.8	12.3	12.1
pimelic acid	0.0	0.0	19.7	16.1	0.0	0.0
suberic acid	0.0	0.0	0.0	0.0	0.0	0.0
azelaic acid	12.6	17.2	24.3	29.1	13.5	13.7
sebacic acid	0.0	0.0	0.0	0.0	0.0	0.0
Keto-diacids						
alpha keto succinic acid	27.5	28.1	27.7	30.0	0.0	27.3
alpha keto glutaric acid	0.0	0.0	0.0	0.0	0.0	0.0
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
Carbonyls						
glycolaldehyde	0.0	26.6	70.0	70.2	26.6	26.6
glyoxal	0.0	0.0	0.0	0.0	0.0	0.0

	3217U	3218U	3219U	3220U	3221U	3222U
Keto-monoacids						
4-oxopentanoic acid	27.1	25.0	24.3	24.6	24.7	25.6
5-oxohexanoic acid	0.0	0.0	0.0	0.0	0.0	0.0
glyoxylic acid	81.7	75.5	75.2	77.8	74.2	74.0
cis-pinonic acid	34.6	34.6	33.5	33.7	33.5	0.0
Diacids						
oxalic acid	501.4	411.3	540.3	415.1	367.6	366.3
malonic acid	0.0	0.0	0.0	0.0	0.0	0.0
succinic acid	13.2	7.2	7.6	7.7	3.0	4.1
glutaric acid	17.4	14.1	15.7	14.2	11.6	11.5
adipic acid	13.9	12.6	12.8	14.1	13.5	12.7
pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	0.0	0.0	0.0	0.0	0.0
azelaic acid	17.6	0.0	0.0	17.2	15.2	14.2
sebacic acid	0.0	0.0	0.0	0.0	0.0	0.0
Keto-diacids						
alpha keto succinic acid	49.4	34.0	34.1	42.6	34.0	31.9
alpha keto glutaric acid	160.3	155.5	0.0	157.1	0.0	153.7
alpha keto adipic acid	153.7	0.0	0.0	0.0	152.6	0.0
beta keto adipic acid	80.2	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	0.0	0.0	0.0	0.0
Carbonyls						
glycolaldehyde	71.0	70.3	70.4	70.5	70.1	70.1
glyoxal	739.0	438.4	639.4	224.1	93.3	93.8

	3223U	3224	3228	3343	3344
Keto-monoacids					
4-oxopentanoic acid	0.0	0.0	14.3	0.0	0.0
5-oxohexanoic acid	0.0	0.0	0.0	0.0	0.0
glyoxylic acid	0.0	71.9	72.7	0.0	0.0
cis-pinonic acid	0.0	0.0	0.0	0.0	0.0
Diacids					
oxalic acid	0.0	0.0	366.7	0.0	0.0
malonic acid	0.0	0.0	0.0	0.0	0.0
succinic acid	0.0	1.2	3.2	1.5	1.3
glutaric acid	0.0	0.0	11.5	0.0	0.0
adipic acid	0.0	0.0	11.8	11.3	0.0
pimelic acid	0.0	0.0	0.0	0.0	0.0
suberic acid	0.0	0.0	0.0	0.0	0.0
azelaic acid	0.0	0.0	0.0	0.0	0.0
sebacic acid	0.0	0.0	0.0	0.0	0.0
Keto-diacids					
alpha keto succinic acid	0.0	39.3	30.2	0.0	0.0
alpha keto glutaric acid	0.0	0.0	0.0	0.0	0.0
alpha keto adipic acid	0.0	0.0	0.0	0.0	0.0
beta keto adipic acid	0.0	0.0	0.0	0.0	0.0
gamma-keto pimelic acid	0.0	0.0	0.0	0.0	0.0
Carbonyls					
glycolaldehyde	0.0	70.2	70.0	0.0	0.0
glyoxal	0.0	112.4	0.0	0.0	0.0

Cloud water blank data:

	3241 rinse	3242 blank
Keto-monoacids		
4-oxopentanoic acid	0.0	0.0
5-oxohexanoic acid	0.0	0.0
glyoxylic acid	0.0	0.0
cis-pinonic acid	0.0	0.0
Diacids		
oxalic acid	0.0	0.0
malonic acid	0.0	0.0
succinic acid	1.4	1.6
glutaric acid	0.0	0.0
adipic acid	0.0	0.0
pimelic acid	0.0	0.0
suberic acid	0.0	0.0
azelaic acid	0.0	0.0
sebacic acid	0.0	0.0
Keto-diacids		
alpha keto succinic acid	0.0	0.0
alpha keto glutaric acid	0.0	0.0
alpha keto adipic acid	0.0	0.0
beta keto adipic acid	0.0	0.0
gamma-keto pimelic acid	0.0	0.0
Carbonyls		
glycolaldehyde	26.6	0.0
glyoxal	0.0	0.0