Connecting Cloud Water Inorganic and Organic Chemical Composition at Whiteface Mountain

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Connecting Cloud Water Inorganic and Organic Chemical Composition at Whiteface Mountain

Summary Report

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Abstract

The research reported here investigated Whiteface Mountain cloud water molecular composition with a focus on sulfur and nitrogen-containing organic compounds that influence acidic deposition in the Adirondack Mountains. To our knowledge, this study represents the first identification of high-molecular weight organic compounds—measured by electrospray ionization coupled with ultrahigh resolution mass spectrometry—in cloud water at Whiteface Mountain. The unique data were combined with routine monitoring data by the Adirondack Lakes Survey Corporation for cloud water inorganic ion concentrations, total organic carbon concentrations, and pH. Combined with air mass trajectory modeling and satellite-based wildfire imagery, the chemical data showed influences of Canadian wildfire emissions, urban air pollution, and trace gas emissions from forests on the composition and acidity of summertime Whiteface Mountain cloud water. Cloud water acidity was positively correlated with the average oxygen: carbon ratio of the high-molecular weight organic compounds. Individual organic compound tracers showed evidence of aqueous-phase reactions that changed the composition of the cloud water, particularly the formation of sulfur-containing and oligomeric compounds. Overall, the cloud water molecular composition depended on air mass source influence and reflected aqueous-phase reactions involving biogenic, urban, and wildfire precursors.

Keywords

Whiteface Mountain, cloud water, sulfur, nitrogen, organic
Acknowledgments

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1 Context

Similar to sulfate formation upon dissolution and oxidation of sulfur dioxide (SO₂) in cloud droplets (Mohnen and Kadlecck, 1989), water-soluble organic gases can also be incorporated into cloud droplets and undergo aqueous reactions (Blando and Turpin, 2000). Aqueous reactions have been suggested as an important source of organic matter in the atmosphere (Ervens et al., 2015; Herrmann et al., 2015). However, only limited evidence of cloud-phase reactions involving high-molecular weight organic compounds has been reported (Boone et al., 2015; Feng and Möller, 2004; Lee et al., 2011, 2012; Pratt et al., 2013; Sagona et al., 2014; van Pinxteren et al., 2016; Zhao et al., 2013). Therefore, an examination of high-molecular weight organic compounds present in cloud water is crucial to improve our current understanding of air quality and deposition of material to the ecosystem.

Laboratory studies have shown that aqueous-phase reactions can lead to the formation of organonitrate and organosulfate compounds (Darer et al., 2011; Minerath et al., 2008; Minerath and Elrod, 2009; Perri et al., 2010), which change the fate of particle-phase nitrate and sulfate. Organosulfates are suggested to be formed from acid-catalyzed reactive uptake of epoxides onto sulfate aerosol (Surratt et al., 2010), as well as in-cloud radical-radical reactions involving sulfate radicals (Nozière et al., 2010; Perri et al., 2010; Schindelka et al., 2013).

Aqueous-phase processes may also produce high-molecular weight compounds, such as oligomers (Ervens et al., 2011). Laboratory studies have shown the production of oligomers in bulk aqueous solutions from the photochemical oxidation of smaller organic compounds (Ervens et al., 2011). Oligomers have been observed in ambient cloud water (Boone et al., 2015; Pratt et al., 2013; Zhao et al., 2013); however, oligomer formation is expected to be favored in aqueous aerosol, compared to cloud droplets (Ervens et al., 2011). Yet, with few studies reporting the molecular composition of high-molecular weight compounds, it is difficult to assess the potential importance of these aqueous-phase derived compounds and their impacts on organic aerosol composition and wet deposition to ecosystems (Hallquist et al., 2009).
Whiteface Mountain in New York State has a long history of cloud water monitoring and studies. An in-depth summary of cloud water studies on Whiteface Mountain has been published elsewhere (Schwab et al., 2016a). Whiteface Mountain cloud water is more acidic than rainwater with its higher sulfate and nitrate concentrations (Aleksic et al., 2009), which are attributed to fossil fuel combustion (Dukett et al., 2011). Cloud deposition of total soluble sulfur accounts for 80–90% of total sulfur deposition during June–September (Baumgardner et al., 2003).
### 2 Objectives

The objectives of this study were to investigate the presence of sulfur- and nitrogen-containing organic compounds and aqueous-phase reactions that impact sulfate and nitrate concentrations in cloud water at Whiteface Mountain, NY. This work focuses on cloud water samples that were collected during August–September 2014 that provided an opportunity to investigate biogenic, wildfire, and urban-influenced air masses, providing a variety of precursor gases and particles to influence cloud water composition. We sought to answer two specific research questions:

- Are sulfur- and nitrogen-containing organic compounds present in summertime cloud water at Whiteface Mountain, and if so, what is their molecular composition?
- How does the presence of these compounds depend on air mass source and cloud water inorganic ion and total organic carbon concentrations, as well as pH?
3 Whiteface Mountain Cloud Water Collection and Analysis

Cloud water samples were collected during August–September 2014 at Whiteface Mountain (44.3659° N, 73.9026° W; summit observatory 1483 m above mean sea level [AMSL]) in the Adirondack Mountains in New York State. An in-depth site description is published elsewhere (Schwab et al., 2016b). Sampling times are provided in Table 1. Cloud water collection and analysis efforts by the Adirondack Lakes Survey Corporation (ALSC) closely follow the original guidelines established by the Environmental Protection Agency’s (EPA) Clean Air Status and Trends Network (CASTnet) program in 1994. An omni-direction passive collector (Aleksic and Dukett, 2010) collected cloud water samples when the following conditions were met: cloud liquid water content > 0.05 g m⁻³ (to indicate the presence of clouds); temperature > 2°C (to avoid freezing of the sampler); wind speed > 2 m s⁻¹ (to assist with cloud water collection by the sampler); and no precipitation (to isolate cloud droplets only). A field blank was collected at the summit of Whiteface Mountain by pouring deionized water into a sample container. Routine analyses of inorganic ions (SO₄²⁻, NO₃⁻, Cl⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺, NH₄⁺), pH, and TOC are performed by the ALSC, as described elsewhere (Baumgardner et al., 2003). Average August–September values of TOC and SO₄²⁻ from 2010–2015 are presented in Table 2. Visit http://www.adirondacklakessurvey.org to access the data.

Table 1. Summary of Sampling Times and Inorganic Ion, pH, and TOC Concentrations for Cloud Water Samples from Whiteface Mountain Observatory

Cloud water samples were collected with 3 h resolution (local time: EDT). Values below the method limit of detection for Na⁺ are noted as “bdl.” Ninety-five percent confidence intervals are shown for August–September 2014 averages.

<table>
<thead>
<tr>
<th>Event</th>
<th>Sample ID</th>
<th>Sampling Start Time</th>
<th>SO₄²⁻</th>
<th>NO₃⁻</th>
<th>Cl⁻</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>NH₄⁺</th>
<th>pH</th>
<th>TOC mg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biogenic</td>
<td>A1</td>
<td>8/16/2014 18:00</td>
<td>4.6</td>
<td>4.9</td>
<td>0.3</td>
<td>1.6</td>
<td>0.8</td>
<td>bdl</td>
<td>0.45</td>
<td>7.6</td>
<td>5.25</td>
<td>0.73</td>
</tr>
<tr>
<td></td>
<td>A2</td>
<td>8/17/2014 06:00</td>
<td>9.7</td>
<td>6.3</td>
<td>0.3</td>
<td>0.7</td>
<td>0.4</td>
<td>bdl</td>
<td>0.30</td>
<td>9.2</td>
<td>4.79</td>
<td>1.46</td>
</tr>
<tr>
<td></td>
<td>A3</td>
<td>8/17/2014 18:00</td>
<td>3.6</td>
<td>3.2</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
<td>bdl</td>
<td>0.37</td>
<td>6.7</td>
<td>4.94</td>
<td>2.16</td>
</tr>
<tr>
<td>Urban</td>
<td>B1</td>
<td>9/2/2014 06:00</td>
<td>69.4</td>
<td>30.7</td>
<td>2.7</td>
<td>2.2</td>
<td>0.8</td>
<td>4.3</td>
<td>0.87</td>
<td>79.5</td>
<td>4.18</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td>B2</td>
<td>9/2/2014 18:00</td>
<td>10.1</td>
<td>10.2</td>
<td>0.7</td>
<td>0.3</td>
<td>0.2</td>
<td>bdl</td>
<td>0.02</td>
<td>12.7</td>
<td>4.86</td>
<td>1.19</td>
</tr>
<tr>
<td>Wildfire</td>
<td>C1</td>
<td>8/4/2014 18:00</td>
<td>100.1</td>
<td>158.3</td>
<td>6.5</td>
<td>18.0</td>
<td>6.2</td>
<td>0.9</td>
<td>5.13</td>
<td>311.8</td>
<td>4.05</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>8/5/2014 06:00</td>
<td>103.2</td>
<td>176.6</td>
<td>7.9</td>
<td>20.8</td>
<td>6.6</td>
<td>1.3</td>
<td>5.38</td>
<td>373.5</td>
<td>4.10</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td>8/6/2014 18:00</td>
<td>9.4</td>
<td>13.3</td>
<td>1.2</td>
<td>2.3</td>
<td>1.1</td>
<td>0.4</td>
<td>1.30</td>
<td>33.0</td>
<td>4.54</td>
<td>7.86</td>
</tr>
<tr>
<td>Aug-Sept 2014 average values</td>
<td>32 ± 9</td>
<td>38 ± 12</td>
<td>9 ± 8</td>
<td>7 ± 3</td>
<td>2 ± 1</td>
<td>11 ± 2</td>
<td>1.6 ± 0.5</td>
<td>66 ± 11</td>
<td>4.8 ± 0.1</td>
<td>3.1 ± 0.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2. Average August–September TOC and Sulfate Cloud Water Concentrations at Whiteface Mountain, NY

<table>
<thead>
<tr>
<th>Year</th>
<th>TOC (mg L⁻¹)</th>
<th>SO₄²⁻ (µM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>4.09</td>
<td>53.7</td>
</tr>
<tr>
<td>2011</td>
<td>3.15</td>
<td>47.7</td>
</tr>
<tr>
<td>2012</td>
<td>4.16</td>
<td>54.2</td>
</tr>
<tr>
<td>2013</td>
<td>3.00</td>
<td>45.8</td>
</tr>
<tr>
<td>2014</td>
<td>3.06</td>
<td>32.3</td>
</tr>
<tr>
<td>2015</td>
<td>4.18</td>
<td>50.5</td>
</tr>
</tbody>
</table>

Cloud water samples and a field blank for mass spectrometric analysis were pre-concentrated using solid-phase extraction (Strata™-X polymeric SPE sorbents), according to the method of Zhao (et al. 2013) to enhance detection and to reduce potential matrix effects from inorganic ions. TOC concentrations of each cloud water sample after SPE ranged from 15–398 mg L⁻¹, with original TOC concentrations shown in Table 1. It should be noted that lower molecular weight organic compounds (i.e., most isoprene oxidation products), including some organosulfates, are expected to be removed during extraction (Zhao et al., 2013).

A 12-tesla Bruker SolariX FTICR mass spectrometer (Billerica, MA) was used to collect ultrahigh-resolution mass spectra of the cloud water samples. The detailed instrument parameters and analysis procedures, optimized during dissolved organic matter experiments, have been described previously (Kujawinski and Behn, 2006; Minor et al., 2012; Tfaily et al., 2015). A standard Bruker electrospray ionization (ESI) source was used to generate negatively charged molecular ions to target analysis of oxidized organic compounds. Samples were first diluted in LC-MS grade acetonitrile to similar TOC concentrations 15 to 45 mg L⁻¹, and then introduced through a syringe pump at a flow rate of 3.0 µL min⁻¹ through a 200 µm i.d. fused silica transfer tube. Experimental conditions were as follows: needle voltage, +4.5 kV; Q1 set to 100 m/ž; heated glass coated metal capillary operated at 180°C, and the ion accumulation time was adjusted for best spectral quality. These parameters were chosen based on previous experiments that optimized complex organic matter characterization (Tfaily et al., 2011, 2012, 2013). Two hundred individual scans were co-added, and the average resolving power (m/Δm) was >450,000 at 451 Da. Mass spectra were calibrated by two dissolved organic matter homologous series separated by 14 Da (−CH₂ groups), and the mass accuracy was calculated to be <1 ppm for singly charged ions ranging across the mass spectral distribution (m/ž 100–1000). A solvent blank of acetonitrile was also analyzed. A threshold was set to assign peaks with S/N > 15 from the spectra of all samples. Only sample ion peaks with intensities at least 100 times higher than those in either blank or acetonitrile were retained for further data analysis.
Assignments were made with elements limited to C, H, O, N, and S, with S=0-1, N=0-2, and the minimum number of O atoms per detected S or N was set to be 3. Assignments were limited to mass error of ± 0.5 ppm. All $^{13}$C isotopic peaks were removed. These conservative limits of data processing and assignments resulted in approximately 430–2300 peaks identified per sample (up to ~60% of the total number of detected peaks, after removal of $^{13}$C and blank peaks). A complete list of assigned peaks is provided in Cook (et al. 2017).

Sources of the air masses arriving at the sampling site were evaluated using NOAA Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) analysis (Stein et al., 2015). Six-day backward air mass trajectories were run from the beginning of the sample collection time at a starting height of 1500 m amsl, based on the Whiteface Mountain Observatory altitude (1483 m). Modeled mixed layer depth for each trajectory was examined to determine the influence of sources (e.g., forests and urban areas) within the atmosphere boundary layer. To investigate whether samples were likely influenced by wildfires, the NOAA Hazard Mapping System Fire and Smoke Product (http://www.ospo.noaa.gov/Products/land/hms.html) was used along with the backward air mass trajectories. The smoke product is divided into categories (light, moderate, heavy smoke) as determined via satellite images collected using Geostationary Operational Environmental Satellite system (GOES), Advanced Very High Resolution Radiometer (AVHRR), and MODerate resolution Imaging Spectroradiometer (MODIS) images.
4 Project Findings

Overall, Whiteface Mountain cloud water samples show a correlation between water acidity and the average oxygen-to-carbon atomic ratios (O:C) of the high-molecular weight compounds detected as negative ions by ESI-FTICR MS (Figure 1). It is important to note that the molecular composition of the cloud water reflects both the precursor aerosol and any aqueous-phase processing that occurred within the cloud droplets, as well as within the aqueous aerosol prior to cloud droplet activation and following cloud droplet evaporation. The average pH of the cloud water samples was 4.6 ± 0.7 (95% confidence interval), reflective of increasing cloud water pH at the site over the past several decades due to reductions in SO$_2$ and NO$_x$ emissions (Schwab et al., 2016a). The average O:C ratio of the high-molecular weight negative ions was 0.505 ± 0.004. To investigate the role of precursor sources on the identities of the dissolved organic compounds in the cloud water, samples were grouped based on backward air mass trajectories (Figure 2) apportioned to (a) biogenic (August 16–17, 2014), (b) urban (September 2, 2014), and (c) wildfire (August 4–6, 2014) sources. The average O:C ratios of the grouped biogenic, urban, and wildfire-influenced cloud water samples were 0.460 ± 0.008 (95% confidence interval), 0.489 ± 0.007, and 0.534 ± 0.005, respectively. The following sections discuss the cloud water chemical composition as a function of air mass influence.

Figure 1. Correlation between Cloud Water pH and Average O:C Ratio

Correlation between cloud water pH and average O:C ratio of the measured high-molecular weight organic compounds (negative ion mode, m/z 100–1000) by air mass source influence.
4.1 Biogenic (Forest) Influence

For the cloud water samples collected on August 16–17, 2014 (A1–A3, Table 1), the air mass had traveled from the Canadian boreal forest before passing over Detroit, MI and Buffalo, NY prior to arrival at Whiteface Mountain (Figure 2). The measured cloud water pH was 4.79–5.25, less acidic than samples collected under greater urban or biomass burning influence, as well as the August–September
2014 average pH (4.8 ± 0.1, 95% confidence interval) seen in Table 1. These cloud water samples had the lowest nitrate, sulfate, chloride, and ammonium concentrations compared to the other samples. Notably, the measured TOC and sulfate concentrations were 0.73–2.16 mg L⁻¹ and 3.6–9.7 μM, respectively, which are below the August–September 2014 averages of 3.1 ± 0.8 mg L⁻¹ and 32 ± 9 μM (Table 1), as well as the August–September 2010–2015 averages.

The A2 cloud water sample is shown in Figure 3 with nitrogen-containing, sulfur-containing, and oxygenated organic compounds (CHNO, CHNOS, CHOS, and CHO) compounds highlighted. Corresponding number fractions of the assigned organic compound types are also shown in Figure 3. For the biogenic-influenced cloud water samples (A1–A3), CHO compounds compose 51–56%, by number, of the dissolved organic species identified. CHO compounds potentially arising from aqueous reactions were identified by comparison to laboratory studies of the aqueous photooxidation of compounds produced from emissions from trees: α-pinene (Aljawhary et al., 2016) and isoprene (Nguyen et al., 2012a; Renard et al., 2015). CHOS and CHNOS compounds account for 14% and 7–9%, respectively, of the measured organic compounds in the A1 and A2 samples; lower percentages were observed for sample A3, consistent with the lower sulfate concentration in A3 (Table 1). These biogenic-influenced cloud water samples contained several unique CHOS and CHNOS compounds with relatively low O:C (0.05–0.4) and H:C (0.7–1.1) ratios, compared to the sulfur-containing organic compounds in other cloud water samples. Many organosulfates and nitrooxy-organosulfates, previously reported in laboratory studies, ambient aerosols, and cloud water as derived from monoterpenes (which are primarily emitted from pine trees), \(^1\) were detected in the biogenic-influenced cloud water samples—also consistent with monoterpane emissions along the air mass trajectories (Guenther et al., 2006). In this study, the required solid-phase extraction step precluded the detection of isoprene-derived organosulfates, which would have been removed prior to analysis. Hydrolysis products (or precursors) of most of the identified organosulfates and organonitrates were also found in the cloud water samples, consistent with laboratory studies (Darer et al., 2011; Hu et al., 2011).

\(^1\) Boone et al., 2015; Hamilton et al., 2013; Inumia et al., 2007a, 2007b, 2009; Kristensen et al., 2016; Kristensen and Glasius, 2011; Lin et al., 2012; Mazzoleni et al., 2012; Nguyen et al., 2012b; Nozière et al., 2010; O’Brien et al., 2014; Pratt et al., 2013; Stone et al., 2012; Surratt et al., 2008).
Figure 3. Negative Ion Mass Spectra and Compound Type Number Fractions of Compound Types for Cloud Water Samples

Negative ion mass spectra (left) and compound type number fractions (right) of compound types (CHO, CHNO, CHOS, and CHNOS) for representative cloud water samples collected on (a) August 17, 2014 6:00–9:00 a.m. EDT (A2), under northern forest (biogenic) influence combined with urban pollution, (b) September 2, 2014 6:00–9:00 a.m. EDT (B1), under urban pollution influence, and (c) August 4, 2014 6:00–9:00 p.m. EDT (C1), under the influence of Canadian wildfires.

CHNO compounds contributed 26% by number in the A1 and A2 samples. The A3 sample, characterized by less urban influence (Figure 2), featured a greater number of CHNO compounds, as well as a higher fraction (38%). Among the CHNO compounds, unique compounds with two N atoms (~30% of total CHNO compounds) were observed in the biogenic-influenced samples (A1–A3). Several likely dinitroaromatics compounds, including C₆H₆N₂O₆, C₇H₆N₂O₅, C₇H₆N₂O₆, and C₉H₈N₂O₆, were identified in these biogenic-influenced samples only. The formation of dinitroaromatics has been reported to originate from aqueous-phase radical nitration of mono-nitroaromatics (Krofič et al., 2015). Since no possible mono-nitroaromatics were observed in the samples, this suggests either a different formation pathway or that complete reaction had occurred.
4.2 Urban Influence

The cloud water samples collected on September 2 from 6:00–9:00 a.m. EDT (B1) and 6:00–9:00 p.m. EDT (B2) were characterized by significant urban influence, with air mass trajectories traveling from the southwest across multiple metropolitan areas—including Buffalo, NY, Detroit, MI, and/or Cleveland, OH (among others)—prior to arrival at Whiteface Mountain (Figure 2). Elevated sulfate (10.1–69.4 μM) and acidity (pH 4.18–4.86) but similar TOC (1.19–2.11 mg L⁻¹) were measured for the cloud water samples, compared to the biogenic-influenced period (Table 1). The sulfate concentrations are representative of August–September 2014 averages of 32 ± 9 μM (95% confidence interval) as well as August–September 2010–2015.

The mass spectrum of the B1 cloud water sample is shown in Figure 3. A total of 2276 oxidized organic compounds were identified in the B1 sample, highlighting the diversity and complexity of the cloud water molecular composition. The CHO compounds were the most prevalent at 44–53%, by number, similar to the other air mass influences. Notably, CHNO compounds account for 36–43% of the identified compounds, generally much higher than the number fractions (as well as absolute numbers) observed in the biogenic-influenced cloud water samples. This is likely due to the influence of elevated NOₓ emissions in urban locations because of fossil fuel combustion. Twenty-four percent of the CHNO compounds in the urban-influenced samples were composed of more than 23 carbon atoms, compared to only 3% and 12% of the CHNO in the biogenic and wildfire-influenced samples, respectively, suggesting the influence of long-chain, fossil fuel-derived organic precursors in these urban-influenced samples.

CHOS and CHNOS account for 7–10% and 3–4% by number, respectively, of the identified organic compounds in the urban-influenced samples. A fraction of the CHOS compounds, unique to sample B1, were characterized by low O:C (0.05–0.25) and H:C (0.6–1.2) ratios, similar to previous cloud water observations by Zhao (et al. 2013). Notably, aliphatic organosulfate species derived from photooxidation of long-chain alkane precursors (C₁₀₋₁₂)—including dodecane, cyclodecane, and decalin and recently observed in laboratory and urban ambient aerosol studies²—were detected in the B1 cloud water sample.

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² Riva et al., 2016; Tao et al., 2014.
consistent with the urban air mass influence. Similar to the northern biogenic-influenced cloud water, many likely monoterpenoid-derived organosulfates and nitrooxy-organosulfates\(^3\) as well as corresponding hydrolysis products (or precursors) were observed in the B1 and B2 cloud water samples, due to the air mass over forested areas of the southeast and Midwest United States (Figure 2).

### 4.3 Canadian Wildfire Influence

Backward air mass trajectories combined with NOAA Hazard Mapping System and Smoke Product data indicate influence from Canadian wildfire smoke during August 4–6, 2014 at Whiteface Mountain (Figure 4). Cloud water pH ranged from 4.05–4.54, generally lower than the biogenic and urban-influenced samples and similar to the August–September 2014 average of 4.8 ± 0.1. The cloud water inorganic ion concentrations were the highest observed in this study, although sample C3 had lower inorganic ion concentrations than the C1 and C2 samples (Table 1). Elevated K\(^+\) concentrations, commonly used as a tracer of biomass burning (Artaxo et al., 1994), were present in the wildfire samples (1.30–5.38 µM), compared to the non-wildfire conditions such as biogenic and urban samples that had 0.02–0.87 µM (Table 1). A positive correlation between K\(^+\) and TOC concentrations was observed, with increased TOC mass concentrations (7.86–16.6 mg L\(^{-1}\)) in wildfire-influenced cloud water, compared to non-wildfire conditions (0.73–2.16 mg L\(^{-1}\)) as well as the August–September 2010–2015 averages. Notably, there appear to be a greater diversity of oligomeric compounds present in the wildfire samples (Figure 3), which is likely a combination of the identities of the specific organic compounds present at high concentrations in the smoke as well as the potential role of acidity (as observed through cloud water acidity), resulting in the production of the observed oligomeric species, likely in aqueous aerosol prior to cloud droplet activation (Ervens et al., 2011).

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\(^3\) Nguyen et al., 2012b; Surratt et al., 2008.
Figure 4. NOAA HYSPLIT Backward Air Mass Trajectory and Corresponding Changes in Cloud Water Molecular Composition

NOAA HYSPLIT 144 h (6 day) backward air mass trajectory (white line, with 6 h resolution, shown as black dots) and corresponding changes in cloud water molecular composition, shown as compound type number fractions during the wildfire event (sample C1). Green, yellow, and red shading on the map represents low, moderate, and high amounts of smoke, respectively, as defined by the NOAA Hazard Mapping System Fire and Smoke Product. Visit http://www.ospo.noaa.gov/Products/land/hms.html for more information.

Biomass burning is one of the largest sources of methylglyoxal (Fu et al., 2008), and aqueous-phase reactive uptake of methylglyoxal has been suggested to be a significant source of organic aerosol through the formation of carboxylic acids, organosulfates, and oligomers (Altieri et al., 2008; Ervens et al., 2011). During wildfire influence, oligomeric species were observed in cloud water samples, with the addition of up to six C₃H₄O₂ (methylglyoxal) monomers to glycolic acid, pyruvic acid, and CHNO.

4 Fu et al., 2009; Zhao et al., 2006.
acid, malonic acid, malic acid, glyoxylic acid, and succinic acid-based compounds. The masses corresponding to these oligomeric series were also observed by Altieri (et al. 2008) in bulk aqueous-phase laboratory studies of the photooxidation of methylglyoxal, suggesting the importance of methylglyoxal-hydroxyl radical reactions for oligomer formation. Notably, pyruvic acid is one of the most abundant photooxidation products of methylglyoxal (Altieri et al., 2006; Lim et al., 2013). Modeling suggests that methylglyoxal oligomerization primarily occurs in aqueous aerosols, rather than during cloud processing (Lim et al., 2013; Tan et al., 2010). Syringol (2,6-dimethoxyphenol) and guaiacol (2-methoxyphenol) are also emitted in significant quantities from biomass burning, and previous studies have examined the aqueous-phase photooxidation of syringol and guaiacol (Yu et al., 2014, 2016), showing production of several CHO compounds that were also observed in the wildfire-influenced cloud water studied here.
5 Project Implications

This work identified the presence of a wide variety of sulfur- and nitrogen-containing, high-molecular weight organic compounds in cloud water at Whiteface Mountain. Many of these compounds were likely formed through aqueous-phase reactions within aerosols and cloud droplets, showing the importance of chemical modifications during atmospheric transport. To distinguish between aerosol and cloud-phase reactions, future measurements of the aerosols serving as seeds for the cloud droplet formation are required. A number of the nitrogen-containing compounds identified have important climate, health, and ecosystem implications because of their known light-absorbing (direct absorption of radiation) and mutagenic properties (Purohit and Basu, 2000; Zhang et al., 2011, 2013), suggesting that further studies are needed to understand the fate of these compounds in the earth system. The fates of the nitrogen- and sulfur-containing compounds are important to consider following deposition to the ecosystem as some organonitrate and organosulfate compounds may undergo hydrolysis in freshwater releasing nitrate and sulfate, respectively (Darer et al., 2011). Lastly, given increasing wildfire frequency and intensity globally (Jolly et al., 2015), we are currently conducting an examination of the frequency of wildfire influence on cloud water at Whiteface Mountain and assessing how this changing cloud water composition.

Given the long history of the Whiteface Mountain Observatory, the 2016 Whiteface Mountain Cloud Chemistry Workshop—led by Mary Barth (National Center for Atmospheric Research), Annmarie Carlton (University of California, Irvine), and Sara Lance (University at Albany)—called for a coordinated investigation of the effects of clouds on atmospheric composition, with a future large-scale field campaign to be proposed at the site. Visit https://nar.ucar.edu/2016/acom/61-whiteface-mountain-cloud-chemistry-workshop for details. The results of the project played a significant role in informing the science objectives of this future field campaign:

- Quantify the clear-sky bias in chemical characterization of the troposphere.
- Identify key oxidants driving aqueous-phase chemistry, especially pertaining to organic compounds.
- Quantify how aerosol characteristics and gas-phase composition change as a result of cloud processing.
- Identify chemical tracers for cloud processing.
- Quantify entrainment and transport of chemical constituents into the free troposphere.
- Determine the importance of aqueous-phase biological processes on aqueous chemistry.
6 Conclusions

This study represents only the second determination of high-molecular weight organic molecular composition in cloud water at Whiteface Mountain, NY (Sagona et al., 2014) and the first using ultrahigh-resolution mass spectrometry. The cloud water samples were analyzed by electrospray ionization (ESI) coupled to Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) in negative ion mode to characterize high-molecular weight oxidized organic compounds. Nitrogen-containing, sulfur-containing, and oxygenated organic compounds (CHNO, CHNOS, CHOS, and CHO) were identified in the cloud water and examined in the context of inorganic ion concentrations, pH, and total organic carbon (TOC) concentrations. The average O:C ratios of the oxygenated high-mass organic compounds increased with decreasing cloud water pH, suggesting the possibility for aqueous acid-catalyzed (prior to cloud droplet activation, or during/after cloud droplet evaporation) and/or radical (within cloud droplet) oxidation reactions contributing to the dissolved organic compounds. However, without knowledge of the organic aerosol composition prior to cloud formation, it is not possible to distinguish between aqueous aerosol and cloud droplet processes in this study. Identified high-molecular weight compounds were compared to lists of molecular tracers of aqueous-phase reactions, identified in previous laboratory studies to gain further insights into the aqueous-phase processing of biogenic, urban, and wildfire-influenced air masses. Cloud water samples from different air masses featured notable differences in the detected compounds. A higher absolute number and number fraction of CHNO compounds were observed during the wildfire and urban air mass periods, compared to biogenic influence, likely due to greater NOx influence. In addition, observations of likely dinitroaromatics during all air mass influences, potentially from aqueous nitration of nitroaromatic compounds, have important implications because of their light-absorbing and mutagenic properties (Purohit and Basu, 2000; Zhang et al., 2011, 2013). During wildfire influence, the cloud water showed evidence of aqueous SOA formation, including oligomer formation involving methylglyoxal (Altieri et al., 2008; Yasmeen et al., 2010) and aqueous-phase reactions of syringol and guaiacol (Yu et al., 2014, 2016). Monoterpene-derived organosulfates and organonitrates (Surratt et al., 2008) were observed in the cloud water during all air mass influences, similar to previous cloud water studies (Boone et al., 2015; Pratt et al., 2013), and indicative of the influence of emissions from forests. Notably, long chain alkane-derived organosulfates (Riva et al., 2016) were observed in cloud water when urban influence was present. This study provides a detailed understanding of the sulfur- and nitrogen-containing compounds present in cloud water at Whiteface Mountain, showing a diversity of organic compounds that may deposit to the ecosystem.
References


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