

Chemical Characterization of Cloud Water from Whiteface Mountain, NY

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Abstract

Clouds play an important role in the Earth's climate through active participation in the hydrological cycle (precipitation) and by affecting the total albedo of the planet. The cloud formation process, in which supersaturated water condenses onto particles, results in a unique aqueous chemical environment within cloud droplets. Very few studies have examined high molecular weight organic compounds present in cloud water. These soluble organic compounds in cloud water are hypothesized to comprise a significant mass fraction of atmospheric aerosols upon cloud droplet evaporation. To study the organic composition of cloud water, five samples from June to September from Whiteface Mountain have been collected and analyzed using LTQ-Orbitrap mass spectrometer with electrospray ionization. NOAA HYSPLIT backward air mass trajectory analysis was performed to determine the source regions of the particles impacting the cloud water. Relationships between organic and inorganic compounds were analyzed through comparisons of the concentrations of total organic carbon and inorganic ions with pH and organic compound classes, as determined by mass spectrometry.

Introduction

Clouds play a major part in the processing of atmospheric organic matter (AOM) (Blando and Turpin, 2000; Collett et al., 2008; Mazzoleni et al., 2010; Ervens et al., 2011; Herckes et al., 2013). Organic aerosols (OA) comprise a significant fraction of submicron particles, and secondary organic aerosol (SOA), in particular, is typically the most dominant portion of the total organic aerosol (Fuzzi et al., 2006; Kanakidou, et al., 2005; Zhang et al., 2007; Ervens et al., 2011). SOA is formed when volatile organic compounds

are oxidized in the atmosphere, creating semi-volatile gas phase species which can partition into the particle phase (Ervens et al., 2011). Compounds are further oxidized and subsequently cumulative, leading to the enhanced SOA production (Blando and Turpin, 2000). The overall effect of these organics on the global climate is still very uncertain (Goldstein and Galbally, 2007).

Hygroscopic atmospheric particles allow for water uptake and formation of cloud droplets via the condensation of water vapor onto these particles termed cloud condensation nuclei (CCN) (Sun, et al., 2006). Clouds play an important role in the Earth's climate through active participation in the hydrological cycle and by affecting the total albedo of the planet (Pöschl 2005). Also, cloud droplets are sites for aqueous chemical reactions. It has been suggested that SOA can be produced during fog and cloud processing, during which aqueous reactions result in the formation of less volatile species in the aerosol phase when the cloud droplets with the absorbed organic molecules evaporate, leaving modified particles behind (Aumont et al., 2006; Blando and Turpin 2000). Previous studies hypothesized that organic compounds are oxidized in cloud water (Blando et al., 2000). As suggested by Fuzzi et al. (2001), the interactions between soluble gases and non-activated aerosols, aqueous-phase reactions, and other meteorological conditions will significantly influence the cloud chemical composition in the process of cloud evolution. Despite many laboratory-based studies (Ervens et al., 2011), few ambient studies have investigated in the organic molecular composition of cloud water and relationships to inorganic cloud water chemistry. By characterizing organic molecules in cloud water, the comparison between inorganic ions and organic components and origins of air mass can be further investigated.

We present chemical data from cloud water collected at Whiteface Mountain, NY. This will help to determine the elemental composition, seasonal variation, and interrelationship of inorganic ions and organic compounds of cloud water. Previously, Aleksic et al. (2009) reported long-term measurements of cloud water from 1994-2006; this study focused on the trends and inter-relationships between inorganic ions. To our knowledge, this represents the first detailed study of high molecular weight organic compounds in cloud water in the northeastern United States.

2. EXPERIMENTAL

Cloud water samples were collected from June to September, 2013 at Whiteface Mountain (44.4 N, 37.9W, 1500 m AMSL) in New York (Figure 1). A total of sixteen cloud water samples were collected; here we focus on 5 samples. An omni-directional passive collector was used to collect the cloud water. The instrument collected samples when following conditions were met: cloud liquid water content $> 0.05 \text{ g/m}^3$; $> 2 \text{ }^\circ\text{C}$; wind speed $> 2 \text{ m/s}$, and the cloud was not precipitating. The measurements and analysis were performed by the Adirondack Lake Survey Corporation. Methods and procedures are described by Isil et al. (2000) and Baumgardner et al. (2003).

Total organic carbon (TOC) and pH values were measured of collected samples were measured by the Adirondack Lake Survey Corporation. Water soluble inorganic ions (including SO_4^{2-} , NO_3^- , Cl^- , Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and NH_4^+) were also measured.

Samples for mass spectrometry analysis were prepared by mixing cloud water and acetonitrile 30/70 by volume. A LTQ-Orbitrap mass spectrometer, coupled with electrospray ionization, was used to determine the molecular composition of individual

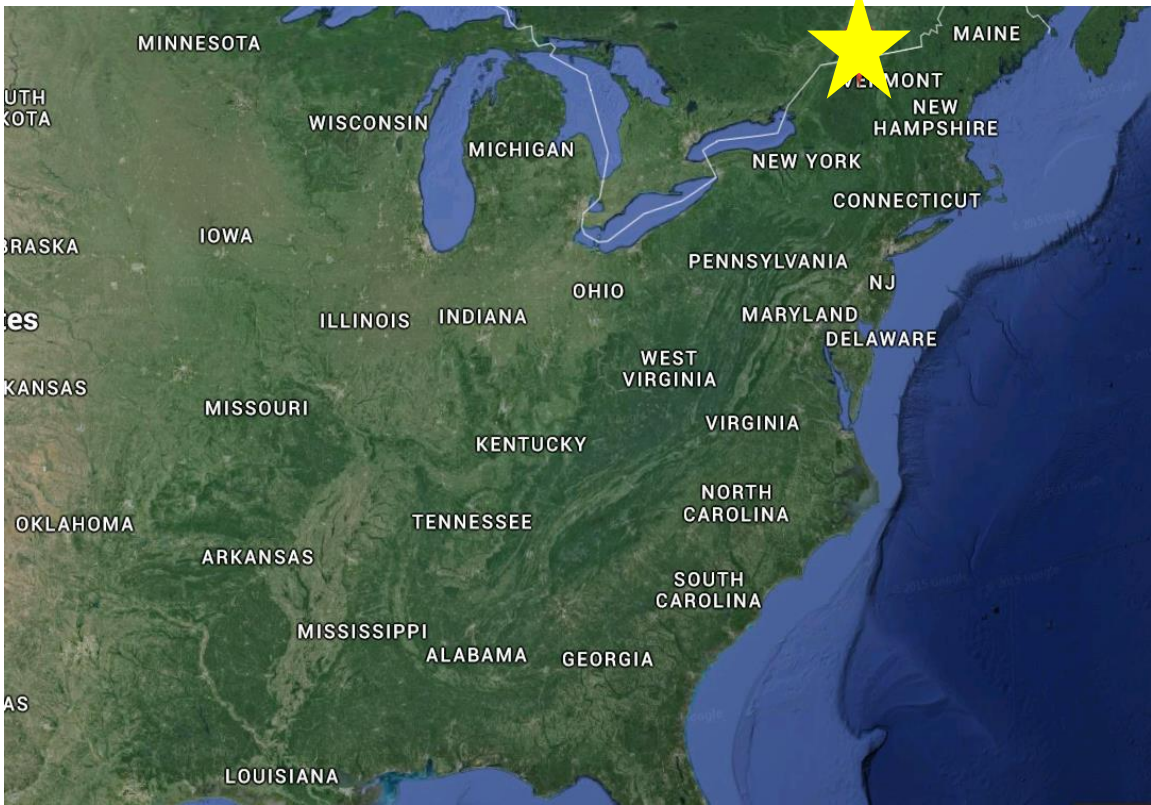


Figure 1. Location of Whiteface Mountain, the yellow star



Figure 2. Scheme of sampling site on the top of Whiteface Mountain (Adirondack Lake Survey)

organic compounds in the cloud water. Negative molecular ions at 100-400 m/z were examined. A criterion was set to isolate mass spectral features with signal to blank intensities of 5 and signal to noise levels of 3 and to eliminate undesired peaks. The Formula Calculator v. 1.1, developed at the National High Magnetic Field laboratory (<http://magnet.fsu.edu/~midas/download.html>), was set to allow up to 50 carbon (C), 100 hydrogen (H), 15 oxygen (O), 5 nitrogen (N), and 3 sulfur (S) atoms per molecular ion in negative mode. We have utilized Kendrick mass defect analysis to sort CH_2 homologous ion series (species with a specific value of double bond equivalents (DBE) and heteroatom content differs in $-(\text{CH}_2)_n$) (Zhao, et al., 2013). For individual elemental composition $\text{C}_c\text{H}_h\text{N}_n\text{O}_o\text{S}_s$, DBE was determined by Eq. (1)

$$\text{DBE} = c - h/2 + n/2 + 1 \quad (1)$$

Sulfur and oxygen are divalent and nitrogen is trivalent in Eq. (1). Therefore, the DBE calculation does not account for tetravalent and hexavalent S or pentavalent N (Mazzoleni, et al, 2010). A total of five samples were used for further analysis because of more reasonable assignment rates.

Air mass sources were investigated by using air mass backward trajectories from NOAA HYSPLIT database. EDAS mode was chosen because of its higher resolution over U.S region than GDAS.

3. Results and Discussion

3.1 Air mass origin

We have focused here on two particular events (June 27 and Sept. 10, 2013) because of their similar air mass trajectory pathways. Both trajectories show air masses that

traveled through the southern and middle U.S. before arriving at Whiteface Mountain (Figure 3).

The pathways for June 27 and September 10 suggest that their organic compositions should be similar, but we observed that the three samples contain different fractions of organic compound classes. Since most of the trajectories were in the mainland of U.S, it is reasonable to assume that the marine environment did not have major contributions to the formation of air mass, as suggested by the ratio of Cl^-/Na^+ and Mg^+/Na^+ . The air mass back trajectories had passed over Toronto. These larger populated metropolitan area likely introduced aerosols (a fraction of which can act as cloud condensation nuclei) and anthropogenic gases (such as SO_2), resulting in higher nitrate and sulfate concentrations (Hutchings et al., 2008).

3.2 Organic Molecular Composition

For the five cloud water samples, elemental compositions of each sample were determined, with negative ions divided into four subgroups: CHO, CHON, CHOS, and CHONS (Table 1). In this study, more than 200 individually measured masses were assigned, which demonstrates the chemical complexity of cloud water. As suggested by Altieri et al. (2008) and Reinhardt et al. (2007), a reaction system with few components can give hundreds of individually measured masses. Thus, elemental compositions for each sample are expected to be different.

CHO and CHON compounds were the most frequently observed compound types in the cloud water, in agreement with the significant presence of oxidized organic material in other cloud water studies (Zhao et al, 2013). CHO compounds were the most abundant

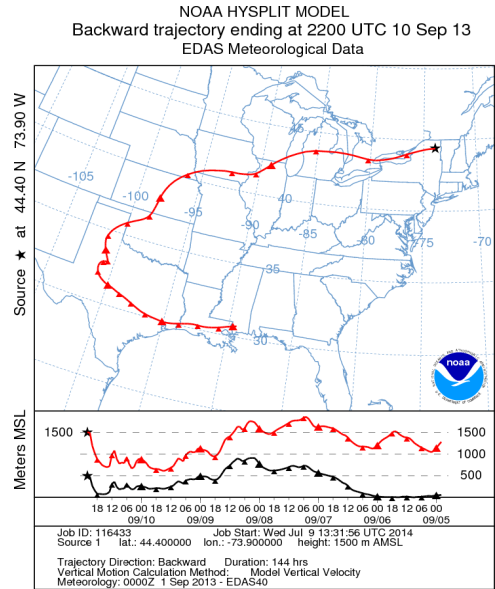
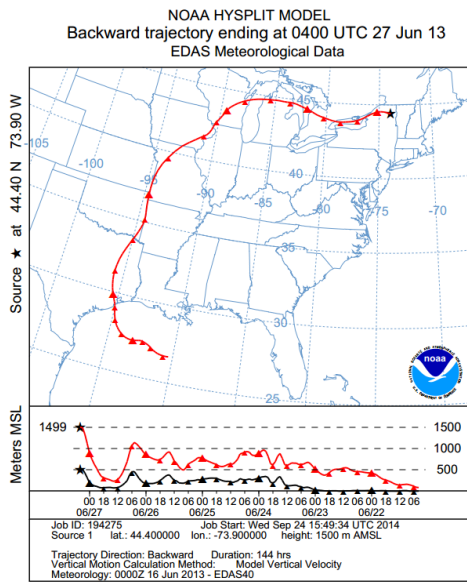


Figure 3. NOAA HYSPLIT 144 h backward air mass trajectories for the Jun. 27 (left) and Sep. 10, 2013 (right) samples.

Table 1: The numbers of compounds identified for each subgroup and the assignment rate for each cloud water sample are shown. Collection times were recorded as Eastern Standard Time.

<i>Sample</i>	<i>CHO</i>	<i>CHON</i>	<i>CHOS</i>	<i>CHONS</i>	<i>Assignment rate</i>
<i>6/24/2013 10:00</i>	18	3	7	3	40%
<i>6/27/2013 00:00</i>	17	7	0	3	38%
<i>9/10/2013 03:00</i>	75	19	14	20	38%
<i>9/10/2013 18:00</i>	16	8	9	3	38%
<i>9/11/2013 03:00</i>	13	6	5	3	42%

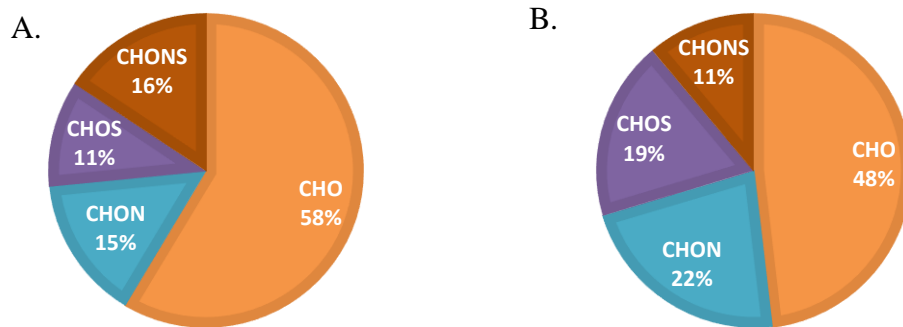


Figure 4. Fractional number contributions of compound classes corresponding to cloud water sampled on Sep. 10 (A) and Sep. 11(B).

for all five samples (Figure 4), in agreement with previous studies of rainwater (Altieri et al., 2012; Mazzoleni et al., 2012). Samples were collected during separate day and night periods, and we can see from Table 1 that the composition of subgroups of each sample did not vary a lot.

A van Krevelan diagram is a plot of the atomic ration of H:C vs O:C for each of the individual assigned molecules (Figure 5). Oxidation/reduction (horizontal), hydration (diagonal), hydrogenation (vertical), and alkylation (diagonal) reactions can be observed from van Krevelen diagrams for atmospheric samples (Kim et al., 2003; Wu et al., 2004; Heald et al., 2010., Mazzoleni et al., 2010). Although the pattern is not observed for our samples possibly due to insufficient sample size, it is observed that more assigned molecules are located on the left side of the diagram ($O:C < 0.5$). Aliphatic compounds are expected to be characterized by a low O:C ratio (<0.5) and high H:C ratio (>1.5) (Mazzoleni et al., 2010), while molecules located in the lower left ($O:C < 0.3$, $H:C < 1$) are typically aromatic compounds with high DBE values (Zhao et al., 2013). Therefore, it is likely that more aliphatic compounds than aromatic molecules were present in our cloud water samples. The CHON compounds generally have lower O/C ratios than the CHO compounds, suggesting that the compounds are not as oxidized. The CHOS compounds (Figure 5) are characterized by high O/C ratios, suggesting the presence of organosulfate compounds (Altieri, et al., 2009). There were only 32 CHONS assigned compounds in the five samples. The majority of the CHONS compounds had $O/C < 1.0$, indicating a lower degree of oxidation than the CHOS compounds, more similar to the CHO and CHON compounds.

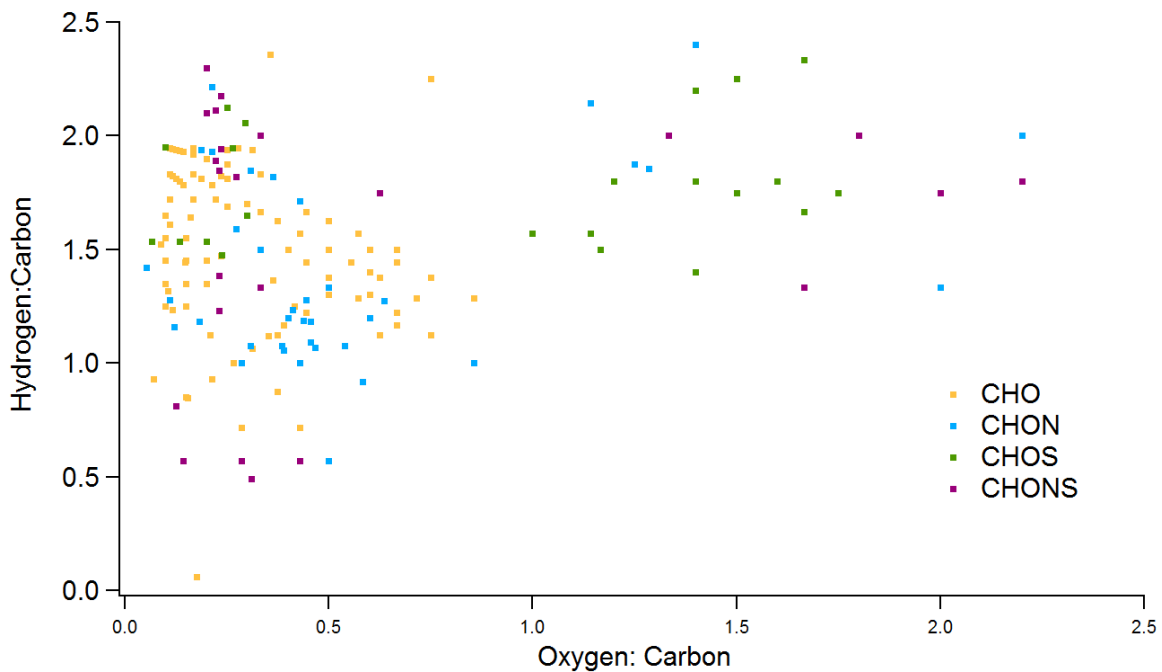


Figure 5. van Krevelen diagram of H:C vs O:C ratio for 249 assigned compounds ($C_cH_hO_oN_nS_s$) in the five cloud water samples.

Overall, 40% of the total ions were assigned for the five cloud water samples. The remaining observed mass peaks were unidentified possibly due to the presence of inorganic compounds and organic compounds significantly affected by salts. For further analysis, it is proposed that by doing solid phase extraction (SPE), the samples will be concentrated and purified such that higher signal will be yielded.

3.3 Inorganic ions

Inorganic ions, total organic carbon, and pH were measured for the cloud water samples. As suggested by Collett et al. (2002), Whiteface Mountain is typically greatly influenced by acidic anthropogenic emissions; however, this was not the case in our study. The average pH of the collected cloud water was 5.0, which is considerably higher than previous studies (Guo et al., 2012). The relatively low nitrate or sulfate concentrations, with respect to other mountain sites, may have led to a higher pH value (Table 2); overall, there was minor influence from acid forming species (e.g., sulfate) when compared to other studies of the same region (Collett et al., 2002).

Additionally, the ammonium concentration was slightly higher than previous studies (Guo et al., 2012), which leads to a more complete neutralization of acidic cloud water and a higher pH value. The greater ammonium concentration is likely due to the influence of agricultural emissions (Collett et al., 2002). Also, total organic carbon (TOC) was determined as a measure of organic compounds presented in cloud water. Larger TOC value means that there was higher concentration of all organic carbon atoms bonded in the organic molecules of a given sample. It is possible that higher TOC content was induced by more combustion or other organic contaminants. Furthermore, inorganic ions

Table 2. Inorganic ion concentrations, pH, and TOC values for 5 samples collected at Whiteface Mountain

<i>SAMPLE</i>	<i>SO₄²⁻ (mg/L)</i>	<i>NO₃⁻ (mg/L)</i>	<i>Cl⁻ (mg/L)</i>	<i>pH</i>	<i>TOC (mg/L)</i>
<i>6/24/2013 10:00</i>	13.76	16.62	0.96	5.08	20.16
<i>6/27/2013 00:00</i>	5.17	13.43	0.16	4.89	13.18
<i>9/10/2013 03:00</i>	7.88	4.51	0.21	4.24	3.61
<i>9/10/2013 18:00</i>	7.66	4.16	0.11	5.98	5.01
<i>9/11/2013 03:00</i>	11.56	9.32	0.31	6.82	9.52

also decreased with decreasing TOC values, which might suggest that the amount of inorganic ions is correlated with organic molecules.

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The relationship between inorganic ions and organic molecules was investigated. We hypothesized that they are positively related to each other because inorganic sulfate and nitrate might react with organic molecules. In addition, the oxidation of SO₂ in cloud

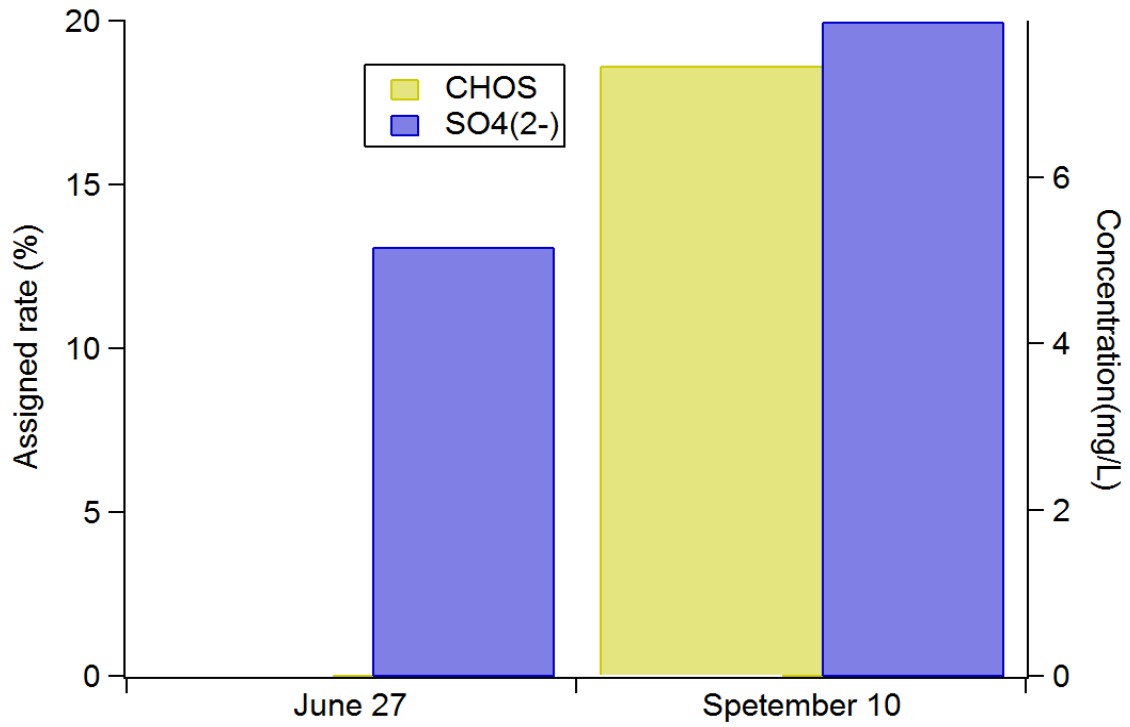


Figure 6. Comparison of inorganic sulfate and CHOS compounds for Jun 27th and Sep 10th in negative mode

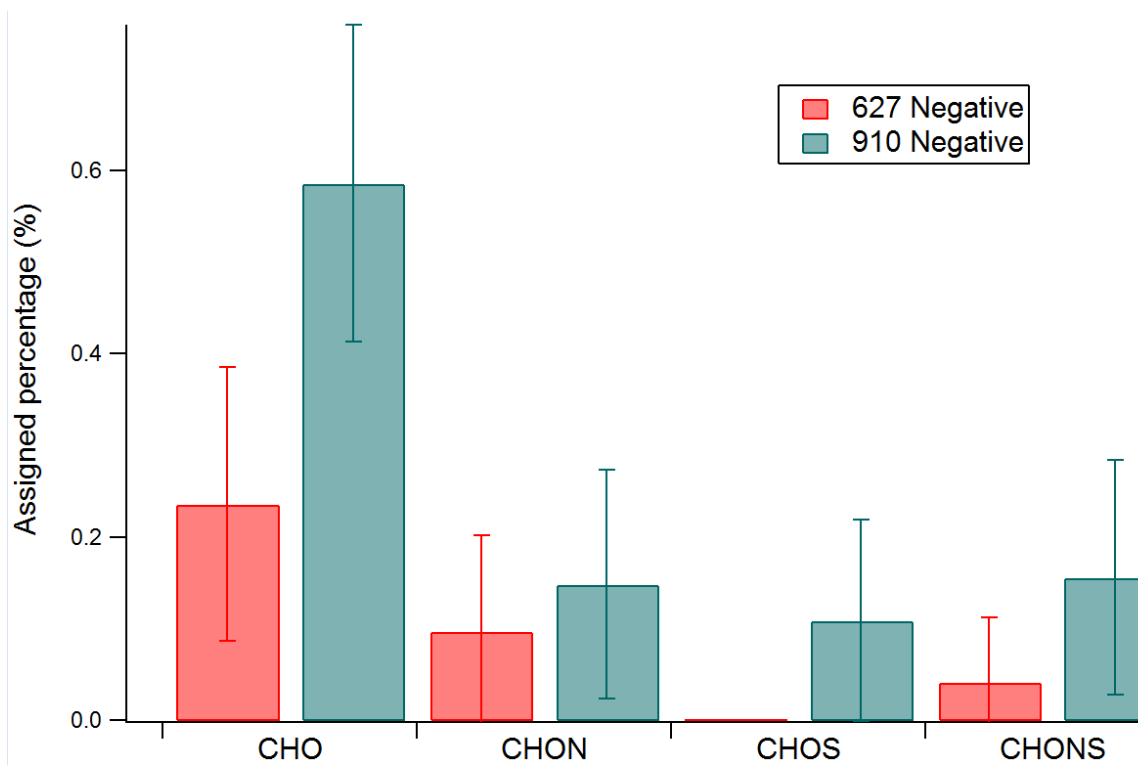


Figure 7. Comparison of CHOS compound fractional contributions

droplets is likely to produce sulfate efficiently in summer and to give a higher SO_4^{2-} concentration (Guo et al., 2012). The sulfate concentration was observed to be higher in the September sample, and CHOS compounds were more prevalent then as well (Figure 6). CHOS compounds were a greater fraction of the total compounds on September 10th, compared to June 27th, possibly due to cloud processing of SO_2 and organic compounds (Figure 7).

Higher concentration of soil/dust components (Ca^{2+} and Mg^{2+}) were recorded, as well as the higher pH values, when compared to typical concentrations measured at Whiteface Mountain (Hutchings et al., 2008) (Table 2 and 3). Greater portions of calcium and magnesium might also lead to the higher average pH values (Hutchings et al., 2008). Comparison of Cl^-/Na^+ and Mg^+/Na^+ values provide insights into the origin of the air masses. The average ratios of Cl^-/Na^+ (1.42) and of Mg^+/Na^+ (1.14) are far from the literature values of 1.17 and 0.1, respectively, for sea water (Chemistry of Sea Water). In this case, we would suggest that the marine environment does not significant impact these air masses, and our hypothesis is supported by HYSPLIT backward air mass trajectories, showing air mass passed along the mainland of U.S (Figure 3).

4. Conclusions

Five samples of cloud water collected from June to September 2013 were examined for similarities and differences in chemical composition. Total around 40% of organic molecules were characterized into subgroups: CHO, CHON, CHOS, and CHONS. The fractional contribution of subgroups of each sample does not vary a lot among five

Table 3. Comparisons of the concentrations of major inorganic ions in cloud water

<i>SAMPLE</i>	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	NH_4^+ (mg/L)
<i>6/24/2013 10:00</i>	3.20	0.52	0.89	0.53	10.27
<i>6/27/2013 00:00</i>	1.92	0.15	0.09	0.22	5.27
<i>9/10/2013 03:00</i>	0.68	0.10	0.16	0.07	2.21
<i>9/10/2013 18:00</i>	1.92	0.15	0.08	0.14	2.68
<i>9/11/2013 03:00</i>	4.46	0.20	0.19	0.22	5.17

samples. CHO and CHON compounds were the most frequently observed compound types in the cloud water, in agreement with the significant presence of oxidized organic material in other cloud water studies. A van Krevelan diagram demonstrated different forms of organic molecules by comparing O/C and H/C values. The relationship between inorganic ions and organic molecules also has been investigated. The oxidation of SO₂ in cloud droplets is likely to produce sulfate efficiently in summer and to yield a higher SO₄²⁻ concentration. The inorganic ions comparison of Cl⁻/Na⁺ and Mg⁺/Na⁺ also implies that the marine environment does not significantly impact these air masses, and this is confirmed by HYSPLIT backward air mass trajectories, showing air mass was travelling inside of the U.S. And for future studies, SPE should be tried to concentrate and purify the samples, yielding a higher signal level. More possible reasonable molecular assignments will help further analysis.

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