
James J. Schwab1*, Paul Casson1, Richard Brandt1, Liquat Husain1,2, Vincent Dutkewicz1, Douglas Wolfe1, Kenneth L. Demerjian1, Kevin L. Civerolo3, Oliver V. Rattigan3, H. Dirk Felton3, James E. Dukett4

1 Atmospheric Sciences Research Center, University at Albany, State University of New York, Albany and Wilmington, NY 12222, USA
2 School of Public Health, University at Albany, State University of New York, Albany, NY 12222, USA
3 Division of Air Resources, New York State Department of Environmental Conservation, Albany, NY 12233, USA
4 Adirondack Lakes Survey Corporation, Ray Brook, NY 12977, USA

ABSTRACT

Long-term records of condensed-phase chemical data are presented from the Adirondack Mountain region of northern New York, USA. These data records are particularly valuable due to the combinations of aerosol, cloud, and precipitation measurements. Objectives of the research and this overview paper include the evaluation of emission reductions of regulated air pollutants and the observed effects on measured deposition, as well as the implications of changing pollutant concentration levels on human health and climate. Summer season cloud chemistry and year-round wet deposition and particulate matter data from two stations on Whiteface Mountain are presented to highlight some of the research and monitoring activities at this mountain location. Clear decreases in the anion concentrations and increases in pH over the past two decades have been observed in cloud and precipitation results. Large decreases in aerosol sulfate (> 80%) and aerosol optical black carbon (> 60%) have been observed for these species over the nearly 40 year summit observatory data record for these measurements, and decreases in PM2.5 mass, sulfate, nitrate, and ammonium have also been recorded over the shorter 15 year period of measurement at the Marble Mountain Lodge level. The studies cited here highlight some of the past successes of air pollution regulation under the Clean Air Act and Amendments and pave the way for future progress in reducing air pollution.

Keywords: Acidic deposition; Regional air quality; Air pollution regulation; Atmospheric chemistry; Aerosol chemistry; Particulate matter; Black carbon.

INTRODUCTION

Condensed phase species in the atmosphere consist of solid and liquid particles in a wide range of sizes and compositions. The smallest of these are aerosol species, produced from natural processes, and from many types of human influenced or anthropogenic activities. Aerosols are extremely important in their own right, influencing the chemistry of the atmosphere, the earth’s radiative balance, and human and ecosystem health. Furthermore, some aerosols have hygroscopic properties that allow them to grow due to the uptake of water, first to become cloud particles, and sometimes to rain droplets that fall out of the cloud. Thus there is a natural connection and progression from new aerosol particle, to cloud droplet, and finally to rain drop. All of these types of condensed species have both simple and complicated chemical processes occurring at surfaces, and sometimes within the particles and droplets. Deposition of aerosols, cloud droplets, and precipitation are measurable endpoints of the atmospheric processing of the rich array of chemical species that make up these condensed species.

Aerosol sampling at Whiteface Mountain began in 1975 and has been continuous at the summit observatory since 1978 as described in a companion paper (Schwab et al., 2016). These samplers collect TSP (total suspended particles) on cellulose filters and are analyzed for mass, major ions and more recently, black carbon (BC). More details are given below, and Table 1 summarizes the condensed phase measurements currently ongoing at the summit observatory.

*Corresponding author.
E-mail address: jschwab@albany.edu
Table 1. Ongoing Whiteface Summit measurements of condensed phase species.

<table>
<thead>
<tr>
<th>START DATE</th>
<th>PARAMETER</th>
<th>PHASE</th>
<th>METHOD</th>
<th>AGENCY</th>
<th>SEASON</th>
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</thead>
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<tr>
<td>2007</td>
<td>Black Carbon - PM$_{2.5}$</td>
<td>Aerosol</td>
<td>Aetholometer</td>
<td>DOH</td>
<td>Year-round</td>
</tr>
<tr>
<td>1978</td>
<td>Total mass, ions, and elements - TSP</td>
<td>Aerosol</td>
<td>Filters</td>
<td>DOH</td>
<td>Year-round</td>
</tr>
<tr>
<td>1994</td>
<td>SO$_4^{2-}$, NO$_3^-$, Cl$^-$, Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, TOC, NH$_4$</td>
<td>liquid (cloud only)</td>
<td>Atomic absorption spectrometry</td>
<td>ALSC</td>
<td>Spring to fall</td>
</tr>
<tr>
<td>1994</td>
<td>Cloud Liquid Water Content</td>
<td>liquid (cloud only)</td>
<td>Optical forward scatter (Gerber)</td>
<td>ALSC</td>
<td>Spring to fall</td>
</tr>
<tr>
<td>1994</td>
<td>Cloud Particle Surface Area</td>
<td>liquid (cloud only)</td>
<td>Optical side scatter (Gerber)</td>
<td>ALSC</td>
<td>Spring to fall</td>
</tr>
<tr>
<td>1994</td>
<td>Cloud specific conductivity</td>
<td>liquid (cloud only)</td>
<td>Probe/meter at 25°C</td>
<td>ALSC</td>
<td>Spring to fall</td>
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</table>

ALSC = Adirondack Lake Survey Corporation.
DOH = Department of Health (New York State).

Table 2. Ongoing Marble Mountain Lodge measurements of condensed phase species.

<table>
<thead>
<tr>
<th>START DATE</th>
<th>PARAMETER</th>
<th>PHASE</th>
<th>METHOD</th>
<th>AGENCY</th>
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<td>1999</td>
<td>PM$_{2.5}$ Mass</td>
<td>Aerosol</td>
<td>FRM Sampler</td>
<td>DEC</td>
<td>Year-round</td>
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<td>2001</td>
<td>PM$_{2.5}$ Speciation</td>
<td>Aerosol</td>
<td>EPA Chemical Speciation Network - CSN</td>
<td>DEC</td>
<td>Year-round</td>
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<td>2002</td>
<td>PM$_{2.5}$ SO$_4^{2-}$</td>
<td>Aerosol</td>
<td>Thermal reduction to SO$_2$</td>
<td>DEC</td>
<td>Year-round</td>
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<td>2002</td>
<td>PM$_{2.5}$ optical scatter</td>
<td>Aerosol</td>
<td>White light nephelometer</td>
<td>ASRC</td>
<td>Year-round</td>
</tr>
<tr>
<td>2012</td>
<td>PM$_{2.5}$ BC</td>
<td>Aerosol</td>
<td>Aetholometer</td>
<td>DOH/DEC</td>
<td>Year-round</td>
</tr>
<tr>
<td>2000</td>
<td>PM$<em>{2.5}$, PM$</em>{10}$, PM Coarse</td>
<td>Aerosol</td>
<td>TEOM</td>
<td>DEC</td>
<td>Year-round</td>
</tr>
<tr>
<td>1984</td>
<td>Precipitation gauge</td>
<td>Precipitation</td>
<td>Load cell weighing gauge with optical sensor</td>
<td>NADP</td>
<td>Year-round</td>
</tr>
<tr>
<td>1984</td>
<td>Precipitation collector</td>
<td>Precipitation</td>
<td>Covered bucket with optical sensor</td>
<td>NADP</td>
<td>Year-round</td>
</tr>
<tr>
<td>2012</td>
<td>Gaseous SO$_2$, HNO$_3$; particulate SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Ca$^{2+}$, Na$^+$, Mg$^{2+}$, Cl$^-$</td>
<td>Gas, Aerosol</td>
<td>Filter pack</td>
<td>CASTNET</td>
<td>Year-round</td>
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</table>

ASRC = Atmospheric Sciences Research Center.
CASTNET = Clean Air Status and Trends Network (U.S. Environmental Protection Agency).
DEC = Department of Environmental Conservation (New York State).
DOH = Department of Health (New York State).
NADP = National Atmospheric Deposition Program (numerous sponsors).

(TSP) samplers at the Marble Mountain Lodge site from 1975–1988, and high-volume inhalable particulate (PM$_{10}$) samplers from 1998–2005. The current focus at Marble Mountain Lodge is on measurement of fine particulate (PM$_{2.5}$) mass and speciation initiated in 1999 and 2001, respectively. Current aerosol measurements at the Marble Mountain Lodge location are summarized in Table 2. Some early aerosol work at Whiteface is described in a companion paper (Schwab et al., 2016), and a large intensive field campaign took place there is the summer of 2002 as part of the PMTACS-NY project – and EPA PM-Supersites effort (Hogrefe et al., 2004; Rattigan et al., 2006).

Many gas and aerosol species can be incorporated into cloud water, and it has been well established that clouds can contribute substantial nutrient and acidic deposition to high elevation ecosystems (e.g., Lovett et al., 1982; Aneja and Kim, 1993; Miller et al., 1993). EPA sponsored programs monitored cloud water chemistry during warm seasons (i.e., water clouds only) at three fixed mountaintop sites from 1994–1999 – Whiteface Mountain, NY; Clingman’s Dome, TN; and Whitetop Mountain, VA (EPA, 2000). Of these three sites, only Whiteface Mountain remains in operation. In 2001, the Adirondack Lakes Survey Corporation (ALSC) took over the field and laboratory operations at Whiteface, with support from the DEC.

The National Atmospheric Deposition Program (NADP) has monitored precipitation chemistry at predominantly non-urban sites since 1978 (e.g., Lamb and Bowersox, 2000). The NADP National Trends Network (NTN) collects and analyzes precipitation samples on a weekly basis. The NTN site at the Marble Mountain Lodge site at Whiteface was established in July 1984, and is currently one of six NTN sites in the Adirondack Park, all of which are above 460 m. Precipitation chemistry data from this site have
been used extensively to report on trends in acidic deposition in New York and elsewhere across the northeastern US (e.g., Butler et al., 2001; Civerolo et al., 2003; Burns et al., 2006; Driscoll et al., 2007). Prior to the NADP, there was a Multistate Atmospheric Power Production Pollution Study (MAP3S; e.g., Hales et al., 1987) station at Marble Mountain Lodge. The MAP3S was a research-oriented program that collected precipitation chemistry on a daily basis, which operated from 1976–1990. The Marble Mountain Lodge site was one of the original four sites in that network. DEC also operated a precipitation monitoring site at the site from 1989–2012. The DEC wet deposition network consisted of 20 sites located throughout the state in both rural and urban locations. At the end of 2012, the DEC discontinued the existing acid rain monitoring program and transitioned six monitoring locations to the NADP, to ensure consistent monitoring of wet deposition across the region (see Table 2 for details).

Whiteface Mountain, in the High Peaks region of the Adirondack Mountains of northern New York, and downwind of many large pollution sources and urban areas, is well suited to characterizing regionally representative air quality and the impacts of long-range transport. Two companion papers in this issue (Schwab et al., 2016; Brandt et al., 2016) have focused on the history of research and monitoring efforts that have occurred at Whiteface Mountain, with an emphasis on gas-phase chemistry. In this paper, we focus on the long-term measurements of condensed-phase chemistry – namely clouds, precipitation, and particulate matter, and provide valuable long term measurement data of cloud water, precipitation and ambient air species from this region covering an approximate 15 or longer year period. We both review some previous results from published work at Whiteface, and present new data and results as well in the sections that follow.

Site Description

The ASRC Whiteface Mountain Summit Observatory is located on the peak of Whiteface Mountain, Latitude 44°21’58”N and Longitude 73°54’10”W at an elevation of 1,483 meters above sea level. As noted by Schwab et al. (2016) the summit is frequently in cloud, and cloud collection has been an important activity at the Whiteface summit beginning in the 1970s. Due to high and erratic winds, the summit is not an appropriate site for precipitation collection. The Marble Mountain Lodge site is located on the Eastern shoulder of the Whiteface Massif at Latitude 44°23’35”N and Longitude 73°51’33”W with an elevation of 604 meters above sea level. This site is located in a wooded clearing and is where samplers for collection of precipitation and filters for particulate matter mass and composition have been located as described below.

Sampling and Method Descriptions

Summit Cloud Collection

The collector is an omni directional passive collector, also known as an ASRC (Atmospheric Sciences Research Center) collector. The collector consists of two disks separated by vertical bars with Teflon filament strung between the disks. The principle of operation is simple: as winds blow the liquid cloud drops through the collector, cloud water impacts on and adheres to the filaments and gravity draws the water down to a funnel. The cloud water collector is deployed from its protective housing only after the following conditions are met (EPA, 2000): 1) the air liquid water content must be 0.05 grams per cubic meter or greater, indicating the presence of cloud (Seinfeld and Pandis, 2006); 2) the temperature must be two degrees Celsius or greater to prevent freezing; 3) the wind speed must be two meters per second or greater, to move clouds through the collector; and 4) the heated grid rain sensor must indicate that no rain is present, to assure that samples are from non-precipitating clouds.

Summit Particulate Matter Collection and Measurement

24-hour integrated aerosol collection at the Whiteface Mountain summit observatory was initiated in 1978 (Parekh and Husain, 1981) and the program is still going on. The cellulose aerosol filter samples collected at these sites have been archived and carefully stored in the Husain group laboratory. Concentration of sulfate ($\text{SO}_4^{2-}$) is routinely measured using ion chromatography, and ions such as nitrate ($\text{NO}_3^-$), ammonium ($\text{NH}_4^+$), and Ca$^{2+}$ can be measured as well for specific projects. The sampling and analytical measurement methodology yields an uncertainty of 7% or better for $\text{SO}_4^{2-}$, and has been diligently kept the same throughout to enable accurate determination of even small variations in $\text{SO}_4^{2-}$ concentrations, and hence in sulfur dioxide ($\text{SO}_2$) upwind emissions. $\text{SO}_4^{2-}$ mixing ratios are combined with $\text{SO}_2$ measurements made, as described elsewhere in this paper and in Brandt et al. (2016), to obtain total sulfur (TS). These data are collectively used: (1) evaluate temporal and spatial trends of these species across the Northeast over the past 30 years; (2) study the impact of changes in regional emissions on the downwind (i.e., receptor) concentrations; (3) investigate the question of linearity/nonlinearity between regional $\text{SO}_2$ emissions and acid deposition; and (4) develop an empirical model for sulfur transport for the Northeast corridor.

Although Whatman 41 filters have been used in many air sampling programs around the world, there have been questions raised on the retention efficiency of this filter media (Lodge, 1986). Over the years a number of test results have been published to address these concerns (e.g., Husain and Dutkiewicz, 1990). Over a 24 hour sampling period with a high volume sampler the retention of $\text{SO}_4^{2-}$ aerosols was on the order of 95% and for 12 hr samples the retention was 92%. More recent tests using BC aerosols collected on Whatman 41 filters indicated a retention efficiency of 90% (Husain et al., 2008). Since particulate matter has been collected at Whiteface Mountain, NY, daily or every 48 hours since 1978 it was decided to conduct detailed studies of BC over nearly four decades at this location. Because the filter media used has been Whatman 41 filters it was necessary to remove BC particles from C-containing cellulose. A new technique was developed to remove cellulose quantitatively by treating Whatman 41 filters with 70% ZnCl$_2$ at 70°C for an hour. The insoluble BC particles were transferred on to quartz filter, and BC concentration determined using the

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*Schwab et al., Aerosol and Air Quality Research, 16: 841–854, 2016*
Illinois, Urbana-Champaign. The CAL analyzes and quality.

1984. The MAP3S collector, DEC collector, and the NADP
Marble Mountain Lodge location as part of the NTN in
Lodge Precipitation Collection

The CAL analyzes and quality assures NTN samples for pH, specific conductance, NH4+, base cations (Ca²⁺, Mg²⁺, Na⁺, K⁺), and key anions (SO₄²⁻, NO₃⁻, Cl⁻) as per standard protocols (NADP, 2014).

At the Marble Mountain Lodge site, weekly wet deposition samples are collected with an N-CON Systems Co. Inc. Bucket Collector Model 00-120-2 (Crawford, GA) and analyzed at the Illinois State Water Survey’s Central Analytical Laboratory (CAL), located at the University of Illinois, Urbana-Champaign. The CAL analyzes and quality assures NTN samples for pH, specific conductance, NH4+, base cations (Ca²⁺, Mg²⁺, Na⁺, K⁺), and key anions (SO₄²⁻, NO₃⁻, Cl⁻) as per standard protocols (NADP, 2014).

Lodge Precipitation Collection

NADP established a precipitation sampling site at the Marble Mountain Lodge location as part of the NTN in 1984. The MAP3S collector, DEC collector, and the NADP collector were co-located for several years. The NADP site (NY98) remains in operation and is operated by ASRG with support from USGS.

Cloud Chemistry at Whiteface Summit

Cloud deposition has been shown to be the dominant contribution to the total (cloud plus precipitation plus dry) deposition at Whiteface (Baumgardner et al., 2003), providing 80–90% of the total soluble sulfur deposition at

A major change to the sampling and analysis of PM₂.₅ carbon occurred in May 2009. The Quartz carbon module was replaced by a separate sampler, a Model URG-3000N Sequential Particulate Speciation System (URG, Chapel Hill, NC). Analysis of quartz filters for elemental carbon (EC) and organic carbon (OC) was switched to the Interagency Monitoring of Protected Visual Environments IMPROVE_A temperature protocol (Chow et al., 2007) at the Desert Research Institute (Reno, NV) using dual mode detectors with optical transmittance and reflectance methods. In order to provide a consistent trend throughout, data from this newer method were scaled to match those of the older CSN carbon method using collocated measurement data (Rattigan et al., 2011). This amounted to a 4% reduction in the URG EC thermal optical reflectance (TOR) data and a scaling factor of approximately 1.5 for the OC TOR fraction.

Lodge Continuous PM Measurement Methods

PM₂.₅ mass concentrations are measured continuously at the Marble Mountain Lodge site using a ThermoFisher 1405D (formerly a Ruprecht & Patashnick Model 1400AB) Tapered Element Oscillating Microbalance (or TEOM) sampler as part of the New York State DEC sampling network. This instrument is well-described in the literature (Schwab et al., 2004). Measurements of particle SO₄²⁻ and NO₃⁻ were performed on a sub hourly basis from July 2002 to June 2006 using flash volatilization methods, Rupprecht & Patashnick (Albany, NY). The methods consist of particle impaction collection with flash volatilization and subsequent analysis of the evolved gases using either pulsed fluorescence or chemiluminescence for particle SO₄²⁻ and NO₃⁻, respectively. From June 2006 sampling of continuous NO₃⁻ was discontinued and the SO₄²⁻ instrument was replaced with a high temperature thermal reduction method, a Thermo Scientific Model 5020i (Franklin, MA). As the efficiency of the conversion processes for these instruments was not 100% quantititative (Rattigan et al., 2006) the data were normalized to 24 h integrated chemical speciation filter measurements for PM₂.₅ SO₄²⁻ and NO₃⁻. Measurements of PM₂.₅ BC have been performed since September 2012 using a two channel (370 and 880 nm) Model AE-21 Aethalometer® (Magee Scientific, Berkeley, CA). The BC for the two channels are referred to as BC₄₄₅ and BC₈₈₀, respectively. The instrument calculates BC by measuring the rate of change (over a 5 min period) in light attenuation due to particle deposit on a quartz fiber filter. However, as the loading on the filter increases the relationship between light attenuation and BC can become non-linear. Aethalometer® 5 min raw data are corrected for loading and processed into hourly intervals using software provided by the Air Quality Laboratory at Washington University (Turner et al., 2007).

RESULTS AND DISCUSSION

Cloud Chemistry at Whiteface Summit

Cloud deposition has been shown to be the dominant contribution to the total (cloud plus precipitation plus dry) deposition at Whiteface (Baumgardner et al., 2003), providing 80–90% of the total soluble sulfur deposition at
this site for the June through September period. A more recent study (Aleksic et al., 2009) estimated that summer cloud deposition of major ions at the Whiteface summit site was 14 to 28 times higher than the summer rain deposition at the lower elevation Marble Mountain Lodge site. The frequency of cloud (Fig. 1) combined with the relatively high concentrations of pollutants in the cloud water contribute to this high deposition fraction. 2004 is excluded from this plot since major facility repairs limited cloud sampling to just a few manually collected events during July. In 2002, 2006, 2007, 2008, and 2010 all four collection months met the 75% validity criteria and the average cloud frequency for those summers is 34, 49, 36, 54 and 46%.

As noted above, the primary focus of the cloud chemistry program at Whiteface has been the measurement of major inorganic ions, with a special emphasis on sulfate given the provisions of Title IV and Title IX of the 1990 Clean Air Act Amendments. Title IV required a two phase reduction in SO$_2$ emissions of approximately 10 million tons, and Title IX mandated a comprehensive research and monitoring program to track emission reductions and their effects on air quality, deposition, and ecosystems. The first SO$_4^{2-}$ reductions occurred in the early 1990’s, as these time series measurements began, and the second set after 2005. Annual volume weighted cloud chemistry concentrations for SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and H$^+$ ions are shown in Fig. 2. (Volume weighting means that total molar loadings (concentration times event volume) for each event are summed, and then divided by the total volume of cloud collected in all events). There is quite a bit of year-to-year variation, and 2005 concentrations are much higher to the point of being an outlier. We have no good explanation for this high value at this point. The level of year-to-year variation is similar to that observed at Clingman’s Dome, but at this location the highest concentrations are recorded in 2001 and 2007 – in contrast to the relative low SO$_4^{2-}$ at Whiteface Summit in those years (EPA, 2012a). Below we show that at the Marble Mountain Lodge site, aerosol SO$_4^{2-}$ is relatively high in 2005, while precipitation SO$_4^{2-}$ is not. Because of the very high anion concentrations in 2005 cloud water, earlier work that only included data through 2006 (Aleksic et al., 2009) did not detect a significant trend in the cloud SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ concentrations – only in the H$^+$ concentration. Fig. 3 shows the range of values and the pH trend in Whiteface Mountain cloud water for the period 1994–2013. This trend is substantial and shows a steady, if somewhat variable year-to-year, decrease in the acidity of the cloud water at Whiteface in the summer months. The recovery works out to a little over 0.4 pH units per decade for the past twenty years. The reductions in SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and H$^+$ over the 20-year period work out to be 3.8%, 3.7%, 2.8%, and 4.3% per year respectively.

**Black Carbon and Sulfate Measurements at Whiteface Summit**

Black Carbon, sometimes called soot and closely related to elemental carbon (or EC), is emitted into our atmosphere whenever wood, vegetation, coal, oil, or any type of carbon based fuel is incompletely burned. The amount of BC emitted into the atmosphere depends upon the conditions of burning (Flagan and Seinfeld, 1988). In oxygen rich and high temperature conditions less BC will be emitted. The BC in

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**Fig. 1.** Whiteface Summit Cloud Frequency 2001–2010 (ALSC data). Months must have 75% of all five-minute averaged Liquid Water Content (LWC) measurements valid to be included.
the atmosphere exists as sub-micron-size particles, (less than a millionth of a meter). When inhaled, these particles can contribute to cardiopulmonary disease and other health effects (EPA, 2012b). These particles can travel thousands of miles from where they were emitted. In the atmosphere they may absorb sunlight and heat the atmosphere. Black carbon can also be incorporated into snow and ice and have important effects on the albedo in cold regions (Doherty et al., 2010; Brandt et al., 2011; Hadley and Kirchstetter, 2013). They are removed from the atmosphere and deposited on earth largely by precipitation (EPA, 2012b). Thus, BC particles, at least some of them, emitted anywhere in North America or elsewhere, could be present in the atmosphere in the Adirondacks of New York. These particles absorb sunlight, become hot, and warm the atmosphere, modify cloud cover, and hence the climate.

The sources emitting BC are numerous, spread over vast regions, and BC emissions per ton of fuel vary with the type of fuel and combustion conditions. The upwind sources which contributed to the observed BC concentrations at Whiteface Mountain were also investigated. Husain and Dutkiewicz (1990) have shown that much of the \( \text{SO}_4^{2-} \).
(63%), and trace elements (specifically As, Se, Sb, Zn, and V) observed at Whiteface Mountain originated in the industrial Midwestern US. This led to an investigation of the impact of the Midwestern sources on BC observed at Whiteface Mountain (Khan et al., 2006). Black carbon concentrations in ten pollution episodes lasting 10–14 days between 1985 and 2002 were analyzed. The data showed that during all of the BC episodes the air masses passed over high emission areas of NJ, PA, IN, OH, KY, MI, and WI (Khan et al., 2006).

Daily aerosol BC and \( \text{SO}_4^{2-} \) were measured at Whiteface Mountain for the year 1997. The air mass transport pathways were determined using four 72-h backward air trajectories per day from the hybrid single-particle Lagrangian integrated trajectory model (HYSPLIT_4 http://www.arl.noaa.gov/HYSPLIT_info.php). The maximum daily BC and \( \text{SO}_4^{2-} \) were 364 and 28,800 ng m\(^{-3}\), respectively. Black carbon and sulfate showed seasonal variations at Whiteface Mountain Summit. Occurrences of high daily BC were mainly in spring months due to rapid transport from source regions, while peak daily \( \text{SO}_4^{2-} \) concentrations occurred in summer months, emphasizing the secondary nature of aerosol \( \text{SO}_4^{2-} \). BC and \( \text{SO}_4^{2-} \) were highly variable as the weather pattern changed. High BC and \( \text{SO}_4^{2-} \) values were associated with westerly air flow from the industrialized Midwestern U.S. Stagnant conditions at the emission sources often resulted in higher BC and \( \text{SO}_4^{2-} \) observed at Whiteface Mountain. Sector analysis using HYSPLIT_4 air trajectories showed that regions lying between the southwest and northwest of the Whiteface Mountain contributed 81% and 83% of the BC and \( \text{SO}_4^{2-} \), respectively (Khan et al., 2010). The net monthly direct radiative forcing due to BC and \( \text{SO}_4^{2-} \) aerosols varied from −0.05 to −0.50 W m\(^{-2}\), with an annual average of −0.20 ± 0.15 W m\(^{-2}\) (Khan et al., 2010).

Monthly BC concentrations were determined in monthly composites of daily or 48-hour samples from 1978 to 2005. Annual mean BC concentrations were calculated from the monthly data from 1978 to 2005. Mean concentrations for the 1978–1986, and 1987–1996 periods were 550, and 225 ng m\(^{-3}\), respectively. A 59% decrease in mean BC occurred between 1978–1986 and 1987–1996 periods, while an 88% decrease was found between the 1978–1986 and 1997–2005 periods as shown in Fig. 4 (Husain et al., 2008). These decreases are due to Clean Air Act emissions controls and cleaner burning combustion sources.

**Precipitation Chemistry at Marble Mountain Lodge**

Fig. 5 displays the annual volume-weighted concentrations of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and pH, as well as annual precipitation depths at Marble Mountain Lodge in relation to other sites operating in the northeastern US from 1980–2013. Concentrations of \( \text{NH}_4^+ \), \( \text{NO}_3^- \), and \( \text{SO}_4^{2-} \) at Marble Mountain Lodge are generally lower compared to other sites across the region, and pH values are generally toward the high end in the region, likely due to the fact that Whiteface Mountain is generally further north and east than the other sites and therefore more removed from source regions. Precipitation depths at Marble Mountain Lodge are generally near the middle of the regional range.

Over the past three decades, substantial declines in emissions of nitrogen oxides and \( \text{SO}_2 \) have led to declines in acidic deposition over much of the northeastern US (CASTNET, 2015). Concentrations of \( \text{NO}_3^- \) in precipitation at Marble Mountain Lodge are less than half of what they were in the early 1980s, and \( \text{SO}_4^{2-} \) concentrations are roughly 75% lower. At the same time, annual pH levels at

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**Fig. 4.** Annual mean BC concentrations measured at Whiteface Summit, from 1978 to 2005. From Husain et al., JGR, (2008).
Marble Mountain Lodge have increased from < 4.4 in the mid-1980s to > 5 currently. We ran the non-parametric Mann Kendall test for monotonic trends in annual average concentrations for each parameter. While there was no significant trend observed in NH$_4^+$, statistically significant ($p < 0.05$) trends were observed in the other parameters. At Marble Mountain Lodge, concentrations of NO$_3^-$, SO$_4^{2-}$, and H$^+$ have decreased by 2.6 % year$^{-1}$, 4.4 % year$^{-1}$, and 4.7 % year$^{-1}$, respectively, while precipitation has increased slightly at a rate of 0.7 % year$^{-1}$. These trends in concentration are generally consistent with the cloud chemistry at the summit described above, albeit with not so much year-to-year variation.

These precipitation chemistry measurements provide
critical information in the current effort to develop a multi-pollutant ambient air quality standard. In particular, the EPA is charged with periodically reviewing and updating national ambient air quality standards (NAAQS) for criteria pollutants as outlined in the federal Clean Air Act. In its recent review of the secondary standards for sulfur and nitrogen oxides, the EPA stated that there was ample data to document the impacts of these two pollutants on acidifying surface waters, soils, and forests; hence, in 2011 the EPA proposed a first ever multi-pollutant, multi-media NAAQS for oxides of sulfur and nitrogen. The aquatic acidification index (AAI; e.g., Scheffe et al., 2014) was developed to relate ambient air concentrations of sulfur and nitrogen oxides to wet and dry depositional processes, and ultimately to surface water acid neutralizing capacity (ANC).

In 2012, the EPA began monitoring continuous NO$_x$ collocated with a CASTNet monitor at Huntington Wildlife, about 55 km SW of Marble Mountain Lodge. The CASTNet samplers consist of three-stage filter packs that collect gas-phase SO$_2$ and HNO$_3$, and particulate inorganic ions on a weekly integrated basis. The EPA also installed a Radiello passive sampler to collect bi-weekly gas-phase NH$_3$, as per Ammonia Monitoring Network (AMoN) protocols. In order to augment these monitoring efforts, the DEC added CASTNet and passive NH$_3$ samplers at the Marble Mountain Lodge site at Whiteface Mountain and Nick’s Lake Campground, approximately 120 km southwest of Whiteface. These additional measurements will allow New York to characterize nitrogen and sulfur air concentrations and deposition in the region at several locations, to better evaluate the AAI and its possible use in the NAAQS process.

**Lodge Particulate Matter from Filter Samples**

A 15 year record of annual mean PM$_{2.5}$ mass data at Marble Mountain Lodge is shown in Fig. 6. Even back in 2001 the annual PM$_{2.5}$ mass (6.9 µg m$^{-3}$) was well below the annual primary PM$_{2.5}$ NAAQS of 15 µg m$^{-3}$ set in 1997 and the 2012 revised standard of 12 µg m$^{-3}$. Since then PM$_{2.5}$ mass has generally decreased with the annual mean of 3.8 µg m$^{-3}$ in 2014. The decrease, which represents an approximate 40–45% drop in concentration since 2001–2002, is significant at the 95% confidence interval. Note the decrease is not uniform throughout with essentially all the change occurring between 2002 and 2008 as concentrations remain relatively uniform in the past 6–7 years. We hypothesize that this is due to the plateauning of emissions reductions in the mid-late 2000’s. Fig. 7 shows annual mean SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ ion concentrations since 2001. Sulfate, which is the dominant ion species and a major component of PM$_{2.5}$ mass, has similar patterns with a significant decreasing trend. The overall decrease in SO$_4^{2-}$ since 2001 is approximately 1.6 µg m$^{-3}$ or 60%. Like PM$_{2.5}$ mass there is a levelling off in concentrations in recent years but particularly after 2010. Nitrate concentrations are considerably lower than SO$_4^{2-}$ by about a factor of 5–7 reflecting the lack of major sources at this rural background site. Concentrations of NO$_3^-$ have decreased since 2001 by approximately 30–40% although not significant at the 95% confidence interval. Annual mean NH$_4^+$ shows a similar downward trend to SO$_4^{2-}$. A significant decrease of 0.4 µg m$^{-3}$ is observed since 2001 equivalent to an overall drop of 60%. The molar ratio of NH$_4^+$ to SO$_4^{2-}$ lies between 1 and 2 indicating a mixture of ammonium bisulfate and ammonium sulfate. The ratio of the sums of measured equivalent anions over cations is above 1 (range 1.16–1.79) indicating aerosol acidity or missing cations (e.g., Ca$^{2+}$ is not measured).

The corresponding annual trends for carbonaceous elemental and organic carbon, EC and OC, from the CSN network are shown in Fig. 8. The EC annual mean at this

![Fig. 6. Annual mean PM$_{2.5}$ FRM mass from 2000–2014 at Marble Mountain Lodge. Error bars represent the 95% confidence intervals. The solid line through the data is solely a visual aid.](image-url)
Fig. 7. Annual mean PM$_{2.5}$ SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ from 2001–2014 at Marble Mountain Lodge. Error bars represent the 95% confidence intervals. The solid line through the data is solely a visual aid. The background site varies from 0.10 to 0.20 µg m$^{-3}$ which is at or below the detection limit (0.24 µg m$^{-3}$) reflecting the lack of major nearby sources. Annual mean OC concentrations varied from 0.9 to 1.6 µg m$^{-3}$ with highest concentrations after 2004. No uniform trend is observed but rather step jumps, for example between 2004 and 2005 and again in 2007 and 2008 when the annual mean increased by 0.30 µg m$^{-3}$ in both instances. However 2012–2014 concentrations of OC are only a little higher than those measured in 2001. The fraction of total fine PM that is carbonaceous has definitely increased over this period, and further work into this phenomenon at this and other locations in New York State is ongoing.

Seasonal variation also helps determine sources and processes affecting PM$_{2.5}$, and Fig. 9 shows on a seasonal basis highest PM$_{2.5}$ mass concentrations are observed in summer (June, July, August) and lowest in winter (December, January, February) reflecting increased secondary aerosol production during summer months as indicated in the SO$_4^{2-}$ and OC patterns in Fig. 10. In 2001 mean summer PM$_{2.5}$ mass is significantly higher than other seasons which are not significantly different from each other. The summer/winter ratio was approximately a factor of 2. By 2013 mean seasonal concentrations have decreased by 2–3 µg m$^{-3}$ but the seasonal pattern remains the same. The summer/winter seasonal amplitude for SO$_4^{2-}$ is also a factor of 2 although not significant. The OC shows a stronger seasonal gradient with concentrations a factor of 3 higher in summer vs winter which is significant. Fig. 11 shows that a major change in species composition has occurred since 2001–2002 when SO$_4^{2-}$ was the dominant mass species representing 30–35% of the PM$_{2.5}$ compared to 2013-2014 which shows organic mass, OM (defined as 1.8 × OC for this site, see Bae et al., 2006), is the largest component amounting to approximately 50% of the mass.

The increase in carbon aerosol mass in New York is in contrast to that observed in most of the rest of the continental U.S. (Hand et al., 2013). Hand et al. (2013) did not offer an explanation of this anomaly. There has been a renewed emphasis on wood burning as a renewable resource in New York, but that is also true in New England.
states with different trends in carbonaceous aerosol mass. Still, the largest contribution to OC is in the summer (Fig. 10), and this observation indicates biogenic carbonaceous secondary aerosols may be more important than primary emissions from biofuel combustion. This is an important question that merits much more detailed research.

**Fig. 9.** Mean seasonal PM$_{2.5}$ mass at Marble Mountain Lodge in 2001 versus 2013. DJF represents months December, January and February and the error bars are the 95% confidence intervals.

**Fig. 10.** Mean seasonal SO$_4^{2-}$ and OC for 2002–2003 and 2012–2013 at Marble Mountain Lodge. DJF represents months December, January and February and the error bars are the 95% confidence intervals.
SUMMARY

These data sets, from two levels operated as part of the Whiteface Mountain research station, illustrate the value of long-term environmental monitoring. The cloud water and precipitation chemistry have been and continue to be a valuable resource for evaluating the ecosystem effects of atmospheric deposition of acidic sulfate and nitrate to this important and sensitive ecosystem. This information will be very valuable moving forward as the regulatory community decides whether to implement the aquatic acidification index (AAI). Specifically, the data clearly show decreases in acidic anions and increases in pH over the past two decades, which reflect well the decreases in emissions of acidic precursors mandated by Clean Air Act regulations. Sulfate in cloud water and precipitation has decreased by roughly a factor of three or more over the past 20 years, and $\text{NO}_3^-$ has decreased by more than a factor of two.

Similarly, the even longer data record for aerosol BC at the summit observatory shows a clear decrease in concentration (greater than 60%), again related to efficiency and regulation, but also of great importance to earth’s radiative balance and climate. Ongoing research into BC’s effect on climate is continuing at this location.

The PM$_{2.5}$ data record of 15 years at the Marble Mountain Lodge site also shows clear signs of a decrease in total mass and SO$_4^{2-}$ concentration, but an increase in the concentration of carbonaceous particulate matter. This switchover has important, but not fully explored implications for pollution control strategies and health and ecosystems response.

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DISCLAIMER

Although this manuscript was reviewed internally, it does not necessarily reflect the views or policies of the DEC or supporting agencies.

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