



Atmospheric Chemistry Measurements at Whiteface Mountain, NY: Cloud Water Chemistry, Precipitation Chemistry, and Particulate Matter

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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 PM_{2.5} 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. The New York State Department of Environmental Conservation (DEC) operated total suspended particulate

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Table 1. Ongoing Whiteface Summit measurements of condensed phase species.

START DATE	PARAMETER	PHASE	METHOD	AGENCY	SEASON
2007	Black Carbon - PM _{2.5}	Aerosol	Aetholometer	DOH	Year-round
1978	Total mass, ions, and elements - TSP	Aerosol	Filters	DOH	Year-round
1994	SO ₄ ²⁻ , NO ₃ ⁻ , Cl ⁻ , Ca ²⁺ , Mg ²⁺ , Na ⁺ , K ⁺ , TOC, NH ₄	liquid (cloud only)	Atomic absorption spectrometry	ALSC	Spring to fall
1994	Cloud Liquid Water Content	liquid (cloud only)	Optical forward scatter (Gerber)	ALSC	Spring to fall
1994	Cloud Particle Surface Area	liquid (cloud only)	Optical side scatter (Gerber)	ALSC	Spring to fall
1994	Cloud pH	liquid (cloud only)	Probe/meter	ALSC	Spring to fall
1994	Cloud specific conductivity	liquid (cloud only)	Probe/meter at 25°C	ALSC	Spring to fall

ALSC – Adirondack Lake Survey Corporation.

DOH – Department of Health (New York State).

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

START DATE	PARAMETER	PHASE	METHOD	AGENCY	SEASON
1999	PM _{2.5} Mass	Aerosol	FRM Sampler	DEC	Year-round
2001	PM _{2.5} Speciation	Aerosol	EPA Chemical Speciation Network - CSN	DEC	Year-round
2002	PM _{2.5} SO ₄ ²⁻	Aerosol	Thermal reduction to SO ₂	DEC	Year-round
2002	PM _{2.5} optical scatter	Aerosol	White light nephelometer	ASRC	Year-round
2012	PM _{2.5} BC	Aerosol	Aetholometer	DOH/DEC	Year-round
2000	PM _{2.5} , PM ₁₀ , PM Coarse	Aerosol	TEOM	DEC	Year-round
1984	Precipitation gauge	Precipitation	Load cell weighing gauge	NADP	Year-round
1984	Precipitation collector	Precipitation	Covered bucket w/ optical sensor	NADP	Year-round
2012	Gaseous SO ₂ , HNO ₃ ; particulate SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ , Ca ²⁺ , Na ⁺ , Mg ²⁺ , Cl ⁻	Gas, Aerosol	Filter pack	CASTNET	Year-round

ASRC – Atmospheric Sciences Research Center.

CASTNET – Clean Air Status and Trends Network (U.S. Environmental Protection Agency).

CSN – EPA Chemical Speciation Network - <http://www.epa.gov/ttnamtl1/speciepg.html>.

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 (PM₁₀) 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 in 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 (SO_4^{2-}) is routinely measured using ion chromatography, and ions such as nitrate (NO_3^-), ammonium (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 SO_4^{2-} , and has been diligently kept the same throughout to enable accurate determination of even small variations in SO_4^{2-} concentrations, and hence in sulfur dioxide (SO_2) upwind emissions. SO_4^{2-} mixing ratios are combined with 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 to: (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 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 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

thermal optical method (Li *et al.*, 2002).

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 ASRC with support from USGS.

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, NH_4^+ , base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), and key anions (SO_4^{2-} , NO_3^- , Cl^-) as per standard protocols (NADP, 2014).

Lodge Particulate Matter Collection and Measurement – Integrated Filter Samples

The Marble Mountain Lodge site was chosen as a regional rural background site for the New York State $\text{PM}_{2.5}$ Federal Reference Method (FRM) Monitoring network. Since there are no large sources of $\text{PM}_{2.5}$ in the vicinity the site measurements are typically the lowest in the state and representative of the rural region (Schwab *et al.*, 2004). Sampling for $\text{PM}_{2.5}$ mass commenced in July 1999. Sample collection is carried out over a 24h integrated period, operated midnight to midnight the following day, and reported as ambient temperature and pressure concentrations in accordance with the U.S. Air Quality Standards for $\text{PM}_{2.5}$. Initially sampling was setup on a daily schedule but changed to a 1 in 6 day schedule in 2007. The sampler is a Thermo Scientific Model 2025 Partisol Plus Sequential Air Sampler (Franklin, MA). Particle flow is directed through a PM_{10} size-selective inlet followed by a Well Impactor Ninety-Six (WINS) impactor which provides the 2.5 μm cut-point. The sample flow is volumetrically controlled and directed onto a 47 mm PTFE filter which is maintained within 5°C of ambient.

Measurements of $\text{PM}_{2.5}$ species composition commenced in May 2001 as part of the Chemical Speciation Network (CSN). $\text{PM}_{2.5}$ species measurements are key to understanding the sources contributing to $\text{PM}_{2.5}$ particle mass. Sampling was initially performed using a Rupprecht & Patashnick Model 2300 Partisol Speciation Sampler (Albany, NY). The sampler was replaced by a MetOne Spiral Aerosol Speciation Sampler (Grants Pass, OR) in October 2007. Sample collection operated from midnight to midnight based on a 1 in 3 day schedule for the first few years, but switched to a 1 in 6 day schedule in 2006. The speciation sampler consists of 3 individual modules each with independent flow control and size selective inlet. A Teflon module is used for $\text{PM}_{2.5}$ mass and element analysis while Nylon and Quartz modules are employed for major ions and carbonaceous material, respectively. Analysis of the FRM and CSN filters (with one exception, described below) is performed at RTI International (Durham, NC).

A major change to the sampling and analysis of $\text{PM}_{2.5}$ 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

$\text{PM}_{2.5}$ mass concentrations are measured continuously at the Marble Mountain Lodge site using a ThermoFisher 1405D (formerly a Rupprecht & 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 SO_4^{2-} and NO_3^- 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 SO_4^{2-} and NO_3^- , respectively. From June 2006 sampling of continuous NO_3^- was discontinued and the SO_4^{2-} 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% quantitative (Rattigan *et al.*, 2006) the data were normalized to 24 h integrated chemical speciation filter measurements for $\text{PM}_{2.5}$ SO_4^{2-} and NO_3^- . Measurements of $\text{PM}_{2.5}$ 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 BC_{UV} and BC_{IR} , 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

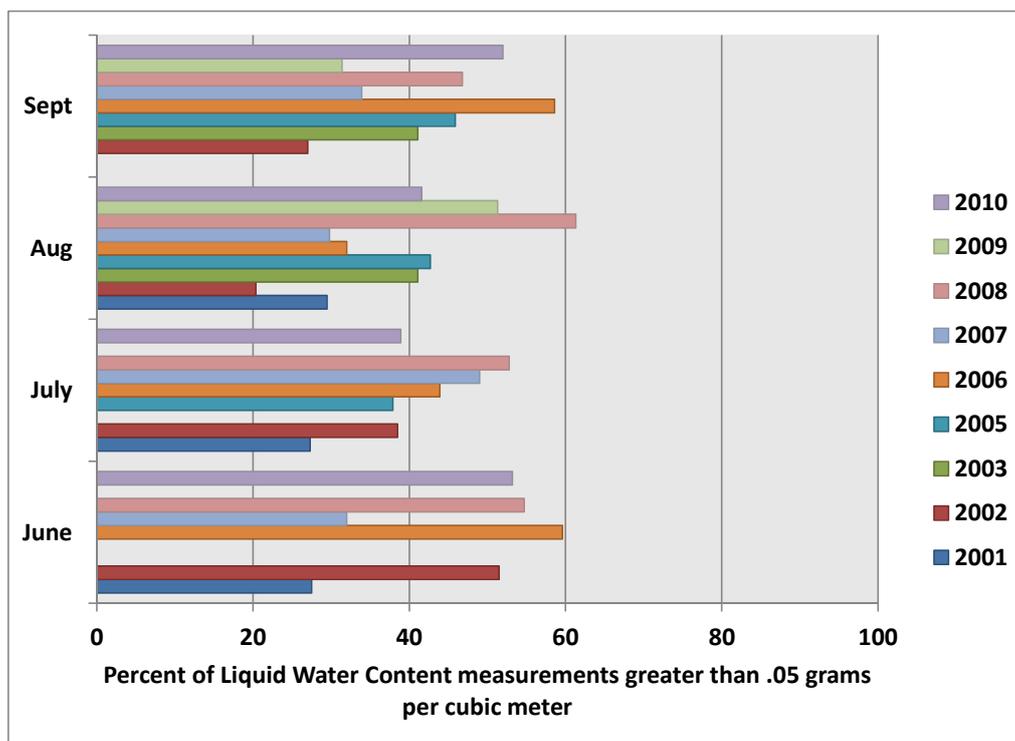


Fig. 1. Whiteface Summit Cloud Frequency 2001–2010 (ALSC data). Months must have 75% of all five-minute averaged Liquid Water Content (LWC) measurements valid to be included.

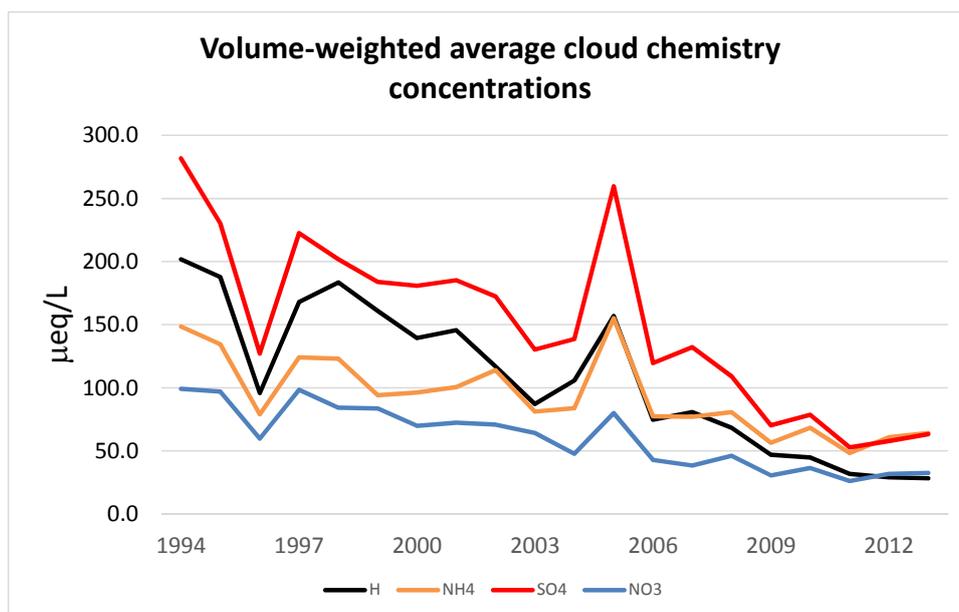


Fig. 2. Volume-weighted summertime cloud chemistry concentrations at Whiteface Summit (EPA-MADPRO and ALSC data). Note that some years have many fewer samples than others – see text and also Fig. 3 below.

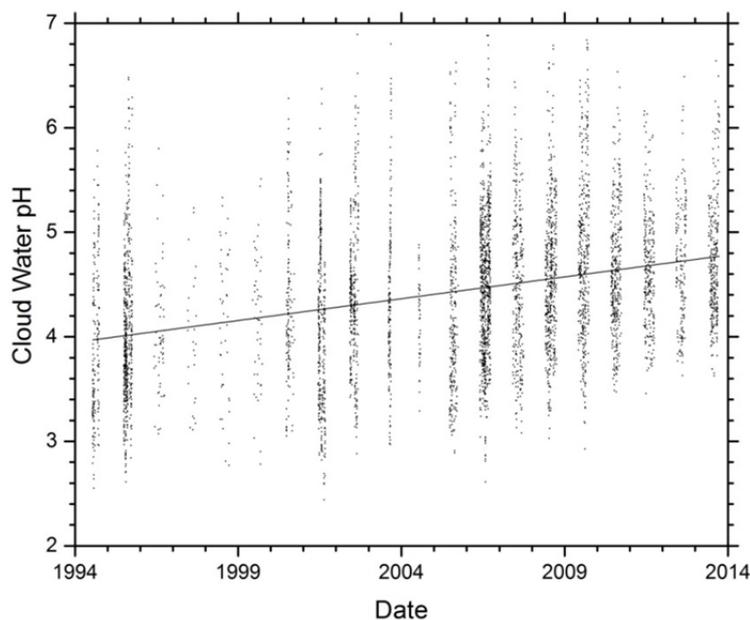


Fig. 3. All cloud water pH measurements, and a fitted linear trend line, for the summer season cloud water analysis program at Whiteface Summit (EPA-MADPRO and ALSC data).

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 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 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 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 SO_4^{2-} concentrations occurred in summer months, emphasizing the secondary nature of aerosol SO_4^{2-} . BC and SO_4^{2-} were highly variable as the weather pattern changed. High BC and 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 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 SO_4^{2-} , respectively (Khan *et al.*, 2010). The net monthly direct radiative forcing due to BC and SO_4^{2-} aerosols varied from -0.05 to -0.50 W m^{-2} , with an annual

average of $-0.20 \pm 0.15 \text{ W m}^{-2}$ (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 NH_4^+ , NO_3^- , 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 NH_4^+ , NO_3^- , and SO_4^{2-} at Marble Mountain Lodge are generally low compared to other sites across the region, and pH values are generally toward the high range 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 SO_2 have led to declines in acidic deposition over much of the northeastern US (CASTNET, 2015). Concentrations of NO_3^- in precipitation at Marble Mountain Lodge are less than half of what they were in the early 1980s, and SO_4^{2-} concentrations are roughly 75% lower. At the same time, annual pH levels at

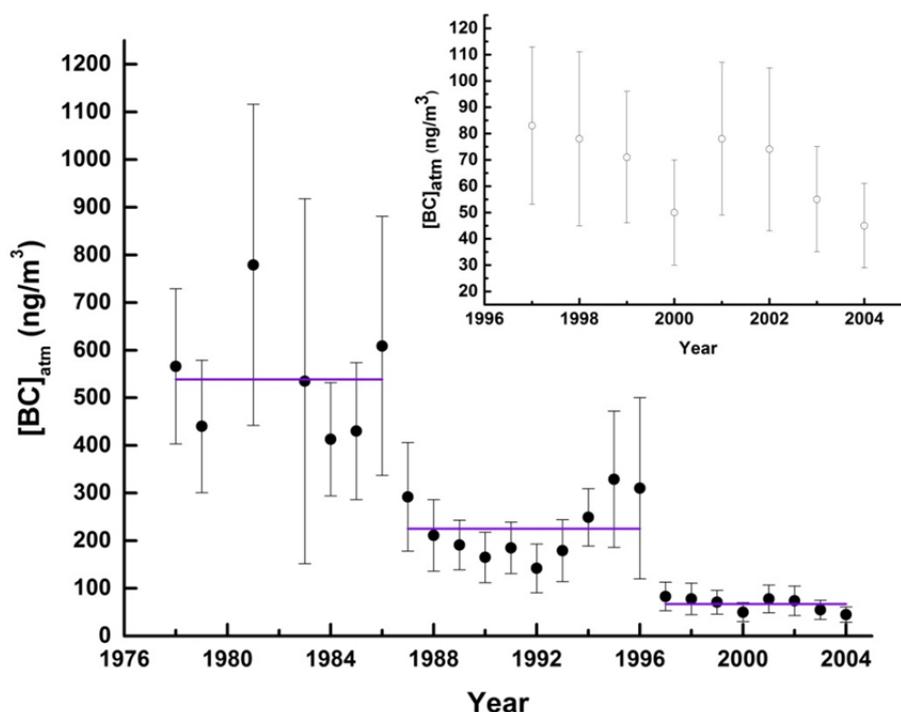


Fig. 4. Annual mean BC concentrations measured at Whiteface Summit, from 1978 to 2005. From Husain *et al.*, JGR, (2008).

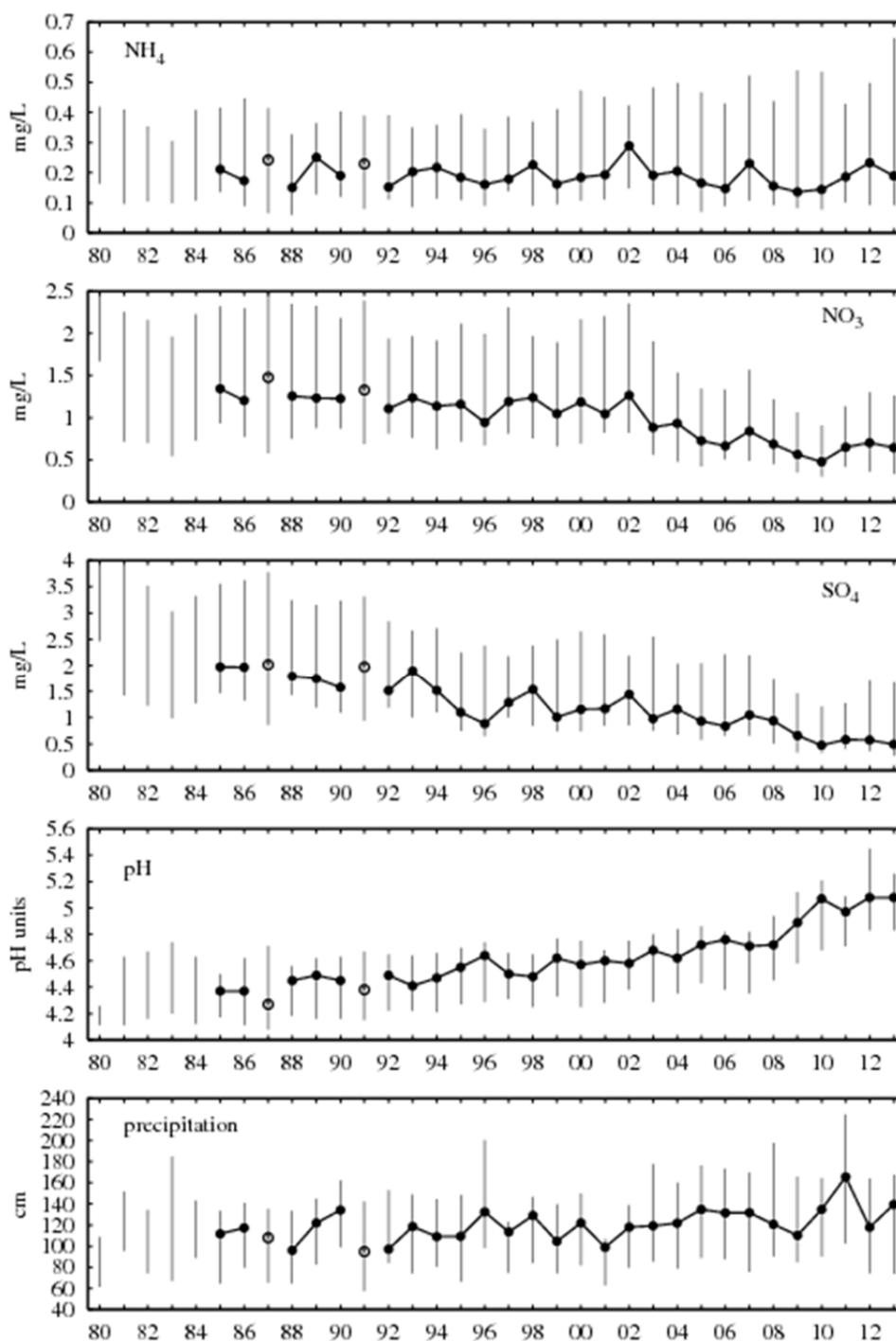


Fig. 5. Precipitation depths and chemistry measured at Marble Mountain Lodge. The data are shown as circles; filled circles denote years with at least 75% valid data, while open circles denote years with between 50–75% valid data. The error bars denote the range in concentrations across 25 long-term sites in the northeastern US (the states of Maryland through Maine) in operation in any given year.

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 $2.6\% \text{ year}^{-1}$, $4.4\% \text{ year}^{-1}$, and $4.7\% \text{ year}^{-1}$, respectively, while precipitation has increased slightly at a rate of $0.7\% \text{ year}^{-1}$. 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_y 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 $\text{PM}_{2.5}$ mass data at

Marble Mountain Lodge is shown in Fig. 6. Even back in 2001 the annual $\text{PM}_{2.5}$ mass ($6.9 \mu\text{g m}^{-3}$) was well below the annual primary $\text{PM}_{2.5}$ NAAQS of $15 \mu\text{g m}^{-3}$ set in 1997 and the 2012 revised standard of $12 \mu\text{g m}^{-3}$. Since then $\text{PM}_{2.5}$ mass has generally decreased with the annual mean of $3.8 \mu\text{g m}^{-3}$ 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 plateauing 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 $\text{PM}_{2.5}$ mass, has similar patterns with a significant decreasing trend. The overall decrease in SO_4^{2-} since 2001 is approximately $1.6 \mu\text{g m}^{-3}$ or 60%. Like $\text{PM}_{2.5}$ 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 $0.4 \mu\text{g m}^{-3}$ 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

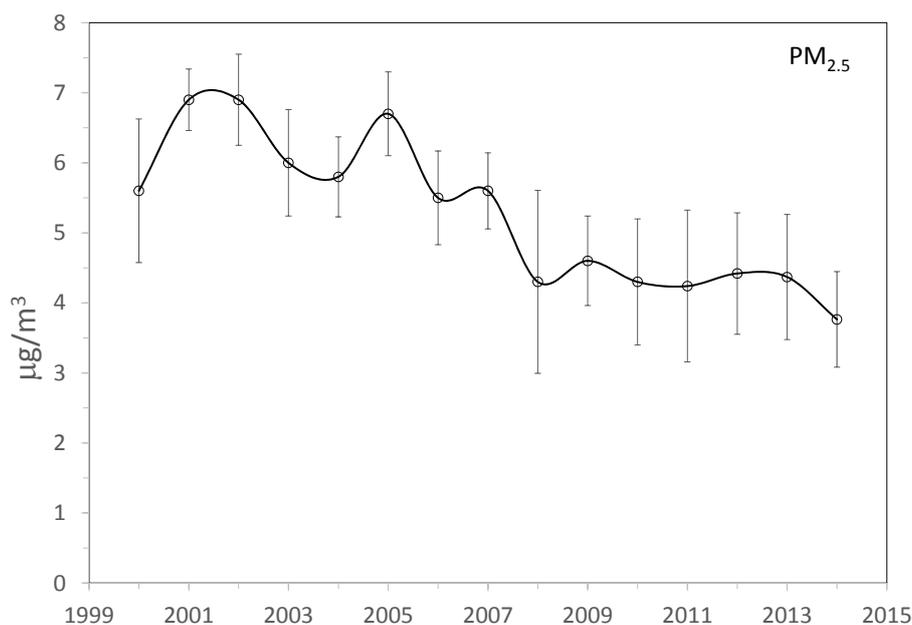


Fig. 6. Annual mean $\text{PM}_{2.5}$ FRM mass from 2000–2014 at Marble Mountain Lodge. Error bars represent the 95% confidence intervals. The solid line through the data is solely a visual aid.

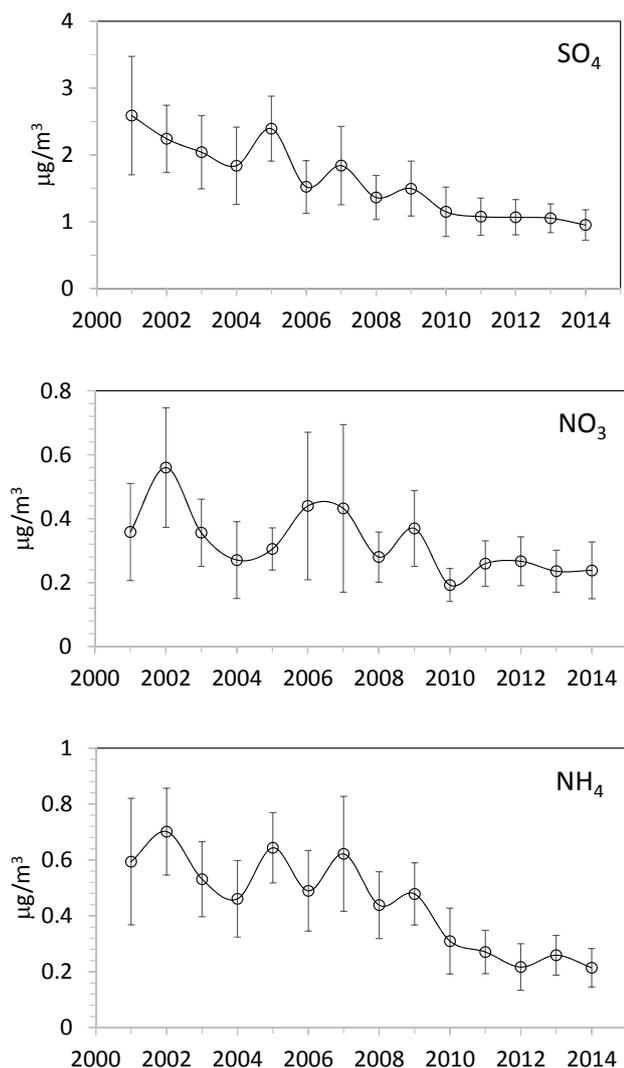


Fig. 7. Annual mean $\text{PM}_{2.5}$ SO_4^{2-} , NO_3^- and NH_4^+ from 2001–2014 at Marble Mountain Lodge. Error bars represent the 95% confidence intervals. The solid line through the data is solely a visual aid.

background site varies from 0.10 to 0.20 $\mu\text{g m}^{-3}$ which is at or below the detection limit (0.24 $\mu\text{g m}^{-3}$) reflecting the lack of major nearby sources. Annual mean OC concentrations varied from 0.9 to 1.6 $\mu\text{g m}^{-3}$ 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 $\mu\text{g m}^{-3}$ 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 $\text{PM}_{2.5}$, and Fig. 9 shows on a seasonal basis highest $\text{PM}_{2.5}$ mass concentrations are observed in summer (June, July, August) and lowest in winter (December, January, February) reflecting increased secondary aerosol

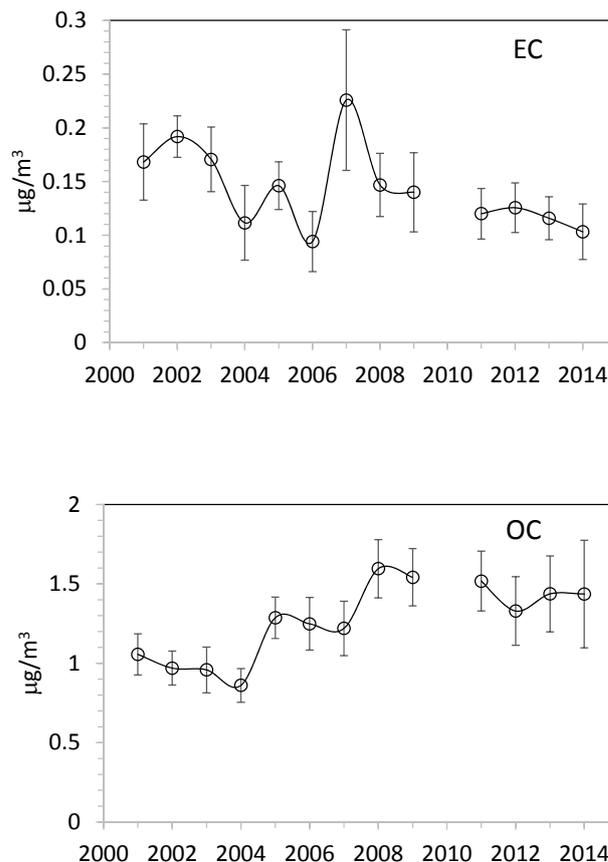


Fig. 8. Annual mean EC and OC concentrations from 2001–2014 at Marble Mountain Lodge. Error bars represent the 95% confidence intervals. The solid line through the data is solely a visual aid. Due to a change in methods data from 2009 onwards were scaled to match the older CSN method to provide a consistent trend. See text for details.

production during summer months as indicated in the SO_4^{2-} and OC patterns in Fig. 10. In 2001 mean summer $\text{PM}_{2.5}$ 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 $\mu\text{g m}^{-3}$ 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 $\text{PM}_{2.5}$ compared to 2013–2014 which shows organic mass, OM (defined as $1.8 \times \text{OC}$ 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

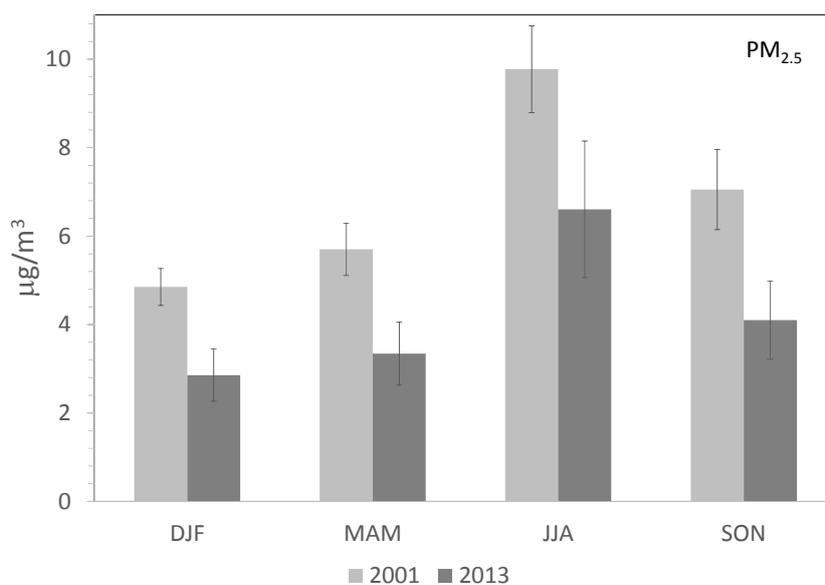


Fig. 9. Mean seasonal PM_{2.5} mass at Marble Mountain Lodge in 2001 versus 2013. DJF represents months December, January and February and the error bars are the 95% confidence intervals.

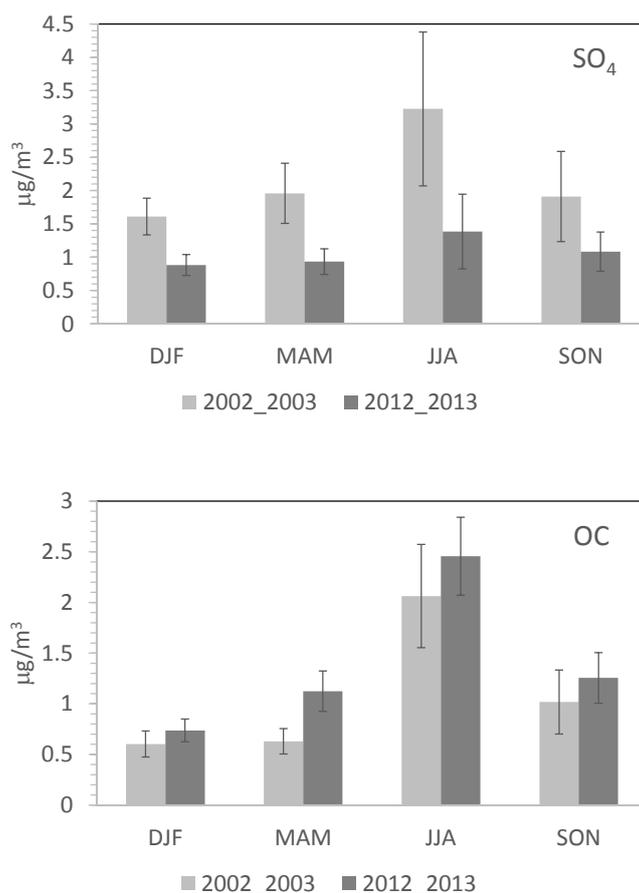


Fig. 10. Mean seasonal SO₄²⁻ and OC for 2002–2003 and 2012–2013 at Marble Mountain Lodge. DJF represents months December, January and February and the error bars are the 95% confidence intervals.

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.

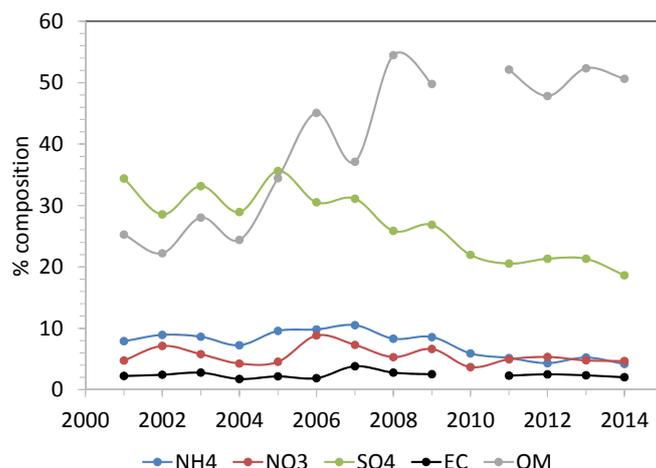


Fig. 11. Percentage species composition of total speciation PM_{2.5} mass at Marble Mountain Lodge. OM is OC × 1.8. There were no carbonaceous measurements for 2010.

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 NO₃ 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 SO₄²⁻ 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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