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Black carbon transport to a remote mountaintop in the northeastern US and relationship with other pollutants

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ABSTRACT

We report Aethalometer black carbon (BC) measurements carried out at 15-min intervals over 30 months at a mountaintop site in northeastern New York, along with co-located measurements of CO, O_3, and SO_2, and high time resolved measurements of $PM_{2.5}$ mass and aerosol sulfate (SO_4) concentrations acquired near the base of the mountain. The mean BC concentration at the site was 84 ng m^{-3} while monthly means varied from 25 to 144 ng m^{-3}. Correcting for the impact of "mountain meteorology" yields an estimated surface equivalent annual mean concentration of 100 ng m^{-3}. Periods of episodic high BC concentrations (>300 ng m^{-3}), however, occurred throughout the year but were longer and more intense during the warmer months. We observed that the concentrations of O_3, SO_2, SO_4, and $PM_{2.5}$ mass, and to a lesser degree CO were often highly correlated with BC concentrations during the episodes, even when air trajectories indicated that the air masses reaching the site had passed through widely varied geographical regions. We report details of three specific BC episodes and examine the relationship between the co-measured species and air trajectories.

1. Introduction

The incomplete combustion of carbon-based fuels (e.g., fossil- or bio-fuels) can lead to the production of soot that includes carbonaceous particulate matter. Both organic and inorganic species are produced. A significant component can be aerosol black carbon (BC); elemental carbon (EC) that is insoluble in polar and non-polar solvents, stable in air and oxygen up to 350–400 °C, has a graphitic like structure, and strongly absorbs energy in the visible range. The terms BC, EC, and soot are often used, but the terms also have operational meanings linked to the method used for analysis. Although we realize that it may not always be entirely accurate, we will simply use BC. Away from large urban sources most BC is found in particulate matter (PM) less than 2.5 μm in diameter ($PM_{2.5}$) but it can also be mixed with other PM. BC in the $PM_{2.5}$ size range can remain suspended in the atmosphere for days and thus be transported over hundreds of km before it falls to the earth as either wet or dry deposition.

Carbonaceous aerosols are a major component of airborne PM and can significantly impact health, atmospheric visibility, and climate. Although aerosols suspended in the atmosphere generally cool the atmosphere by scattering solar radiation, BC strongly absorbs in the visible and IR portions of the spectrum and thus contributes to atmospheric warming. In fact, it has been suggested that BC aerosols are the second largest contributor to global warming, after greenhouse gases (Jacobson, 2002). On a global basis it is estimated that BC contributes ~0.5 W m^{-2} to radiative forcing (Sato et al., 2003), but direct and indirect aerosol interactions may also significantly contribute but have uncertainties that are large (IPCC, 2007). Carbonaceous aerosols significantly contribute to the fine aerosol loading of the atmosphere. For sites in the Northeastern US the BC and organic carbon (OC) contributions to the $PM_{2.5}$ burden average 10 and 32%, respectively for 2006 (USEPA, 2008). Fine PM can penetrate deep into the lungs and cause respiratory and cardiovascular disease (e.g., Dockery et al., 1993; Gwynn et al., 2000; Pope et al., 2002). For the above reasons it is important to (1) characterize BC concentrations ([BC]) where [ ] designates concentration, at different sites and (2) evaluate transported versus local source contributions.

BC is considered a good surrogate for the presence of combustion products. Carbon monoxide (CO) is a colorless and odorless gas that is also a by-product of carbon fuel combustion but unlike BC, CO emissions are highest in highly efficient combustion processes. While BC has a residence time of around a week, CO is relatively

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stable in the atmosphere and has a lifetime of around 60 days (Logan et al., 1981; Crutzen and Zimmerman, 2003). There are a number of studies where Aethalometer [BC] and [CO] were co-measured in urban settings (Baumgardner et al., 2002; Zhang et al., 2007) or directly downwind from large urban centers (Zhou et al., 2009). The authors concluded that the primary factors affecting the [BC] to [CO] ratio were the local ratio of diesel to gasoline usage and the combustion efficiency of the vehicles in the area. Another factor may be the use of low-quality bunker fuel in marine vessels that produce a proportionally large component of BC compared to CO while coal fired power plants emitted very little BC compared to CO. Thus, [BC] and [CO] can help to deconvolute sources of carbonaceous emissions.

Some long-term BC measurements at rural sites have been made by the IMPROVE program (e.g., Malm et al., 2004) including two sites in New York that had sampling initiated in 2001. Concentrations of BC and OC, and water-soluble organics were also measured every third day at two sites in rural New York between November 2002 and August 2005 (Sunder Raman and Hopke, 2007). At the site in western NY, Stockton, [BC] averaged 474 ng m^{-3} while at Potsdam located in the northeastern Adirondacks [BC] averaged 333 ng m^{-3}. Long-range transport was considered to be the major source of carbonaceous aerosols at these sites. There were also 2 rural sites in NY that were part of the USEPA Speciation Trends Network (STN) that have aerosol samples collected for 24 h every 3 or 6 days that are measured for [BC] and [OC] (Schwab et al., 2004). At rural Pinnacle State Park in the Allegheny Plateau [BC] averaged 166 ng m^{-3} for the period February 2001 through February 2003 while over the same period [BC] at Whiteface Mt. Lodge averaged 106 ng m^{-3}. We maintain two rural aerosol-sampling sites in New York that collect suspended PM on a continuous basis with either 24- or 48-h samples (e.g. Husain and Dutkiewicz, 1990). The site at Whiteface Mt. summit has been in operation since 1978 while Mayville started sampling in the summer of 1983. Both sites presently collect continuous 24-h samples. A portion of each of these samples are extracted in Milli-Q water and analyzed for major ions by ion chromatography (Husain and Dutkiewicz, 1990). The Whatman 41 filters that are used, however, cannot be directly analyzed for BC or OC as the filters are cellulose based. Recognizing the lack of any long-term measurements of BC in the region, and the importance of these measurements for the reasons discussed above, a method was developed to dissolve the Whatman filter and redeposit the BC component on a quartz filter so it can be determined in a thermal/optical carbon analyzer (Li et al., 2002). Khan et al. (2006) used this method to determine BC for selected days with episodic high sulfate concentrations ($[SO_4]$) at Mayville and Whiteface Mt. They showed that BC was primarily transported in the same air masses as high $[SO_4]$; air masses from the southwest quadrant that had passed through the industrial Midwest. The archived filters from Whiteface Mt. going back to 1978 were combined into monthly composites and analyzed for [BC] (Husain et al., 2008). During the early 1980's [BC] averaged around 600 ng m^{-3} with mean concentrations during isolated quarters >800 ng m^{-3}. Beginning around 1987 [BC] were decreasing steadily except for a period in the mid- 1990's. From 1997 to 2005 they found the [BC] varied from 40 to 80 ng m^{-3} with an average of 66 ng m^{-3}. They used the BC trend data at Whiteface Mt. to normalize the depth profile of BC measured in dated lake sediments from an isolated lake in the region. Thus, atmospheric BC profiles were evaluated back through 1835 that provided a unique long-term snapshot of atmospheric [BC] in the region.

To further support the long-term BC measurements at Whiteface Mt. and to better understand the source regions impacting the site we initiated 15-min BC measurements with an Aethalometer in July of 2007. Through December 2009 17,000 h of [BC] measurements were recorded. In this paper we present the high time resolved BC data at Whiteface Mt. through December 2009 and compare the BC measurements to co-located 15-min and hourly measurements of [CO], $[O_3]$, and $[SO_2]$, and 3-h measurements of $PM_{2.5}$ mass and $PM_{2.5}$ aerosol $[SO_4]$ from a site located at base of the mountain. The co-located data, along with air trajectories, are used to explore source regions of BC and the interrelationships between these various pollutants in northeastern North America.

2. Methods

The measurements were conducted at Atmospheric Sciences Research Center (ASRC), State University of New York facility at the summit of Whiteface Mountain (1.5 km above mean sea level; 44.366°N and 73.903°W) and at a second site located at the base of the mountain (0.6 km above mean sea level, 44.393°N and 73.859°W). The two sites are <4 km apart and will hereafter simply be referred to as Summit and Lodge, respectively. The sites are in the Adirondack Park of New York State, which is highly rural with little industry. The village of Lake Placid (pop. 2500) is 12 km south southwest of the Summit and is the closest populated area. Overall the population is small so the associated vehicular traffic is also small. The Summit is accessible to the general public via a road that ends in a parking area ~90 m below the summit on the western slope. The summit can be reached via a tunnel to an elevator, or walking trails that are open to the public from Memorial Day through Columbus Day each year. However, the instruments at the Summit station are maintained throughout the year. Local activities do not contribute any significant BC at the summit. Supporting data is given in Appendix 1.

The Aethalometer BC measurements began on 11 July 2007. The high-sensitivity version of the Magee Scientific model AE21 was used. It has a collection area of 0.5 cm^2 and was operated at a flow rate of 5 lpm through a BGI sharp-cut 2.5 μm cyclone with an integration time set at 15 min. The AE21 measures the absorption of light by ambient aerosols collected on a quartz filter tape at 880 and 370 nm to determine [BC] (Hansen et al., 1984). The manufactories recommended specific attenuation coefficients of 16.6 and 39.5, respectively were used to convert the measured light attenuation into BC density. As the 370-nm channel can also be influenced by some fresh OC species like wood smoke or tobacco smoke, only results from the 880 nm channel are reported here. Several papers have concluded that the AE does not have a constant response curve as the filter loads due to multiple scattering and shadowing effects (e.g. Weingartner et al., 2003; Arnott et al., 2005). However, the bias is greatest for fresh soot particles and the shorter wavelength channels. Extensive tests run with this Aethalometer in highly polluted air in Karachi, Pakistan found no measurable bias for the 880 nm channel (Dutkiewicz et al., 2009). Similar tests run with the data set at Whiteface Mt. confirm this result so no correction for loading was applied.

The [BC] measured with this Aethalometer was compared to [BC] collected on Quartz filters and determined with a thermo/optical analyzer using the NIOSH protocol (Husain et al., 2007). The Aethalometer [BC] averaged 20% higher. Ahmed et al. (2009) compared [BC] from Whiteface Mt summit and three other highly varied sites that were extracted from Whatman 41 filters using the method introduced by Li et al. (2002) and analyzed for BC with the NIOSH protocol to [BC] determined on the same filters with a optical Transmissometer from Magee Scientific that uses the same optical channels and attenuation coefficients as the Aethalometer. The regression line passing through origin for the 206 daily samples from the Summit yielded a slope 0.92, with $r^2 = 0.58$. Thus, the two techniques give results which are in good agreement so [BC] at this