Atmospheric Research 137 (2014) 49–57

Contents lists available at ScienceDirect

Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

Long term trends in Black Carbon Concentrations in the Northeastern United States

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ARTICLE INFO

Article history:
Received 3 June 2013
Received in revised form 31 August 2013
Accepted 3 October 2013

Keywords:
Carbonaceous aerosols
Black carbon
Long-term trends
Aethalometer
Wood burning

ABSTRACT

We report BC concentrations, ([BC]), measured using the thermal optical method, in monthly composites of daily particulate samples collected at rural Mayville, NY from 1984 to 2010. The monthly concentrations ranged from 10 to 900 ng m^{-3}, and showed decreasing trend with a slope of −5.5 ng m^{-3} per year, and a 32% decrease over the 27-year period. The monthly [BC] varied weakly with season but generally peaked in late summer. An aethalometer was also used to measure [BC], in real time, every 5 min from May 2008 to December, 2010. Measurements were made at 370 and 880 nm wave-lengths. Although both channels are calibrated as BC, fresh wood combustion emissions include polycyclic aromatic hydrocarbons that enhance the 370 nm channel signal. We utilize this to estimate that the wood burning contributed 18% of the BC on an annual basis, but accounted for ~30% in winter and ~8% during summer. BC concentration from local and transported sources was calculated based on aethalometer BC and HYSPLIT 4 air trajectories. The highest [BC] were associated with air masses that passed through the Ohio River Valley as well as through the Mid-Atlantic States. However, when integrated over time 68% of the BC transported to the site arrived from OH, KY, IN, IL, MI, WI, and southern Ontario.

1. Introduction

Black carbon, also often referred to as elemental carbon (EC) or soot, is a byproduct of incomplete combustion of fossil- or bio-fuels and prescribed or wild fires. We will simply use the term BC, recognizing that it may not always be completely accurate. BC particles are submicron in size but increase in size as they age in the atmosphere (Viidanoja et al., 2002). The average residence time of BC bearing particles is around 6 days so they can be deposited hundreds or thousands of km from their source (Haywood and Shine, 1995). While most suspended particulate matter scatters light, BC strongly absorbs light in the visible and UV range. Thus, it has a significant impact on global warming (e.g., Ramanathan and Carmichael, 2008; McConnell et al., 2007). In fact, BC may be the second largest contributor to global warming after greenhouse gases (Jacobson, 2002) accounting for ~15–30% of global warming estimates (Jacobson, 2001). However, the magnitude of the climate forcing exerted by BC is still uncertain, with a global average value estimated from +0.20 to 1.1 W m^{-2} (Haywood and Shine, 1995; Haywood and Ramaswamy, 1998; Jacobson, 2001, 2002; Christopher et al., 2006; IPCC, 2007; Bond et al., 2013). In addition, BC particles affect visibility and adversely impact our respiratory and cardiac health (e.g., Dockery et al., 1993; Pope et al., 2002; Wichmann et al., 2000; Arimoto et al., 2005; Forastiere, 2004; Rom and Samet, 2006).

We maintain two rural sampling sites in New York State that collect particulate matter on a continuous basis with either 24- or 48-hour samples (e.g. Husain and Dutkiewicz, 1990; Husain et al., 1998). The site at Whiteface Mountain

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http://dx.doi.org/10.1016/j.atmosres.2013.10.003

summit has been in operation since the summer of 1978 while sampling started at Mayville during the summer of 1983. A portion of each of these samples are routinely extracted in Milli-Q water and analyzed for major ions by ion chromatography (Husain et al., 1998). Because Whatman 41 filters are used, they cannot be directly analyzed for BC as this filter is cellulose based. In recognizing the need for long-term measurements of carbonaceous aerosols in the region, and the importance of these measurements for the reasons discussed above, a method was developed to dissolve the Whatman filter and redeposited 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 at Mayville and Whiteface Mt. They showed that BC were primarily transported in the same air masses as high sulfate concentrations; 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). Although [BC] averaged around 600 ng m^{-3} during the early 1980s beginning around 1987 [BC] steadily decreased except for a period in the mid-1990s. From 1997 to 2005 [BC] varied from 40 to 80 ng m^{-3} with an average of 66 ng m^{-3}. The BC trend data at Whiteface Mt. was used to normalize the depth profile of BC measured in dated lake sediments from an isolated lake in the region to evaluate atmospheric BC profiles back through 1835. This technique provided a unique long-term snapshot of atmospheric [BC] in the region.

Here, we report on BC measurements at Mayville, a rural site in western NY State, from monthly composites of the daily filters for 27 continuous years dating back to 1984. To further support the long-term BC measurements at Mayville and to better understand the source regions impacting the site 5-minute aethalometer BC measurements were initiated at Mayville in May of 2008 and continued through 2010 when the site was shut down. The combined data are used to elucidate the importance of regional BC sources and to demonstrate that BC contributions from residential wood burning can be significant at rural northeastern sites during winter.

2. Methods

2.1. Site

The site is located on the roof of the Chautauqua County Office Building in rural Mayville (42.255° north, 79.505° east) located in the westernmost corner of NY State (Fig. 1). There are two four-storey County office buildings at the sampling site along with the associated parking area. The sampling site consists of a 10 cm diameter Al pipe that passes through the wall of the machine room on the roof into a sealed stainless steel box containing 4 high volume air samplers. Thus, there was no size selection of the aerosols. The brushless pumps were equipped with mass flow controllers and were programmed to run 24 h every 4th day at a flow rate of 1.0 m^3 per minute. The filters were 20 × 25 cm Whatman 41 filters. Based on double filter measurements it was determined that the Whatman 41 collection efficiency for aerosol sulfate varied from 92 to 97% depending on sampling conditions (Husain and Dutkiewicz, 1990). As BC primarily reside on submicron sized aerosols and archived Whatman 41 filters were being used to evaluate BC, the collection efficiency of the filter was recently evaluated at 90% with double filters and side by side comparisons with quartz filters (Khan et al., 2010). This retention factor has been applied to all Whatman 41 BC results.

There are weekly tests of the emergency diesel powered generators at the county buildings where the samples are collected and at the county jail located across the street for 1 to 2 h. When winds are calm there are large transient BC peaks. These tests began in 1989 on Friday afternoons and were switched to Mondays in 2002. Because of the highly time resolved aethalometer measurements, the impact from this transient source has been removed from the aethalometer data set. It was determined that a 13% reduction was needed for the filter BC measurements collected after 1989. The site is also 16 km downwind of interstate highway US-90 (NYS Thruway). Thus, it is possible that diesel truck and automobile traffic on this heavily traveled interstate may impact the BC at this site. As we shall later show, employee vehicles in the parking area have minimal impact on [BC] but the impact from I-90 traffic is indeterminate. During winter months wood burning is commonly used for space heating in the area so this may contribute to the BC burden at the site.

2.2. Thermal optical BC measurements

While there are a variety of methods available to measure [BC] on filters, the most commonly used is the thermal optical method using either laser reflectance (TOR) or transmission (TOT) to correct for the production of pyrolized carbon during the oxygen free organic carbon analysis stage. The daily filter collection at Mayville used cellulose Whatman 41 filters which cannot be directly analyzed by thermal optical techniques. Li et al. (2002) developed a method to dissolve away the cellulose filter so the suspended BC can be filtered onto a quartz filter. [BC] measurements were made from monthly composites of the daily filters, made by punching out a one cm diameter disk from each daily filter. BC aerosols were extracted for months with at least 15 days of daily filters using the method developed by Li et al. (2002). The BC was transferred on to quartz filters and concentrations were determined using the TOT NIOSH protocol (Birch and Cary, 1996). Additional discussion of the method can be found in Khan et al. (2010). There were an increased number of filters missed during 2009 and 2010 due to a more limited schedule of the onsite operator. For May through December 2008 monthly [BC] were determined by both TOT and aethalometer methods. Over these 8 months, aethalometer concentrations were 11% higher than those by the TOT technique. For the purpose of minimizing bias in the long term studies, [BC] for June 2008–2010 are based on the aethalometer data which was reduced by 11% as explained above.

We conducted an experiment to evaluate the uncertainty of monthly means when only partial data was available. Two months with complete aethalometer data were selected (July 2009 and January 2010). After daily means were computed 10 and 15 days were randomly removed from each of the two months with 10 trials of each. We found that the relative