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Seasonal variations of elemental carbon in urban aerosols as measured by two common thermal-optical carbon methods

Min-Suk Bae [a,*], James J. Schauer [a], Jay R. Turner [b], Philip K. Hopke [c]

[a] Civil and Environmental Engineering, University of Wisconsin-Madison, Madison, Wisconsin, USA
[b] Energy, Environmental and Chemical Engineering, Washington University, St. Louis, Missouri, USA
[c] Center for Air Resources Engineering and Science, Clarkson University, Potsdam, New York, USA

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ABSTRACT

Two commonly employed laboratory-based elemental carbon (EC) and organic carbon (OC) thermal/optical methods for the analysis of ambient particulate matter were used to analyze 709 twenty-four hour integrated $PM_{2.5}$ samples along with 76 field blanks from the St. Louis-Midwest Supersite in East St. Louis, Illinois. The two laboratory ECOC methods were the Aerosol Characterization Experiment—Asia (ACE-Asia) method based on National Institute of Occupational Safety and Health (NIOSH 5040) method and the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol. As in previous intercomparisons between these two methods, there was excellent agreement for total carbon (i.e. sum of EC and OC), but significant differences were observed in the split between the measured EC and OC. The 709 daily $PM_{2.5}$ samples spanned a time series of two years that allowed an assessment of seasonal relationships between the EC reported by the two methods. Seasonal average ACE-Asia and IMPROVE EC concentration values were highest in the fall and lowest in the spring. Differences between the seasonal average IMPROVE and ACE-Asia EC concentration values were about 40% greater in summer compared to winter. While IMPROVE EC values were always larger than ACE-Asia EC, the EC difference between these methods exhibited a strong seasonal variation with largest differences occurring in the spring and especially summer with the smallest differences in the fall and winter. Seasonal average EC differences (IMPROVE − ACE-Asia) were anti-correlated with molecular markers for biomass burning and mobile source emissions that had wintertime maximum concentrations. The EC difference between methods did have a moderate positive correlation with indicators of secondary organic aerosol and sulfate suggesting that oxidized organic aerosol associated with atmospheric processing or other secondary components of ambient aerosol could be associated with the seasonal differences between these EC measurements.

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1. Introduction

Organic carbon (OC) and elemental carbon (EC) are typically significant contributors to atmospheric fine particulate matter burdens (Hopke, 2009). These two fractions of the carbonaceous aerosol are often measured to support atmospheric particulate matter source apportionment calculations (Schauer et al., 1996; Jaeckels et al., 2007), mass balance calculations on $PM_{2.5}$ (Bae et al., 2006), studies of the radiative impact of aerosols on global climate forcing (Leck et al., 2002), and efforts to understand air pollution exposure and health effects (Oberdorster et al., 2002).

Many different thermal, optical, and thermal/optical carbon analysis methods for OC, EC or black carbon (BC) have been applied throughout the world. Dozens of inter-method and inter-laboratory comparison studies have been conducted. Traditionally, OC and EC measurements have been made by collecting particulate matter on quartz fiber filters that are subsequently analyzed by off-line thermal evolution and combustion techniques (Schmid et al., 2001; Currie et al., 2002). These methods use different hardware and different combinations of temperature profiles and analysis atmospheres to vaporize or combust the carbon-containing compounds with the gaseous products being detected downstream. The thermal evolution process also leads to pyrolysis of some organic compounds and optical methods are used to reassign this portion of the measured elemental carbon (termed the OP fraction) back to organic carbon.

Two commonly used methods for the analysis of OC and EC are the Aerosol Characterization Experiment—Asia (ACE-Asia) method (Schauer et al., 2003) based on National Institute of Occupational Safety and Health (NIOSH 5040) method (Birch and Cary, 1996) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) method (Chow et al., 1993; Chow et al., 2007). The ACE-Asia (NIOSH 5040) method corrects for pyrolysis using laser transmittance (Birch and Cary, 1996; Eller and Cassinelli, 1996), whereas the IMPROVE method corrects for pyrolysis using laser reflectance (Chow et al., 1993). Although both the ACE-Asia and IMPROVE methods differentiate OC and EC by using similar analytical strategies, their hardware, temperature

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* Corresponding author. Atmospheric Sciences Research Center, University of Albany, State University of New York, 251 Fuller Road Albany, NY 12203, USA.
E-mail address: minsbae@hotmail.com (M.-S. Bae).

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profiles, and optical monitoring protocols are not the same and yield different results. The ACE-Asia and IMPROVE methods have been shown in the past to have good agreement for total carbon (TC), which is the sum of OC and EC, but can yield very different splits between OC and EC (Chow et al., 2001; Schmid et al., 2001; Currie et al., 2002; Chow et al., 2004; Subramanian et al., 2006). It has been observed that a fraction of OC is pyrolytically converted to EC during analysis due to the sample becoming visibly darkened with increasing temperature in the oxygen-starved atmosphere (Huebert and Charlson, 2000). This pyrolysis causes darkening of the filter deposit and can be corrected by monitoring the laser light transmittance/reflectance as the sample is being analyzed and noting when the optical response has returned to its original intensity. However, moderate changes in the thermal evolution protocol for an OC and EC analysis can have a large impact on the EC and OC split (Schauer et al., 2003; Chow et al., 2004; Conny et al., 2003; Subramanian et al., 2006). Previous work has suggested that the difference between the EC and OC splits by the ACE-Asia (NIOSH 5040) and IMPROVE methods are due to reactions between oxygen containing minerals and EC particles in the filter deposit (Chow et al., 2001), the pyrolysis characteristics of water soluble organic compounds (Yang and Yu, 2002), charring of adsorbed vapors throughout the filter that is seen differently by the transmittance vs reflectance measurements (Chow et al., 2004) and the different mix of sources contributing to a given atmospheric sample (Schauer et al., 2003; Subramanian et al., 2006).

The IMPROVE method, employed from 1987 through 2004 for the IMPROVE network, was modified in 2005 (Chow et al., 2007). The changes included new hardware (the DRI Model 2001 analyzer replaced the DRI/OGC analyzer) and revisions to the analysis protocol (the IMPROVE_A temperature protocol replaced the IMPROVE temperature protocol). Oxygen in the carrier gas—whether pure helium or oxygen/helium mixture—is now monitored and the temperature probe was moved closer to the filter sample. The IMPROVE_A temperature protocol includes revised temperature setpoints so that the temperature profile at the filter in the DRI Model 2001 analyzer matches the temperature profile at the filter in DRI/OGC analyzer for the original IMPROVE protocol. The IMPROVE_A temperature protocol has 20–40 °C higher setpoint temperature for each step than the IMPROVE temperature protocol shown in Table 1 (Chow et al., 2007).

The present study uses a large number of daily ambient particulate matter samples from an urban site to examine seasonal variations in the relationship between EC measured by the ACE-Asia method and EC measured by the IMPROVE method prior to the method changes noted above. Organic speciation by gas-chromatography/mass spectrometry (GC/MS) was performed on seasonal composites of daily samples to assess relationships between the EC differences between the methods and concentrations of organic compound classes. Although the analysis is limited to one urban site, the results do provide insights into the relationships between the methods that have not been possible with previous studies using a limited number of samples and limited information on carbonaceous aerosol composition.

Table 1
Experimental parameters of the thermal/optical analytical protocols applied in this study.

Gas	ACE-Asia		IMPROVE		
	Hold time (s)	Temperature (°C)	Hold time (s)[a]	Temperature (°C)	Carbon fraction
He	60	340	150–580	120	OC1
He	60	500	150–580	250	OC2
He	60	615	150–580	450	OC3
He	90	870	150–580	550	OC4
He	60	Oven off	–	–	
He:O2	45	550	150–580	550	EC1
He:O2	45	625	150–580	700	EC2
He:O2	45	700	150–580	800	EC3
He:O2	45	775			
He:O2	45	850			
He:O2	120	900			

[a] The residence time at each temperature in the IMPROVE protocol depends on when the flame ionization detector (FID) signal returns to the baseline.

2. Experimental

Two sets of 24-h integrated samples were collected for carbonaceous aerosol analysis at the USEPA funded St. Louis-Midwest Supersite located in East St. Louis, Illinois. The site is about 3 km east of the central business district of St. Louis, Missouri (Bae et al., 2004a). Samples for ECOC analysis were collected downstream of PM$_{2.5}$ cyclones that operated from midnight to midnight. In addition, medium volume PM$_{2.5}$ samplers that operated at 92 lpm collected samples each day from midnight to midnight for organic speciation by gas-chromatography mass spectrometry (GC/MS) analysis.

As previously presented by Bae et al. (2004b), two low volume 24-h integrated samplers were assembled using commercially available components and were specifically designed for the collection of atmospheric particulate matter for OC and EC analysis. The sampling train consisted of a cyclone followed by an organics denuder (Sunset Laboratory) and a downstream 47-mm quartz fiber filter (Pall Gellman, Ann Arbor, Michigan) that was used to collect fine particulate matter samples at a flow rate of 12 lpm. The organics denuder was fabricated with replaceable parallel charcoal-impregnated filter strips to collect gas-phase organic compounds that could adsorb to the downstream quartz fiber filter (Mader et al., 2003). These denuders have been shown to be effective at removing adsorption artifacts (Bae et al., 2004a). The two ECOC low volume samplers were operated on alternating days from June 2001 to May 2003 to collect a daily time series of particulate matter samples for the OC and EC analyses of the present study. A total of 709 daily ambient PM$_{2.5}$ samples were analyzed, along with 76 field blanks and 20 laboratory blanks, by both the ACE-Asia and IMPROVE methods. The ACE-Asia method analysis was performed at the University of Wisconsin-Madison and the IMPROVE method analysis was conducted at the Desert Research Institute (DRI).

The Harvard/EPA Annular Denuder System (HEADS) was used for collecting ambient particulate matter NO_3^-, SO_4^{2-}, and NH_4^+, as well as gaseous SO_2, HNO_3, HNO_2, and NH_3. Ionic compounds were analyzed by ion chromatography (Babich et al., 2000). Samples collected by PM$_{2.5}$ Harvard Impactors were analyzed for elements by X-ray Fluorescence (XRF) Spectroscopy. Desert Research Institute (DRI) performed the ion and elemental analyses.

2.1. OC and EC analysis

A Sunset Laboratory, Inc. (Forest Grove, OR) laboratory thermal/optical ECOC analyzer was used for the ACE-Asia analysis. Details of the ECOC analysis have been previously described in detail (Birch and Cary, 1996; Schauer, 2003) and are only summarized here. Briefly, 1.45 cm^2 punches from the filter samples were heated in a helium atmosphere in four increasing temperature steps while measuring the transmission of a laser light through the filter (Table 1). As carbon compounds were vaporized, they were catalytically oxidized to carbon dioxide and passed through a methanator to reduce the carbon dioxide to methane (Bae et al., 2004b). The methane was then quantified by a flame ionization detector (FID). After the completion of the oxygen-free heating stages, a carrier gas containing 2% oxygen and 98% helium was used to burn off all remaining carbon by heating the sample to 900 °C using six heating steps. The carbonaceous combustion products were fully oxidized to carbon dioxide and reduced to methane which was detected by the FID. After all carbon was oxidized from the sample, a known mass of methane was injected into the sample oven as an internal standard.

The Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer (Chow et al., 1993) was used for IMPROVE analysis; this analyzer is also called the DRI/OGC (Desert Research Institute/Oregon Graduate Center) analyzer (Chow et al., 2007). A 0.5 cm^2 circular punch