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Comparison of two thermal-optical methods for the determination of organic carbon and elemental carbon: Results from the southeastern United States

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ABSTRACT

A total of 333 $PM_{2.5}$ samples were collected at four sites in the southeastern Aerosol Research and Characterization Study (SEARCH) network during four seasons from 2003 to 2005 and were simultaneously analyzed by two common thermal-optical methods, the National Institute of Occupational Safety and Health (NIOSH) method and the Interagency Monitoring of Protected Visual Environments (IMPROVE) method. The concentrations of total carbon measured by the two methods were comparable, whereas the split of organic carbon (OC) and elemental carbon (EC) was significantly different. The NIOSH-defined EC was lower (up to 80%) than that defined by IMPROVE since the NIOSH method applied the transmittance charring correction and a much higher peak inert mode temperature. The discrepancy between NIOSH- and IMPROVE-defined EC showed distinct seasonal and spatial variations. Potential factors contributing to this discrepancy besides the analytical method were investigated. The discrepancy between NIOSH- and IMPROVE-defined EC was larger in the spring compared to winter due to the influence of biomass burning, which is known to emit significant amount of brown carbon that would complicate the split of OC and EC. The NIOSH-defined EC to IMPROVE-defined EC ratio reached its minimum (0.2–0.5) in the summer, when the largest discrepancy was observed. This was most likely to be attributed to the influence of secondary organic aerosol (SOA). Moreover, the discrepancy between NIOSH- and IMPROVE-defined EC was larger in the coastal and the rural sites where the presence of abundant SOA was found based on previous studies in this region, providing supporting evidence that SOA could contribute to the observed discrepancy in summer.

1. Introduction

Carbonaceous aerosol mainly consists of organic carbon (OC) and elemental carbon (EC). OC typically constitute approximately 10–70% of the total dry fine particles with the aerodynamic diameter less than 2.5 micron ($PM_{2.5}$) mass in the atmosphere (Turpin et al., 2000). Of particular interest is the role of EC on climate change and health studies as EC is a strong light absorber and it is enriched in particles from diesel engine exhaust. Accurate measurement of carbonaceous aerosol is essential for a better understanding of its sources, transformation in the atmosphere, and fate. Continuing and increasing attention has been given to how to reduce the uncertainties in the measurement of carbonaceous aerosol, due to its complex impacts on human health (Nel, 2005) and the environment (Ramanathan et al., 2001).

To accurately measure carbonaceous aerosol is one of the most difficult challenges that atmospheric science are still facing today. A variety of measurement techniques has been developed to separate OC and EC, such as the thermal method developed by Novakov (1982), the thermal manganese oxidation method developed by Fung (1990), and the thermal-optical method developed by Huntzicker et al. (1982). Ideally, a loaded filter is exposed to a prescribed temperature protocol first in an inert atmosphere (He) to determine OC and then in an oxidizing atmosphere (He/O_2) to determine EC. However, a fraction of OC has been found to char (or pyrolyze) in the inert mode

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of the analysis. This fraction OC is usually defined as pyrolyzed organic carbon, or PC. PC is light-absorbing and requires an oxidizing atmosphere to evolve off the filter, similar to native EC. As a result, the formation of PC would complicate the split of OC and EC, which is a substantial challenge for the current measurement techniques. Thermal-optical method has been developed to account for the PC formation (Huntzicker et al., 1982). The carbon evolved in the oxidizing atmosphere that is necessary to return the filter reflectance or transmittance to its initial value is considered as PC. Yang and Yu (2002) pointed out that the PC correction in the thermal-optical methods depends on one of the following two assumptions: (1) PC evolves before the native EC in the oxidizing atmosphere, or (2) PC and native EC have the same light attenuation coefficient. However, it has been demonstrated that PC is co-evolved with native EC (Yu et al., 2002; Yang and Yu, 2002, and Subramanian et al., 2006) and is more light-absorbing (Chow et al., 2004; Subramanian et al., 2006, Cheng et al., 2009).

The thermal-optical method is widely used, despite the limitations mentioned above. A variety of operational protocols have been developed (Watson et al., 2005). Two commonly used methods are the National Institute of Occupational Safety and Healthy (NIOSH) method (Birch and Cary, 1996) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) method (Chow et al., 1993). The two methods generally measure the same amount of total carbon (Chow et al., 2001, 2004). However, the discrepancy between the split of OC and EC might be significant. For example, Chow et al. (2004) showed that EC concentration measured by the STN method (similar to NIOSH) was 70–80% lower than that measured by IMPROVE for samples from IMPROVE network. The discrepancy seemed less significant for urban area. For example, EC measured by STN was only about 20% lower than that measured by IMPROVE for samples collected in Hong Kong (Chow et al., 2005). These results indicated that chemical compositions and sources of carbonaceous aerosol could have considerable influence on the thermal-optical split of OC and EC.

Therefore, the objectives of this study are: 1) to better understand if the difference between NIOSH and IMPROVE measurements of carbonaceous aerosol varies with season and space, and 2) to investigate the potential factors contributing to the discrepancy. In this study, $PM_{2.5}$ samples were collected during four seasons from 2003 to 2005 at four long term air-quality monitoring sites in the southeastern United States, which represented urban, coastal and rural areas. These samples were analyzed simultaneously by the NIOSH method and the IMPROVE method to examine the level of discrepancy between EC defined by the two methods, the spatial and seasonal variations of the discrepancy, and what particular sources could lead to the discrepancy.

2. Methods

2.1. Field sampling

Twenty-four hour $PM_{2.5}$ samples were collected by a high-volume sampler (Thermo Anderson) at four sites in the Southeastern Aerosol Research and Characterization Study (SEARCH) monitoring network. Detailed information about the four sites has been given by Hansen et al. (2003). Briefly, the North Birmingham, AL (BHM) and the Jefferson Street, Atlanta, GA (JST) site are located in the industrial/residential area and are referred to as urban site. The Pensacola, FL is located in the coastal area. The Centreville, AL (CTR) site is located in the forest area, thus it is a rural site. All of the four sites are located at the southeastern United States where is generally hilly and is covered heavily by subtropical vegetation. In colder seasons, the area experiences both controlled and uncontrolled biomass burning, while in the warmer months, volatile organic carbon from biogenic sources and transportation provide precursors for significant secondary organic aerosol formation.

The operating flow rate of the high-volume sampler was 1.13 m^3/min and the face velocity was 0.46 m/s. The quartz filters (8×10 in, 2500 QAT-UP) used were from Pall Corp. (Ann Arbor, MI). About 333 samples were collected from October 2003 to October 2005. All the data reported have been corrected by the field blank.

2.2. Sample analysis

The quartz filters were analyzed by both a Sunset Laboratory Thermal/Optical Carbonaceous Aerosol Analyzer (Forest Grove, OR) at Georgia Institute of Technology and a Thermal/Optical Carbon Analyzer at Desert Research Institute. When analyzed by the Sunset analyzer, the NIOSH method was implemented. Briefly, a 1.45 cm^2 punch taken from the quartz filter was first heated to 870 °C in pure He atmosphere and subsequently to 900 °C in the $98\%He/2\%O_2$ atmosphere. Filter transmittance was monitored throughout the analysis. EC is defined as the carbon that is measured after the filter transmittance returns to its initial value in the He/O_2 mode and is referred to as EC_{TOT}. When analyzed by the DRI analyzer, the IMPROVE method was used. Briefly, a 0.5 cm^2 punch was first heated to 550 °C in pure He atmosphere and subsequently to 800 °C in the $98\%He/2\%O_2$ atmosphere. Filter reflectance was monitored throughout the analysis. EC is defined as the carbon that is measured after the filter reflectance returns to its initial value in the He/O_2 mode and is referred to as EC_{TOR}. The key difference between the two methods include: (1) temperature plateaus, especially the maximum temperature in the inert mode which was 870 °C and 550 °C for the NIOSH and IMPROVE protocol respectively; (2) residence time at each plateau, which was fixed in NIOSH but defined by the flattening of carbon signals in IMPROVE; (3) charring correction method, which was transmittance and reflectance for NIOSH and IMPROVE respectively.

The TC concentrations measured by IMPROVE correlated well with that measured by NIOSH ($R^2 = 0.99$, $N = 333$), with a slope of 0.94 and an intercept of zero. The maximum TC loading was found at BHM, which was about 170 μgC/cm^2 (corresponding to an ambient concentration of about 42 μgC/m^3).

3. Results and discussion

3.1. OC and EC concentrations

The OC and EC concentrations defined by the IMPROVE method at the four sampling sites were shown in Fig. 1. The OC concentrations showed distinct seasonal variations, with higher concentrations found during the spring and autumn. The variation was more significant at the two urban sites (BHM and JST) comparing with the coastal site (PNS) and the rural site (CTR). At the two urban sites, the OC concentration in spring was 1.6–2.0 times the concentration in summer, whereas at the coastal and the rural sites, the OC only differed by a factor of 1.3–1.4 during the spring and summer. The EC concentrations also showed seasonal variations. At the two urban sites, the seasonal pattern of EC was similar to that of OC, but the spring peak was not significant at JST. At the coastal and the rural sites, the lowest EC concentration was found in summer.

3.2. Comparison of OC defined by TOR and TOT

As shown in Fig. 2, the OC values measured by the NIOSH approach (OC_{TOT}) were much higher (up to 20%) than those measured by the IMPROVE method (OC_{TOR}). At the two urban sites (BHM and JST) and the coastal site (PNS), the OC_{TOT} was 1.1–1.2 times the value of OC_{TOR} (Fig. 2(a)–(c)). The discrepancy between