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Long-range transport of biomass burning emissions based on organic molecular markers and carbonaceous thermal distribution

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ABSTRACT

Semi-continuous organic carbon (OC), elemental carbon (EC), and organic molecular markers were analyzed using the thermal optical transmittance method at the Gosan supersite (on Jeju Island, Korea), which has been widely used as a regional background site for East Asia. The Carbonaceous Thermal Distribution (CTD) method, which can provide detailed carbon signature characteristics relative to analytical temperature, was used to improve the carbon fractionation of the analytical method. Ground-based measurements were conducted from October 25 to November 5, 2010. During the sampling period, one high OC concentration event and two characteristic periods were observed. Considering the thermal distribution patterns, the relationship between the EC and black carbon (BC) by optical measurements, the backward trajectories, the aerosol optical thickness, the PM_{10} concentrations from the 316 PM-network sites that were operated by the Ministry of Environment in Korea, and the organic molecular markers, such as levoglucosan, PAHs, and organic acids, we concluded that the event was influenced by long-range transport from biomass burning emissions. This study discusses the CTD analysis with organic molecular marker concentrations, extracts and interprets additional carbon fractions from a semi-continuous data set, and provides knowledge regarding the origin of carbon sources and their behaviors.

1. Introduction

Carbonaceous aerosols are classified as either organic carbon (OC) or as elemental carbon (EC) and are the main components of aerosols in the atmosphere (Rattigan et al., 2010). Carbonaceous aerosol sources include stationary and mobile combustion sources and biological sources. In addition, carbonaceous aerosols result from the oxidation of anthropogenic and natural gaseous organic species, which form reaction products that condense to form secondary organic aerosols (SOAs). The complex chemistry of organic aerosols and the associated precursors of SOAs present major challenges for measuring, modeling, and developing control strategies to mitigate the effects of carbonaceous aerosols. EC is emitted from combustion processes (Mader et al., 2003) and is called black carbon (BC) in optical measurements (Gray et al., 1986; Huntzicker et al., 1986; Turpin et al., 1991). Carbonaceous aerosols comprise a large portion of particulate matter (Hopke, 2009) and significantly impact the climate due to the optical properties of OC and EC (Bates et al., 1998; Jacobson, 2001; Leck et al., 2002; Raes et al., 2000). Organic aerosols can modify the hydroscopic properties of other aerosols and impact their ability to serve as condensation nuclei for cloud formation (Seinfeld and Pandis, 1998).

As concern has increased regarding the impacts of carbonaceous aerosols on climate and human health (Chow et al., 2002; Cyrys et al., 2003; Lena et al., 2002), many methods have been developed to measure the concentrations of carbonaceous aerosols in the atmosphere. Among these techniques, collecting aerosols on quartz fiber filters is widely used in laboratory-based chemical analyses (Birch, 1998; Birch and Cary, 1996; Chow et al., 1993; Noble and Prather, 1996; Seinfeld and Pandis, 1998). One important carbonaceous aerosol measurement is the thermal-optical measurement of OC and EC. The OC and EC are measured by progressively heating a punch from the quartz fiber filter to higher temperatures. Next, the evolved gasses are oxidized to carbon dioxide before being analyzed with a Nondispersive Infrared Detector (NDIR) (Birch, 1998; Chow et al., 1993, 2001; Johnson et al., 1981; Noble and Prather, 1996). This method of analyzing OC and EC can be used to determine their concentrations. These OC and EC concentrations can be used to determine the potential sources of OC and EC by using the source apportionment model. In addition, these concentrations can be used to identify atmospheric carbon behaviors by using a method that was developed to identify secondary organic carbon based on Deming's least-squares solution, which uses the OC to EC ratio (Turpin and Huntzicker, 1995).

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General analytical approaches and different simplified analytical carbon fractions, such as OC1, OC2, OC3, OC4, Pyrolyzed Carbon (PC), EC1, EC2, and EC3, have been used to understand the carbon fractions and sources of carbonaceous aerosols (Hwang and Hopke, 2007). The characteristic carbon fractions that are reported by the carbon instruments can be defined by certain time steps, which can be related to the analysis temperature that was preprogrammed into the OCEC instrument. Of the four OC fractions, OC1 is the most volatile and OC4 is the least volatile. Several researchers (Novakov and Corrigan, 1996; Schauer et al., 2003; Peralta et al., 2007; Wang et al., 2010) have employed the thermal analytic method for carbonaceous aerosols and have found that the single Carbonaceous Thermal Distribution (CTD) from converted carbon dioxide (CO_2) evolves differently, depending on its source and chemical composition. Novakov and Corrigan (1996) provided the CTD for the nucleation of cloud condensation from biomass smoke. In addition, Peralta et al. (2007) presented the CTD of aromatic compounds, which varied with the number of aromatic rings. Wang et al. (2010) presented the CTD of gasoline and diesel engine emissions. Kirchstetter and Novakov (2007) showed that the CTD can be related to other inorganic aerosol constituents, such as NaCl. These studies focused on the use of off-line OCEC measurements.

The current CTD analysis method uses semi-continuous in situ OCEC measurements and employs data analysis methods that can use a continuous distribution of evolved carbon, which provides better data integration for understanding the sources of carbonaceous aerosols. In addition, the concentrations of carbonaceous aerosols, including OC and EC, tend to increase during dust storms. Highly specific organic compounds that arise from different aerosol source categories (referred to as molecular markers in this paper) have been extensively used to identify aerosol sources and the distributions of ambient aerosols (Simoneit et al., 1999). Stone et al. (2011) showed that carbonaceous aerosols from biomass burning, coal combustion, and motor vehicles that contained organic and elemental components were included in coarse particle masses measured during dust events due to a strong crustal component of the aerosols mixed with anthropogenic pollution and biomass burning in Gosan, Korea. The present study demonstrates the characterization of organic molecular markers and semi-continuous CTDs during event and non-event periods that occurred in the fall. The organic molecular markers that are of interest include levoglucosan, polyaromatic hydrocarbons (PAHs), hopanes, *n*-alkanes, *n*-alkanoic acids, and aromatic acids. In addition, this paper combines the CTD results with satellite data (e.g., pathways of air masses and aerosol optical thickness (AOT)) to demonstrate the value of integrating these measurements to better understand carbonaceous aerosol sources.

2. Experimental details

2.1. Sampling site

Ground-based measurements were performed at the Gosan supersite (33.29 °N, 126.16 °E) on Jeju Island, Korea. The Gosan supersite is located approximately 100 km south of the Korean peninsula, 500 km northeast of Shanghai, China, and 250 km west of Kyushu, Japan. This site has been regarded as a background monitoring site in East Asia due to its low pollution levels and its geographical conditions (Stone et al., 2011). The Gosan sampling site is located on the coastal area of Jeju Island and is 72 m above sea level. Measurements were taken from October 25 to November 5, 2010.

2.2. Organic carbon (OC) and elemental carbon (EC) analyses

The CTD analyses were performed using standardized OC and EC measurements that were obtained with a semi-continuous OCEC Carbon Aerosol Analyzer (Sunset laboratory Inc.). The thermal-optical transmittance (TOT) method (Birch, 1998; Birch and Cary, 1996) was used to collect $PM_{2.5}$ particles for 45 min on a 1.12 cm^2 quartz fiber filter that was located in the oven of the analyzer. After collecting the aerosols, the filter was heated over a series of temperature steps based on the NIOSH protocol (Birch and Cary, 1996). The analytical procedure consists of three parts. In the first part, the loaded filter is heated to 840 °C in the presence of pure (oxygen-free) helium gas and the organic compounds and pyrolysis products are thermally released from the aerosols on the filter. The desorbed carbon fragments are oxidized to CO_2 by using MnO_2 as a catalyst. Next, the CO_2 is measured by a NDIR detector. In addition, EC is detected in a similar way during the second stage but by using a maximum temperature of 870 °C and an He/O_2 atmosphere. During the last stage, a fixed volume of methane is analyzed as an internal standard for quantification. Throughout the analysis, the difference between OC and EC is determined from the laser transmittance by correcting for the EC formed during the first stage of analysis in the helium atmosphere. To validate the accuracy of the semi-continuous OCEC analyzer, the external calibration was checked across five different injections at different concentrations. The average recovery was 0.98 ± 0.02, and the calibration check had a correlation factor of 0.999. The instrument blank test, which was conducted by completing the analysis without collecting aerosols, was conducted several times to determine the noise and contamination in the instrument and filters.

2.3. Carbonaceous Thermal Distribution (CTD)

The CTD is motivated by the fact that the thermal evolution of carbonaceous aerosols is different than during an instrumental analysis. Fig. 1 shows a description of the CTD approach. Briefly, all of the raw data analyzed using the semi-continuous OCEC Carbon Aerosol Analyzer were extracted, then the instrument internal standard, actual analytical temperature (NIOSH protocol), laser intensity, and split-times were checked. Next, all of the raw data were converted into CO_2 ppm using the conversion algorithms provided by the manufacturing company. The CO_2 ppm from the NDIR detector can be used to calculate the carbon concentration. After blank corrections, the final data were analyzed using a MATLAB program. A series of data sets from a semi-continuous OCEC Carbon Aerosol Analyzer can be displayed as the CTD. The CTD can show different patterns, which are related to the origins and/or chemical structures under the NIOSH temperature protocol. In this study, the CO_2 peaks and the temperature protocol during the entire sampling period are simultaneously provided using the graphical CTD during the entire monitoring period while analyzing the actual temperature and CO_2 levels, as shown in Fig. 1. These results can be presented in one plane as a contour plot.

2.4. Normalized Carbonaceous Thermal Distribution (NCTD)

The Normalized Carbonaceous Thermal Distribution (NCTD) was used for the detailed classification of the organic carbon characteristics. The normalized CO_2 in each bin (in dCO_2 ppm dt^{-1}/OC μg m^{-3} dt^{-1}), which was obtained by dividing each CO_2 concentration by the hourly OC concentration, clarifies the characteristics of the carbonaceous aerosols. The NCTD explains the change in OC relative to the related analytical temperature changes. The NCTD provides a fingerprint that can be used as a signature for source identification. As shown in Fig. 3(b) and Table 1, two characteristics (temperature mode) and one plume event can be observed in the NCTD from October 25 to November 5, 2010.

2.5. Organic molecular marker analysis

While a total of 35 8-hour integrated samples were collected with a high volume sampler for the sampling period, organic molecular markers from five composites related to select sampling events were