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Chemical characteristics and source apportionment of fine particulate organic carbon in Hong Kong during high particulate matter episodes in winter 2003

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ABSTRACT

$PM_{2.5}$ samples were collected at six general stations and one roadside station in Hong Kong in two periods of high particulate matter (PM) in 2003 (27 October–4 November and 30 November–13 December). The highest $PM_{2.5}$ reached 216 μg m^{-3} during the first high PM period and 113 μg m^{-3} during the second high PM period. Analysis of synoptic weather conditions identified individual sampling days under dominant influence of one of three types of air masses, that is, local, regional and long-range transported (LRT) air masses. Roadside samples were discussed separately due to heavy influences from vehicular emissions. This research examines source apportionment of fine organic carbon (OC) and contribution of secondary organic aerosol on high PM days under different synoptic conditions. Six primary OC (POC) sources (vehicle exhaust, biomass burning, cooking, cigarette smoke, vegetative detritus, and coal combustion) were identified on the basis of characteristic organic tracers. Individual POC source contributions were estimated using chemical mass balance model. In the roadside and the local samples, OC was dominated by the primary sources, accounting for more than 74% of OC. In the samples influenced by regional and LRT air masses, secondary OC (SOC), which was approximated to be the difference between the total measured OC and the apportioned POC, contributed more than 54% of fine OC. SOC was highly correlated with water-soluble organic carbon and sulfate, consistent with its secondary nature.

1. Introduction

Organic carbon (OC) and elemental carbon (EC) constitute a significant fraction of airborne particulate matter (PM) mass, ranging from ~10% in remote areas to ~40% in urban areas (Jacobson et al., 2000; Seinfeld and Pandis, 1998). At urban and roadside locations in Hong Kong, the carbonaceous materials are the most abundant component of $PM_{2.5}$ (particles of less than 2.5 μm in diameter), accounting for 44% and 67%, respectively, on an annual average (Louie et al., 2005a,b). Compared with inorganic components in PM, identities of individual organic compounds and their source contributions, are far less understood mainly

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due to the large number of individual organic compounds and a wide variety of emission sources and multiple secondary formation pathways.

Chemical characterization of sources and ambient $PM_{2.5}$ is an essential step to identifying and quantifying major contributing sources to $PM_{2.5}$ in the ambient air. Individual organic tracers, combined with chemical mass balance (CMB) model, have long been demonstrated to be able to provide source apportioning of primary organic aerosols (e.g., Hu et al., 2010; Li et al., 2012; Manchester-Neesvig et al., 2003; Schauer and Cass, 2000; Schauer et al., 1996; Zheng et al., 2002, 2006). In this work, a total of 27 ambient $PM_{2.5}$ samples were collected at six air quality monitoring stations in Hong Kong in two periods of high PM (Period I: 26 October–4 November 2003 and Period II: 30 November–13 December 2003). The highest $PM_{2.5}$ reached 216 μg m^{-3} during the first high PM period and 113 μg m^{-3} during the second high PM period. The objectives of this work are (1) to characterize major components of $PM_{2.5}$ during high PM episodes in Hong Kong; (2) to obtain chemical composition of the organic fraction of $PM_{2.5}$ and to identify and quantify the major contributing sources of fine OC under different episodic conditions.

2. Experimental section

2.1. Samples

The 27 samples were collected at six general air quality monitoring stations (AQMSs) and one roadside station in the AQMS network in Hong Kong. Sample collection was carried out by the Hong Kong Environmental Protection Department (HKEPD). Three of the samples were collocated duplicate samples. Fig. S1 (Fig. S# and Table S# denotes materials provided as supporting information) shows the geographical distribution of the six general stations (CW—Central Western, KT—Kwon Tong, SSP—Sham Shui Po, TC—Tung Chung, TW—Tsuen Wan, YL—Yuen Long) and the Mong Kok (MK) roadside station. Among the general AQMSs, CW and SSP are in mixed residential and commercial neighborhoods; KT and TW are in mixed residential, commercial, and industrial neighborhoods; TC and YL are in new town residential areas. The MK roadside station is located in a busy commercial and residential down town area surrounded by tall buildings. Table 1 lists the locations and sampling dates of individual samples. The $PM_{2.5}$ samples were collected on quartz fiber filters (20×25 cm) prebaked at 550 °C using high-volume air samplers (GT22001; Andersen Instruments, Smyrna, GA, USA) at a flow rate of 1.13 m^3 min^{-1} for 24 h (from midnight to midnight). All the filter samples were stored in a freezer at 4 °C until analysis.

2.2. Analysis of EC and OC

EC and OC were determined using a thermal/optical aerosol carbon analyzer (Sunset Laboratories, Forest Grove, Oregon, USA) (Birch and Cary, 1996). A filter punch of 1×1 cm^2 in size was removed from each filter and loaded into the aerosol carbon analyzer. The thermal analysis conditions (i.e., temperature program and the type of atmosphere) were the same as those established for the NIOSH method 5040 (Wu et al., 2012).

2.3. Extraction and analysis of solvent extractable organic compounds

Half of each filter was spiked with tetracosane—D_{50}, phenanthrene—D_{10}, $CD_3(CH_2)_{14}COOH$, phthalic acid—D_4 and levoglucosan—^{13}C, and then Soxhlet-extracted with a mixture of ~140 mL high purity dichloromethane and ~140 mL high purity methanol. The extract was reduced to ~5 mL using a rotary evaporator and then filtered through glass wool to a test tube and rinsed with dichloromethane. To the extract, 250 μL of high purity acetonitrile was added. Acetonitrile served to replace methanol upon further solvent evaporation to 250 μL. Methanol had to be replaced due to its reaction with silylation reagent N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA), which was used to derivatize –OH and –COOH containing compounds later in the analytical procedure. The samples were then blown down to 200 μL and split into two equal portions of 100 μL and transferred to two vials capped with Teflon-lined lid. One portion was used to analyze non-polar species (e.g., alkanes, polycyclic aromatic hydrocarbons (PAHs), cycloalkanes, hopanes, steranes, and phthalates) using gas chromatography–mass spectrometry (GC–MS). The second portion was silylated by BSTFA and analyzed using GC–MS within 18 h. This portion was used to quantify both acid compounds (i.e., alkanoic acids, alkenoic acids, etc.) and alcohol compounds (i.e., alkanols, levoglucosan, mono-glycerides, cholesterol). The recoveries of a set of 22 selected compounds representing the target compound classes were determined by spiking deuterated standards onto a blank filter. The recoveries ranged from 60% to 99%, demonstrating that our analytical protocol provided acceptable quantitative results.

2.4. Extraction and analysis of water-soluble organic carbon and ion species

The total water-soluble organic carbon (WSOC) was determined by measuring the OC content of aerosol water extracts using a TOC analyzer (Yang et al., 2003). A portion of the filter sample was extracted with 10 mL aliquots of UV–oxidized high-purity water in a sonication bath for 30 min. The water extracts were rid of filter debris and suspending insoluble particles using a syringe filter. A 3-mL aliquot of the extract was used for quantification of carbon content with a total organic carbon (TOC) analyzer. The water extracts were also used for analysis of organic anions (formate, acetate, methanesulfonate, oxalate), inorganic anions (Cl^-, NO_3^-, and SO_4^{2-}) and cations (e.g., NH_4^+, K^+, Na^+, Ca^{2+}, and Mg^{2+}) using an ion chromatography (IC) system (Dionex DX 500). The IC method detail was given by Yang et al. (2004).

The analysis of mono- and dicarboxylic acids, ω-oxo-carboxylic acids, mid-chain ketocarboxylic acids, and aldehydes was carried out using a method developed in our lab (Li and Yu, 2005). Briefly, one-fourth of the 20×25 cm quartz filter was mixed with a mixture of BF_3/BuOH for derivatization. The reaction mixture was washed with water