Atmospheric Research 170 (2016) 112–122

Contents lists available at ScienceDirect

Atmospheric Research

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

Chemical characterization and source apportionment of size-resolved particles in Hong Kong sub-urban area

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ARTICLE INFO

Article history:
Received 21 July 2015
Received in revised form 26 October 2015
Accepted 26 November 2015
Available online 7 December 2015

Keywords:
Aerosol size distribution
Inorganic ions
Carbonaceous aerosol
MOUDI
PMF

ABSTRACT

Size-resolved particulate matter (PM) samples were collected with a 10-stage Micro-Orifice Uniform Deposit Impactor (MOUDI) at a sub-urban site (Tung Chung) in Hong Kong for four non-consecutive months representing four seasons from 2011 to 2012. Major chemical components were water-soluble anions (i.e., Cl^-, NO_3^-, and SO_4^{2-}), cations (i.e., NH_4^+, Na^+, K^+, and Ca^{2+}), organic and elemental carbon and elements. Both chemical mass closure and positive matrix factorization (PMF) were employed to understand the chemical composition, resolve particle size modes, and evaluate the PM sources. Tri-modal size distributions were found for PM mass and major chemical components (e.g., SO_4^{2-}, NH_4^+, and OC). Mass median aerodynamic diameters (MMADs) with similar standard deviations ($1.32 < \sigma < 1.42$) were 0.4, 0.7 and 3.8 μm, consistent with condensation, droplet and coarse modes. A bi-modal distribution peaking at condensation and droplet modes was found for EC, with a single mode peaking at 3.8 μm for Cl^-. Besides secondary SO_4^{2-}, carbonaceous aerosol dominated the condensation mode with 27% by engine exhaust and 18–19% each by residual oil combustion (shipping) and coal/biomass burning. Secondary SO_4^{2-} is also the most dominant component in the droplet mode, accounting for 23% of PM mass, followed by an industrial source (19%). Engine exhaust, secondary NO_3^-, and sea salt each accounted for 13–15% of PM mass. Sea salt and soil are the dominated sources in the coarse mode, accounting for ~80% of coarse mass.

1. Introduction

Airborne particulate matter (PM) scatters and absorbs sunlight, causing direct and indirect effects on Earth's radiation balance, visibility impairment, climate change, and human health (Penttinen et al., 2001; Seinfeld and Pandis, 2006; Watson, 2002). These effects are related to particle sizes and chemical compositions (Huang and Yu, 2008; Malm and Pitchford, 1997; Milford and Davidson, 1987; Sloane et al., 1991). Based on size-resolved measurements from a Micro-Orifice Uniform Deposition Impactor (MOUDI), Sloane (1983) and others quantified scattering efficiencies based on Mie theory (Sloane et al., 1991; Sloane and Wolff, 1985). Major chemical components (e.g., sulfate [SO_4^{2-}], nitrate [NO_3^-], and organics) have been used to understand the particle growth mechanisms as well as the physical and chemical characteristics (Howell and Huebert, 1998; Huang et al., 2006a; John et al., 1990; Kim et al., 2003; Plaza et al., 2011; Tang, 1996; Tsai et al., 2012; Wang et al., 2013).

Past studies in Hong Kong have showed high concentration for SO_4^{2-}, organic matter (OM), and elemental carbon (EC) in the submicron-mode, greatly influence local visual range and human health (Gao et al., 2015; Yao et al., 2002, 2003b; Zhuang et al., 1999b), similar to observations from other countries (John et al., 1990; Kim et al., 2003; Plaza et al., 2011). Chow et al. (2008) observed a SO_4^{2-} size distribution that was multi-modal and wider at an urban site than the uni-modal distribution found at a rural site in central California. Bian et al (2014) found significant size distribution changes over the past 20 year periods when compared with the three inorganic compounds (i.e., SO_4^{2-}, NO_3^-, and NH_4^+) at the same site. $PM_{2.5}$ or PM_{10} source apportionment studies have been conducted in Hong Kong via different receptor models (Fung and Wong, 1995; Guo et al., 2009; Lee et al., 1999), e.g. Multivariate Regression Analysis, Principal Component Analysis with Absolute Principal Component Scores technique (PCA-APCS), Chemical Mass Balance (CMB), and Positive Matrix Factorization (PMF), finding contributions from engine exhaust, secondary aerosols, residual oil combustion, fresh and aged sea salt, soil, coal combustion and biomass burning. Only few source apportionment studies investigated have examined contribution to different size ranges (Contini et al., 2014; Han et al., 2006; Kim et al., 2003), but not in Hong Kong.

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http://dx.doi.org/10.1016/j.atmosres.2015.11.015
0169-8095/

The Tung Chung (TC) site is a newly developed sub-urban area in Hong Kong, located in the centerline of the Pearl River Delta (PRD) region. It is a gateway to Macau and mainland China, with ~78,400 inhabitants (*2011 Census*) and increasing industrial and commercial activities, such as coal-fired power plants, airports, seaports, and local traffic (Wang et al., 2005; Zhou et al., 2014). Therefore, it is essential to understand the air pollution in this area.

The objectives of this study are to: 1) investigate the particle size distribution of water-soluble ions and carbon; and 2) determine resolved size mode and source apportionment by the Positive Matrix Factorization (PMF) receptor model applied to MOUDI (Model 110, MSP Corp. Minnesota, U.S.A.) data.

2. Methods

2.1. Sampling site and sampling periods

The TC site (22.17 °N, 113.56 °E) is on the northern coast of Lantau Island and southwest of Hong Kong (Fig. 1). It is a new town area, ~3 km from the Hong Kong International Airport. MOUDI samplers were placed on a three story building which was established by Hong Kong Environmental Protection Department (HKEPD). Sampling was conducted for 27 days and covers four periods: August/September (2011), November/December (2011), February/March (2012), and May (2012), representing summer, fall, winter, and spring seasons, respectively. Sample duration was 24 h, from 10:00 a.m. to 10:00 a.m. the next day local standard time (LST). Table 1 details the sampling dates and daily meteorological conditions.

2.2. Size-resolved particle measurements

The ten-stage MOUDI includes the following aerodynamic particle diameter ranges with 30 L/min flow rate: 0.056–0.1, 0.1–0.18, 0.18–0.32, 0.32–0.56, 0.56–1.0, 1.0–1.8, 1.8–3.2, 3.2–5.6, 5.6–10, and 10–18 μm. One MOUDI contained 47 mm Teflon-membranes Filters (Pall Sciences, New York, U.S.A.) and another contained 47 mm quartz-fiber filters (QMA, Whatman, Maidtone, England) as substrates. Backup filters were 37 mm. The spacer (0.05 in. in thickness) provided by MSP Corp. (MN, U.S.A.) was placed between adjacent stages to compensate for the lower jet-to-plate distance caused by the filter thickness (Huang et al., 2006b; Bian et al., 2014). Fujitani et al. (2006) reported that quartz-fiber filter artifacts are minimal compared with aluminum foils or Teflon-membrane filter for PM concentrations of ~42 μg/m^3.

Ions and carbon were analyzed on quartz-fiber filters with mass and elements analyzed on Teflon-membrane filters. During the sampling periods, the effect of particle bounce should be negligible since the relative humidity (RH) was high, ~60% to 80% (Chow et al., 2005; Huang et al., 2004; Milford and Davidson, 1987).

Before sampling, quartz-fiber filters were prefired at 900 °C for 3 h to minimize organic artifacts (Chow et al., 2010a; Ho et al., 2006; Watson et al., 2009). Both the Teflon-membrane and quartz-fiber filters were weighed before and after sampling, using a microbalance (Model MC5, Sartorius, Goettingen, Germany) with a sensitivity of ±1 μg in the 0–250 mg range. Before weighing, filters were equilibrated in a desiccator for 24 h at temperature (25 ± 5 °C) and RH (35 ± 10%) controlled environment. After weighing, filters were stored air-tight in a refrigerator (<4 °C) to minimize evaporation of volatile components. Sample flow rates within ±10% of the specification were verified at the beginning and end of each sampling period.

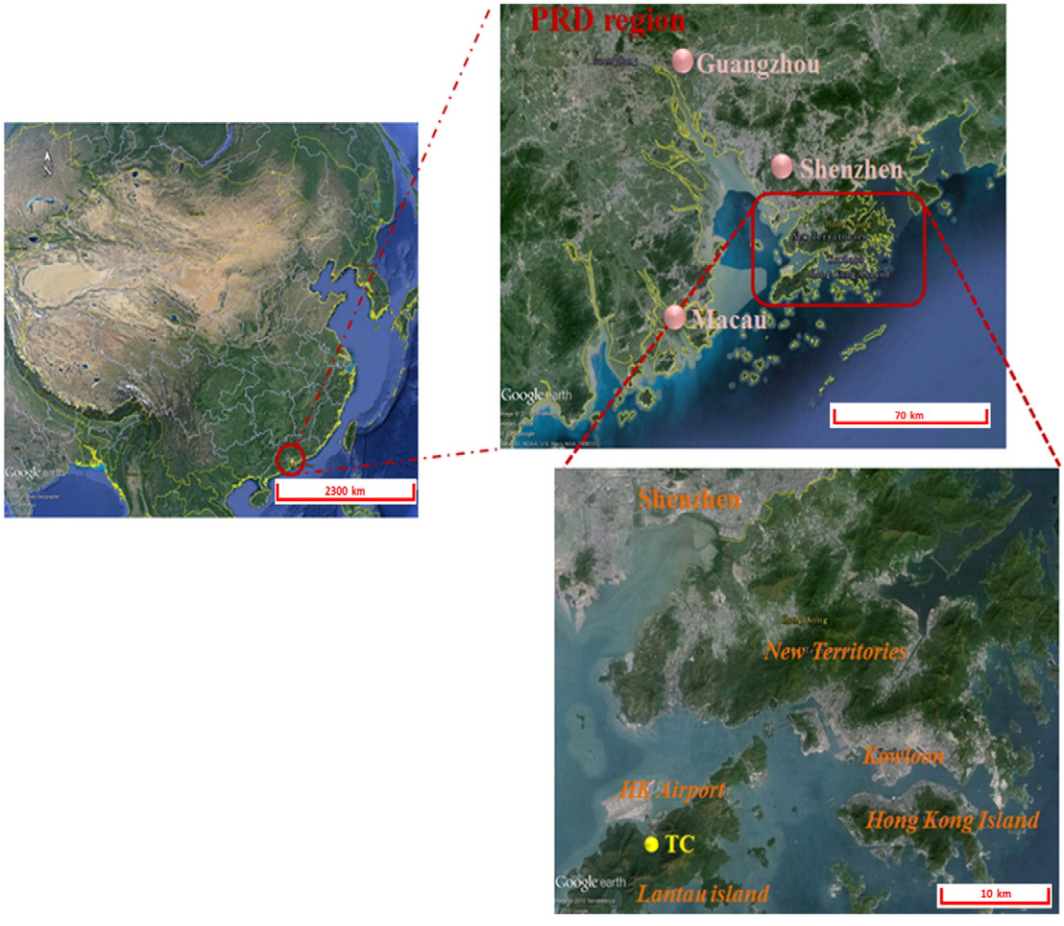

Fig. 1. Location of sampling site, at the Tung Chung monitoring station (TC), Hong Kong.