Atmospheric Environment 166 (2017) 110–119

Contents lists available at ScienceDirect

Atmospheric Environment

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

Size distributions of hydrophilic and hydrophobic fractions of water-soluble organic carbon in an urban atmosphere in Hong Kong

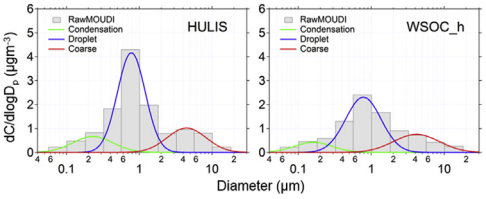
Nijing Wang [a], Jian Zhen Yu [a, b, *]

[a] Fok Ying Tung Graduate School, Hong Kong University of Science & Technology, Hong Kong, China
[b] Department of Chemistry and Division of Environment, Hong Kong University of Science & Technology, Hong Kong, China

HIGHLIGHTS

- Both hydrophilic and hydrophobic fractions of water-soluble organic carbon (WSOC) had a dominant droplet-mode.
- Organic materials contributed more than the inorganic ions to the water-soluble mass on particles smaller than 0.32 μm.
- The hydrophobic WSOC component on the coarse mode were found to come from condensation mode particles through coagulation.
- The hydrophobic WSOC component was well-correlated with sulfate in all size modes.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 March 2017
Received in revised form
28 June 2017
Accepted 4 July 2017
Available online 6 July 2017

Keywords:
Size distribution
HULIS
Hydrophilic WSOC
Urban Hong Kong

ABSTRACT

Water-soluble organic carbon (WSOC) is a significant part of ambient aerosol and plays an active role in contributing to aerosol's effect on visibility degradation and radiation budget through its interactions with atmospheric water. Size-segregated aerosol samples in the range of 0.056–18 μm were collected using a ten-stage impactor sampler at an urban site in Hong Kong over one-year period. The WSOC samples were separated into hydrophilic (termed WSOC_h) and hydrophobic fractions (i.e., the humic-like substances (HULIS) fraction) through solid-phase extraction procedure. Carbon in HULIS accounted for 40 ± 14% of WSOC. The size distribution of HULIS was consistently characterized in all seasons with a dominant droplet mode (46–71%) and minor condensation (9.0–18%) and coarse modes (20–35%). The droplet mode had a mass median aerodynamic diameter in the range of 0.7–0.8 μm. This size mode showed the largest seasonal variation in abundance, lowest in the summer (0.41 μg/m^3) and highest in the winter (3.3 μg/m^3). WSOC_h also had a dominant droplet mode, but was more evenly distributed among different size modes. Inter-species correlations within the same size mode suggest that the condensation-mode HULIS was partly associated with combustion sources and the droplet-mode was strongly associated with secondary sulfate formation and biomass burning particle aging processes. There is evidence to suggest that the coarse-mode HULIS largely originated from coagulation of condensation-mode HULIS with coarse soil/sea salt particles. The formation process and possible sources of WSOC_h was more complicated and multiple than HULIS and need further investigation. Our

* Corresponding author. Department of Chemistry, Hong Kong University of Science & Technology, Hong Kong, China.
E-mail address: jian.yu@ust.hk (J.Z. Yu).

http://dx.doi.org/10.1016/j.atmosenv.2017.07.009

measurements indicate that WSOC components contributed a dominant fraction of water-soluble aerosol mass in particles smaller than 0.32 μm while roughly 20–30% in the larger particles.

1. Introduction

Water soluble organic carbon (WSOC) is a major fraction of organic carbon in ambient aerosol formation. Analytically it is feasible to further divide WSOC into two fractions, hydrophilic part and hydrophobic part using solid-phase extraction (SPE). Such a demarcation is useful in disentangling the role of organics in interacting with atmospheric water. The approach using an SPE step was initially developed to remove the inorganic salts, which are major aerosol constituents and co-exist with WSOC, as the inorganic salts would interfere chemical characterization of the aerosol organics in many advanced analytical instruments (e.g., LC/MS). The commonly employed SPE stationary phases include silica with carbon chain (alkyl- or aryl-bonded silicas), function-bonded silica, alumina etc. (Hennion, 1999). In practice, this SPE separation step also removes the more hydrophilic fraction WSOC. The fraction that is retained on the SPE and later eluted with an organic solvent (e.g., methanol) is the hydrophobic part of WSOC, also called humic-like substances (HULIS) as they share similar spectroscopic properties to macromolecular humic substances in terrestrial and aquatic environments (Graber and Rudich, 2006; Kiss et al., 2002; Sannigrahi et al., 2006; Zappoli et al., 1999). Due to their surface active property and light absorbing ability (Dinar et al., 2006; Hoffer et al., 2006; Kiss et al., 2005), HULIS is expected to be an active component in cloud condensation nuclei (CCN) process (Gysel et al., 2004) and contribute to atmospheric light absorption (Lukacs et al., 2007). Recent studies also showed that HULIS contains redox active components contributing to health effects by ambient PM through catalyzing the generation of reactive oxygen species (Dou et al., 2015; Lin and Yu, 2011; Verma et al., 2012).

The ambient measurements of HULIS in PM_{10} and $PM_{2.5}$ for different locations have suggested that biomass burning and secondary formation through in-cloud processing as major sources for HULIS (Havers et al., 1998; Decesari et al., 2001; Gelencser et al., 2002; Kiss et al., 2002; Cavalli et al., 2004; Krivácsy et al., 2008; Salma et al., 2008; Lin et al., 2010a; Kuang et al., 2015; Park and Son, 2016). Most of the previous studies focused on the hydrophobic part of WSOC (i.e., HULIS) (Lin et al., 2010b; Kuang et al., 2015), the hydrophilic part in WSOC (here named as WSOC_h) was rarely commented on.

Size distribution of ambient aerosol is important in understanding aerosol properties, possible sources and formation pathways. Up to now, size distributions of organic and elemental carbon (OCEC), WSOC and ion species have been extensively studied (e.g., McMurry and Zhang, 1989; Yu et al., 2004a,b, 2010; Huang and Yu, 2008; Park et al., 2013; Wang et al., 2013; Bian et al., 2014). In comparison, only three studies reported the size distribution of HULIS (Lin et al., 2010b; Salma et al., 2013; Park and Son, 2016) and the measurement period was limited to only 1–2 weeks to one month. There is no research reporting the ambient size distribution of hydrophilic part of WSOC. In this study, one-year size-resolved aerosol samples were collected at an urban site in Hong Kong. Size distribution information of both hydrophobic and hydrophilic WSOC, together with size-segregated data of OCEC and major ion species, were obtained. The main objective of this work is to identify the size distribution characteristics of HULIS and WSOC_h in an urban environment and to determine the size-specific relative importance of organic and inorganic water-soluble mass, providing data for further understanding the role of water-soluble organics in visibility impairment and CCN formation. An additional objective is to gain knowledge of the sources and possible formation pathways of the two WSOC fractions in different size range through comparison with the size distribution data for other major species (WSOC, OC, EC and ion species).

2. Method

2.1. Sample collection

The ambient size-resolved aerosol were collected in Tsuen Wan (22°22′18″ N, 114°06′52″ E), a general air quality monitoring station of Hong Kong Environmental Protection Department (HKEPD). The sampler was located on the roof top of a 17 m building. Size-segregated samples were collected onto pre-baked 47 mm quartz fiber filters using a micro-orifice uniform deposit impactor (MOUDI, MSP Corp., Shoreview, MN, USA), operating in a nonrotating mode and at a flow rate of 30 L min^{-1}. The sampler has 10 size stages in an aerodynamic diameter range of 0.056–18 μm. In order to compensate the reduced space between each adjacent impactor plate caused by quartz filters, special spacers of 0.127 cm (MSP Corp., Shoreview, MN, USA) were used in the sampler. The MOUDI sampler was returned to the laboratory for cleaning by alcohol after each sampling.

The duration of each sample was 48 h (0:00 a.m. to 0:00 a.m.) and one sample was collected every 12 days from September 2013 to August 2014. Due to operational mistakes, samples collected in April 2014 were not valid. In late August and early September 2013, additional four sets of samples were collected. The sampling program yielded a total of 32 valid sets of samples. Two field blank samples were collected in each sampling trip. The collected filters were stored in polycarbonate petri-slide dishes lined with pre-baked aluminum foil and placed in a refrigerator at −18 °C before analysis.

2.2. Chemical analysis

Half of each 47-mm substrate filter was used for WSOC and HULIS analysis, while the other half was used for analysis of ions and OCEC. The filter portion was extracted with 15 mL ultrapure water in an ultrasonic bath for 45 min. The extracts were filtered through a 0.45 μm PTFE (polytetrafluorethylene) syringe filter (Millipore, Billerica, MA, USA) and analyzed for WSOC using a TOC analyzer (Shimadzu TOC-V_{CPH}, Japan). The instrument response was calibrated using sucrose. Due to relatively lower WSOC concentration for size-segregated samples, large volume of injection (200 μL) was applied.

The method for HULIS isolation and qualification was adopted from our previous work (Lin et al., 2010b), which was modified from the one developed by Varga et al. (2001). In brief, 4.0 mL of the water extract was acidified to pH = 2 using HCl and loaded on a SPE cartridge (Oasis HLB, 30 μm, 60 mg, Waters, USA). Before use, the cartridge was activated, cleaned and equilibrated by methanol, pure water and 0.01 M HCl in succession. The sample-loaded