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Variations of aerosol size distribution, chemical composition and optical properties from roadside to ambient environment: A case study in Hong Kong, China

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HIGHLIGHTS

- Roadside particles displayed higher number concentration but smaller size than those at the ambient site.
- Ambient particles showed strong UV-light absorbing properties.
- Both BC coatings and BrC sources play significant roles in the evolution of light-absorbing properties.

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ABSTRACT

This study investigated the "roadside-to-ambient" evolution of particle physicochemical and optical properties in typical urban atmospheres of Hong Kong through collection of chemically-resolved $PM_{2.5}$ data and $PM_{2.5}$ size distribution at a roadside and an ambient site. Roadside particle size distribution showed typical peaks in the nuclei mode (30–40 nm) while ambient measurements peaked in the Aitken mode (50–70 nm), revealing possible condensation and coagulation growth of freshly emitted particles during aging processes. Much higher levels of anthropogenic chemical components, i.e. nitrate, sulfate, ammonium, organic carbon (OC) and elemental carbon (EC), but lower levels of OC/EC and secondary inorganic aerosols (SIA)/EC ratios appeared in roadside than ambient particles. The high OC/EC and SIA/EC ratios in ambient particles implied high contributions from secondary aerosols. Black carbon (BC), a strong light absorbing material, showed large variations in optical properties when mixed with other inorganic and organic components. Particle-bound polycyclic aromatic hydrocarbons (*p*-PAHs), an indicator of brown carbon (BrC), showed significant UV-absorbing ability. The average BC and *p*-PAHs concentrations were 3.8 and 87.6 ng m^{-3}, respectively, at the roadside, but were only 1.5 and 18.1 ng m^{-3} at the ambient site, suggesting BC and *p*-PAHs concentrations heavily driven by traffic emissions. In contrast, $PM_{2.5}$ UV light absorption coefficients ($b_{abs\text{-}BrC,370nm}$) at the ambient site (4.2 Mm^{-1}) and at the roadside site (4.1 Mm^{-1}) were similar, emphasizing that particle aging processes enhanced UV light-absorbing properties, a conclusion that was also supported by the finding that the Absorption Ångström coefficient (AAC) value at UV wavelengths ($AAC_{\_UV\ band}$) at the ambient site were ~1.7 times higher than that at the roadside. Both aqueous reaction and photochemically produced secondary organic aerosol (SOA) for ambient aerosols contributed to the peak values of $b_{abs\text{-}BrC,370nm}$ in ambient particles at midnight and around noon, highlighting that secondary BrC had different sources and particle aging in the atmosphere affected BrC and BC properties and related aerosol light absorption.

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1. Introduction

Particulate matter (PM) in the atmosphere has been a major environmental concern at local, regional and global scales owing to its adverse impacts on human health (Grahame, 2009; Kampa and Castanas, 2008; Kreyling et al., 2004; Nel, 2005) and its important roles in climate change through radiative forcing and aerosol-cloud interaction (Pöschl, 2005; Tagaris et al., 2009; Von Schneidemesser et al., 2015). Traffic emissions are known to be a major source of $PM_{2.5}$ ($d_p < 2.5$ μm) in densely populated mega-cities (Lonati et al., 2006; Slezakova et al., 2007; Westerdahl et al., 2005). After being released from traffic emissions, PM undergoes rapid evolution through various physical and chemical processes, and thus displays different properties in near-source and ambient environments. The number concentration of vehicle-emitted ultrafine particles (6–220 nm) decreased exponentially with distance downwind from a freeway via atmospheric dispersion and coagulation processes, and different sizes (e.g., 6–25, 25–50, 50–100 and 100–220 nm) of particles behave quite differently in the atmosphere. Mass concentrations of PM and its chemical components, including organic aerosol (OA), black carbon (BC), sulfate, nitrate, ammonium and trace elements, differ significantly between rural, suburban and urban atmospheres (Gomiscek et al., 2004; Schwarz et al., 2008).

PM has significant light-absorbing impacts on urban atmosphere and leads to enhanced radiative forcing. BC in the atmosphere is the most potent absorbing component of PM in visible wavelengths (400–700 nm), contributing to ~71% of global solar energy absorption (Ramanathan and Carmichael, 2008; Bond et al., 2013). However, there is a growing body of evidence showing that certain organic aerosols, which are referred to as "brown carbon (BrC)", also have strong absorption abilities at near-ultraviolet wavelengths, adding further uncertainty to aerosol radiative forcing estimation (Mohr et al., 2013; Feng et al., 2013; Jo et al., 2015). Pure BC is formed in open combustion or in internal combustion engines, exists as a graphite-like structure with 10–50 nm spherules, and is believed to be chemically stable in the atmosphere (Bond and Bergstrom, 2006; Ramanathan and Carmichael, 2008; Wentzel et al., 2003); while BrC contains a rather large variety of primary and secondary organic compounds from natural and anthropogenic sources. The molecular structure of BrC is complex and includes polycyclic aromatic hydrocarbons (PAHs), humic-like substances and biopolymers (Alexander et al., 2008; Desyaterik et al., 2013; Hoffer et al., 2006). Both primary and secondary PAHs which belonging to BrC components contribute significantly to UV absorbing properties (Andreae and Gelencsér, 2006).

Pure BC is rarely found in the atmosphere because it readily adsorbs organic and inorganic compounds such as components of BrC, semi-volatile organic compounds, and sulfuric acid as a consequence of aging processes, thus leading to complex light absorptive properties (Kotzick and Niessner, 1999; Levitt et al., 2007; Liu and Smallwood, 2011; Qiu et al., 2012; Shen et al., 2017). Lack and Cappa (2010) applied the core/shell Mie theory and found a reduction of BC light-absorption if coated by BrC compared to pure BC related shell scattering (Bond and Bergstrom, 2006). The extent of reduction depends on BrC coating thickness and pure BC absorption properties, and can be up to 50% for 400 nm and 25% averaged across the visible radiation spectrum for reasonable core/shell diameters ($diameter_{core}/diameter_{shell} > 0.55$). In a field study near a busy freeway in Los Angeles, Ning et al. (2008) found that nearly 50% of volatile PAHs with high vapor pressure evaporated from the particle phase while less volatile PAHs (3–4 ring) remained in the particle phase together with BC particles during the short dispersion process from roadway to roadside, indicating the dynamic role of organics in the coating of fresh soot particles. Hence, observations of changes in the physicochemical properties of BC and BrC and their state (e.g. coatings) in this dynamic atmosphere may provide information on the evolution of optical, chemical and aerodynamic properties of PM. These changes influence atmospheric properties including cloud formation, radiative heating/cooling atmospheric lifetimes, and lung deposition (Bond et al., 2013).

In this study, measurements of aerosol particles in roadside and ambient environments in Hong Kong were conducted using online and offline methods. The study is aimed to (1) explore the diurnal and spatial pattern of PM number distribution and in relation to traffic flow; (2) investigate the evolution of $PM_{2.5}$ chemical characteristics from roadside to ambient aerosols in an urban environment; and (3) determine the impact of aging processes on the light-absorbing properties of roadside and ambient aerosols.

2. Methodology

2.1. Sampling location

Field campaigns were conducted at two sites in Hong Kong with different PM pollution characteristics (Fig. 1). The first site was a typical roadside site next to Lai Chi Kok (LCK) road in Sham Shui Po, Kowloon where fresh emissions from traffic sources are dominant, and the second one was in Kowloon Tong (KLT) representing typical urban ambient environment with well mixed and aged aerosols distant from traffic sources.

Lai Chi Kok Road (LCK): The site is situated at about 5 m away from the curbside of LCK road, a busy urban arterial with no stationary pollution sources nearby. Residential buildings of 8–10 stories height bound both sides of this near roadway site. The topography is typical in the city with street canyon effects and suppressed dispersion of on-road emissions. It is 0.3 km from the Sham Shui Po Ambient Air Quality Monitoring Station of the Hong Kong Environmental Protection Department.

Kowloon Tong (KLT): The site is located on the rooftop of a 30 m high building in Kowloon Tong district, about 1 km from the Sham Shui Po Ambient Air Quality Monitoring Station of the Hong Kong Environmental Protection Department. Previous investigations carried out at this site demonstrated it as representative of the urban ambient environment with no direct emission sources surrounding the site (Ning et al., 2013). The distance between the LCK and KLT sites is about 1 km, with multi-story urban residential buildings and city roadways between the sites.

2.2. Online and offline measurements

A combination of online and offline measurements was conducted during January 25–February 1, 2016 at LCK and during February 15–March 15, 2016 at KLT. BC was monitored continuously at seven wavelengths (370, 470, 520, 590, 660, 880, and 950 nm) using an Aethalometer 42 (AE42, Magee Scientific, USA), set at a flow rate of 2.4 L min^{-1} with 5-min interval throughout the sampling period, from which the aerosol absorption coefficient (b_{abs}) was calculated. The particle size distribution (18.1–532.5 nm) was continuously monitored using a Scanning Mobility Particle Sizer (DMA 3082 in tandem with CPC 3775, TSI Inc., USA) with scan, retrace, and purge time set at 50, 6, and 10 s, respectively. Data reduction and analysis of the SMPS output were performed using Aerosol Instrument Manager software (version 10.0, TSI Inc.). A Photoelectric Aerosol Sensor (PAS, 2000; Eco-chem, USA) was deployed to measure the particle-bound surface PAHs (*p*-PAHs). The flow rate of the PAS2000 was set at 2.0 L min^{-1} with data