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Nighttime aqueous-phase secondary organic aerosols in Los Angeles and its implication for fine particulate matter composition and oxidative potential

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HIGHLIGHTS

- Organic and elemental carbon concentrations were measured continuously in two seasons.
- Secondary organic carbon was quantified using the EC-tracer method.
- Time-integrated fine and ultrafine PM samples were collected and analyzed.
- Secondary organic aerosol tracers were detected in high quantities during nighttime.
- Intrinsic oxidative potential of nighttime samples exhibited elevated levels.

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ABSTRACT

Recent investigations suggest that aqueous phase oxidation of hydrophilic organic compounds can be a significant source of secondary organic aerosols (SOA) in the atmosphere. Here we investigate the possibility of nighttime aqueous phase formation of SOA in Los Angeles during winter, through examination of trends in fine particulate matter (PM2.5) carbonaceous content during two contrasting seasons. Distinctive winter and summer trends were observed for the diurnal variation of organic carbon (OC) and secondary organic carbon (SOC), with elevated levels during the nighttime in winter, suggesting an enhanced formation of SOA during that period. The nighttime ratio of SOC to OC was positively associated with the relative humidity (RH) at high RH levels (above 70%), which is when the liquid water content of the ambient aerosol would be high and could facilitate dissolution of hydrophilic primary organic compounds into the aqueous phase. Time-integrated collection and analysis of wintertime particles at three time periods of the day (morning, 6:00 a.m.–9:00 a.m.; afternoon, 11:00 a.m.–3:00 p.m.; night, 8:00 p.m.–4:00 a.m.) revealed higher levels of water soluble organic carbon (WSOC) and organic acids during the night and afternoon periods compared to the morning period, indicating that the SOA formation in winter continues throughout the nighttime. Furthermore, diurnal trends in concentrations of semi-volatile organic compounds (SVOCs) from primary emissions showed that partitioning of SVOCs from the gas to the particle phase due to the decreased nighttime temperatures cannot explain the substantial OC and SOC increase at night. The oxidative potential of the collected particles (quantified using a biological macrophage-based reactive oxygen species assay, in addition to the dithiothreitol assay) was comparable during afternoon and nighttime periods, but higher (by at least ~30%) compared to the morning period, suggesting that SOA formation processes possibly enhance the toxicity of the ambient particles compared to mobile-source dominated primary emissions in the Los Angeles area.

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1. Introduction

Particulate matter (PM) is widely recognized as one of the most human health significant environmental pollutants, exposure to which may lead to multiple adverse health effects, ranging from respiratory problems to cardiovascular, neurodevelopmental and gastrointestinal disorders (Delfino et al., 2014; Li et al., 2015; Peters et al., 2001; Schwarze et al., 2006). Organic components constitute a significant portion of atmospheric aerosols (as much as 50% or more by mass (Jimenez et al., 2009; Petit et al., 2014)) and have been subject to extensive research in recent years, due to their substantial impacts on multiple environmental aspects including the climate, visibility and human health (Hand et al., 2012; Mauderly and Chow, 2008; Russell et al., 1997).

Organic aerosols are comprised of hundreds of individual compounds that either have primary origin (known as primary organic aerosols, directly emitted from mainly combustion sources, namely vehicular emissions and biomass burning) or are formed through secondary transformations of primary organics (known as secondary organic aerosols-SOA) (Jimenez et al., 2009). Several studies have demonstrated that secondary organics comprise a substantial portion of organic aerosols in the Los Angeles basin (LAB) (Fine et al., 2008; Hayes et al., 2013; Williams et al., 2010; Zhang et al., 2012). Moreover, a number of recent investigations have reported that a considerable fraction of the oxidative potential of PM can be attributed to the secondary organics and even hypothesized that they may be more toxicologically potent compared to their primary precursors. For instance, enhanced oxidative potential of photochemically-aged secondary particles compared to primary particles were reported in both chamber studies as well as direct ambient measurements (Antiñolo et al., 2015; McWhinney et al., 2013a, 2013b; Rattanavaraha et al., 2011; Verma et al., 2009). While these investigations underscore the importance of SOA in terms of the overall PM-induced health effects, the mechanisms leading to enhanced SOA toxicity in the atmosphere are still poorly understood.

One major pathway of SOA formation is through gas-phase photochemical oxidation of primary organics followed by condensation of low volatility products into the particle phase (Kroll and Seinfeld, 2008). Another possible pathway of SOA production in the ambient air, which has been explored more recently, involves aqueous phase formation of low volatility organic compounds through dissolution of hydrophilic organic precursors in the bulk of the pre-existing water droplets and subsequent heterogeneous oxidation reactions in the liquid phase (Ervens et al., 2011; Lim and Turpin, 2015). Recent kinetic models suggest that the SOA formed through this latter process might have a substantial contribution to the total SOA mass (Lim et al., 2010; Volkamer et al., 2009).

Despite the importance of the relative impact of different SOA formation mechanisms on the aerosol's bulk chemistry and toxicity, there is currently very limited real world atmospheric observations addressing this topic. In a series of initial measurements, we observed a substantial increase in the nighttime concentration of organic carbon (OC), which fostered the hypothesis that these higher OC levels might be due to aqueous-phase formation of SOA occurring during that time period. We tested this hypothesis by 24-h continuous measurements of size distribution and OC content of fine particles ($dp < 2.5$ μm—PM2.5) during two contrasting seasons. The observed enhanced nighttime SOA levels during the cold season prompted us to further investigate a second hypothesis of whether this phenomenon impacts the organic aerosol composition and oxidative potential. To investigate this hypothesis, we conducted additional time-integrated measurements of individual organic compounds and oxidative potential of PM (using a macrophage-based biological assay as well as the Dithiothreitol (DTT) assay), in ultrafine (PM0.18, $dp < 0.18$ μm) and accumulation (PM0.18–2.5, 0.18 μm $< dp <$ 2.5 μm) size fractions, during the winter season. Our time-integrated measurements were performed on both ultrafine and fine PM size fractions, because the emission/formation mechanisms that were the focus of our investigations produce PM in different size ranges. While PM from primary organic emission sources (e.g. vehicular emissions) are mostly partitioned in the ultrafine size range (Morawska et al., 2008; Sardar et al., 2005), aqueous-phase SOA, which is the main objective of this study, predominantly forms PM in the accumulation mode (Cabada et al., 2004; Pandis et al., 1993).

2. Methodology

2.1. Sampling period and location

Time-integrated particle collection, as well as continuous measurements, were conducted at the particle instrumentation unit of the University of Southern California, located in central Los Angeles, about 150 m downwind of the Interstate 110 freeway. Continuous (i.e. hourly) monitoring of ambient organic carbon (OC), elemental carbon (EC) and particulate matter size distribution was performed during two periods, from August to mid-October of 2014 (referred to herein as "summer" or "warm season"), and from December 2014 to February 2015 (referred to herein as "winter" or "cold season"). Hourly-averaged temperature and relative humidity data during the warm season and cold season periods are summarized in Figure S1 (supplementary information).

In addition to the continuous monitoring, weekly time-integrated PM collection was also conducted in the cold season, during three time periods of the day, namely morning (6:00 a.m.–9:00 a.m.), afternoon (11:00 a.m.–3:00 p.m.) and night (8:00 p.m.–4:00 a.m.). These time intervals represent contrasting conditions in terms of particle emission/formation sources. The morning time interval represents the period with dominant impact from fresh vehicular emissions. Afternoon period is when the photochemical activity is highest during the day. Nighttime, in contrast, represents the period of the day with minimal photochemical activity, lowest temperatures and highest atmospheric stability. For the afternoon and night periods, particles were collected in two different size fractions, including ultrafine (PM0.18, $dp < 0.18$ μm) and accumulation modes (0.18 μm $< dp <$ 2.5 μm). For the morning period, however, only the ultrafine particles (PM0.18) were collected and analyzed, in order to minimize the potential impact of residual secondary organic aerosols in the morning samples.

2.2. Sampling methods and equipment

Hourly PM2.5 EC and OC data were collected using a semi-continuous EC-OC analyzer (Model 4, Sunset laboratory Inc., Tigard, OR) operating at 8 L/min, based on the National Institute of Occupational Safety and Health thermal/optical transmittance measurement protocol (NIOSH 5040). A PM2.5 cyclone and a multi-channel carbon denuder were connected upstream of the EC-OC instrument inlet, in order to prevent the adsorption of organic vapors on the quartz filters (Kirchstetter et al., 2001). In each 1-h cycle, 45 min was allocated to sample collection, during which the input air passed through a quartz filter punch (16 mm in diameter), installed inside of a heating oven. Further details about this analytical protocol can be found elsewhere (Arhami et al., 2006; Bae et al., 2004; Birch, 2002; Birch and Cary, 1996; Chow et al., 2011).

Particle size distribution data were collected continuously (with