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Sources and their contribution to two water-soluble organic carbon fractions at a roadway site

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HIGHLIGHTS

- Impact of biomass burning (BB) was examined using black carbon data of two types.
- Non-BB and BB-derived black carbon data were distinguished.
- Tracer method applied to elucidate sources of water-soluble organic carbon (WSOC).
- Non-BB emissions are an important source of hydrophilic and hydrophobic WSOC.

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ABSTRACT

24-h $PM_{2.5}$ samples were collected at a roadway site every 6th day for one year (September 2010 through August 2011) and analyzed for organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), hydrophilic and hydrophobic fractions of WSOC ($WSOC_{HPI}$ and $WSOC_{HPO}$), and ionic species, to provide important seasonal quantitative information on the primary and secondary sources of two WSOC fractions. Five minute black carbon (BC) concentrations were also measured using a seven-channel wavelength aethalometer to investigate the relationship of biomass burning (BB)-derived BC data from a $BC_{@880\ nm}$ tracer method and WSOC. There has been increased interest in the light adsorption of WSOC and water-insoluble OC but most of the tools that have been used to understand these relationships have limited to extracts of filter-based samples. The impact of BB emissions on WSOC fractions was examined using the relationship between ΔBC ($=BC_{@370\ nm} - BC_{@880\ nm}$) and WSOC (or K^+), and between BB tracers (WSOC and K^+) and BB-derived BC (BC_{BB}) estimated. The moderate correlation ($R^2 = 0.41$) of WSOC and ΔBC during the cold months of November through April may support the contribution of BB emissions to the observed WSOC. Predicted BC_{BB} correlated well with K^+, $WSOC_{HPI}$, and $WSOC_{HPO}$ concentrations (R^2 of 0.65, 0.43, and 0.61, respectively), suggesting BB emissions may have an influence on the WSOC fractions observed.

Contributions of non-BB, BB, and secondary OC (SOC) to both $WSOC_{HPI}$ and $WSOC_{HPO}$ were estimated using a multiple linear regression analysis. The monthly average contribution of non-BB emissions ranged from 12.6% to 29.4% of the $WSOC_{HPI}$ and from 21.5% to 44.1% of the $WSOC_{HPO}$, with high contributions occurring during the cold months and low contributions occurred during the warm months. BB emissions contributed more to $WSOC_{HPI}$ (2.7%–13.1%) than $WSOC_{HPO}$ (0.2%–1.1%), and the SOC contribution to both WSOC fractions was significant. SOC accounted for 57.2%–79.7% of the $WSOC_{HPI}$, and for 55.3%–78.0% of the $WSOC_{HPO}$, with the higher fractions occurring in summer. During the summer the high SOC contributions were consistent with high OC/EC and WSOC/OC ratios. Results of this study suggest that non-BB ("fossil") emissions are likely an important source to $WSOC_{HPI}$ and $WSOC_{HPO}$ observed at this roadway site.

1. Introduction

Atmospheric particulate water-soluble organic carbon (WSOC) accounts for approximately 10–90% of the organic carbon (OC)

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worldwide (Ruellan and Cachier, 2001; Jaffrezo et al., 2005; Park and Cho, 2011; Wonaschütz et al., 2011) and may influence the Earth's radiative forcing by acting as cloud condensation nuclei (Novakov and Penner, 1993; Saxena et al., 1995; Facchini et al., 1999). Many studies have shown that the contribution of WSOC to OC increased from emission sources to a background area (Zappoli et al., 1999; Decesari et al., 2001; Salma et al., 2001; Yu, 2002; Ho et al., 2006) and was higher in summer than in winter (Balasubramanian et al., 2003; Jaffrezo et al., 2005; Park et al., 2006, 2007; Sullivan and Weber, 2006; Pio et al., 2007; Snyder et al., 2009; Park and Cho, 2011).

Biomass burning (BB) emissions are an important primary source of WSOC loadings in the atmosphere (Park et al., 2006; Timonen et al., 2008; Snyder et al., 2009; Saarnio et al., 2010; Zhang et al., 2010; Wonaschütz et al., 2011), but its impact is limited in some regions. In the absence of BB emissions, WSOC is often considered a proxy for secondary organic aerosols (SOA) due to the highly oxidized nature of these water-soluble organic species. For example, particulate WSOC in a large urban center of Tokyo accounted for approximately 75–80% of the SOA mass (Miyazaki et al., 2006; Kondo et al., 2007). A major pathway for SOA formation is the atmospheric oxidation of precursor organic species (Kanakidou et al., 2005; Weber et al., 2007). However, the heterogeneous chemical reactions in clouds (Lim et al., 2005) or haze particles (Volkamer et al., 2007) may also result in significant SOA formation. It has been suggested that the partitioning of organic compounds due to liquid water uptake may be another important route of SOA formation, but its effects on SOA formation were restricted to an urban site dominated by summertime biogenic VOC emissions (Hennigan et al., 2008, 2009). However, in addition to BB emissions and SOA, motor vehicle emissions and fossil fuel combustion are known primary sources of particulate WSOC (Kawamura and Kaplan, 1987; Ruellan and Cachier, 2001; Yu, 2002; Ho et al., 2006; Park and Cho, 2011; Park et al., 2012a). Roadside $PM_{2.5}$ measurements indicated that the WSOC fraction of OC ranged from 0.12 to 0.22 in summer and from 0.23 to 0.32 in winter (Ruellan and Cachier, 2001; Yu, 2002; Ho et al., 2006). These values may be considered an upper limit for $PM_{2.5}$ from motor vehicle emissions. As discussed above, primary emissions and SOA can contribute to ambient WSOC loading. However, studies estimating the source contributions of particulate WSOC were limited (Snyder et al., 2009; Zhang et al., 2010; Cho and Park, 2013). Contributions of BB smoke and SOC to WSOC in $PM_{2.5}$ were estimated in Midwestern United States and Detroit, MI, using a chemical mass balance model (Snyder et al., 2009). Their work, however, did not include emissions from primary non-biomass burning sources of WSOC which could be an important source in urban and industrial locations. Cho and Park (2013) estimated fossil fuel emissions, BB emission, and SOC contributions to the observed WSOC at a high traffic volume location during winter using multiple linear regression analyses. These results have shown that contributions from fossil fuel emissions to the WSOC varied significantly with $PM_{2.5}$ pollution episodes. On average approximately 38% of the observed WSOC was attributed to fossil fuel emissions. Accordingly, more studies are required to estimate the seasonal and monthly contributions of primary non-BB emissions to WSOC over a long-term measurement period.

Measurements of particulate WSOC have been extensively conducted around the world, but most were limited to periods of summer or winter (Miyazaki et al., 2006; Kondo et al., 2007; Weber et al., 2007; Hennigan et al., 2008, 2009; Duong et al., 2011; Park and Cho, 2011; Wonaschütz et al., 2011; Park et al., 2012a, b; Cho and Park, 2013), with the exception of a few studies (Jaffrezo et al., 2005; Timonen et al., 2008; Snyder et al., 2009; Zhang et al., 2010). Our previous studies (Park et al., 2012a, b; Cho and Park, 2013) have focused on qualitative assessments of the total WSOC and its two fractions observed during limited measurement periods. However, the data obtained from the limited sampling periods do not allow an assessment of the monthly and seasonal variability of the sources and composition of carbonaceous aerosols in the region that is impacted from local sources and transport from China. To the best of our knowledge, information on source contributions of fractionated WSOC components over a full year has never been reported. In this study, 24-h $PM_{2.5}$ samples were collected at a roadway site every 6th day for one year between September 2010 and August 2011, and were analyzed for $PM_{2.5}$ mass, EC, OC, total WSOC, hydrophilic WSOC ($WSOC_{HPI}$), hydrophobic WSOC ($WSOC_{HPO}$), oxalate, and water-soluble inorganic components. Concentrations of black carbon (BC) observed at wavelengths of 370 nm and 880 nm were used to distinguish non-BB from BB-derived BC, and to help elucidate sources of WSOC. The goal of this study was to estimate the contribution of primary non-BB emissions, BB emission, and secondary organic carbon to the WSOC fractions ($WSOC_{HPI}$ and $WSOC_{HPO}$) using a multiple linear regression analysis.

2. Experimental

2.1. $PM_{2.5}$ measurements

24-h $PM_{2.5}$ were measured for one year at a university campus (35°11′N, 126°54′E) in Gwangju, Korea (Fig. 1). Gwangju metropolitan city has a population of approximately 1.5 million people and an area of 501.3 km^2. Based on the emission inventory data of criteria air pollutants in 2010, approximately 78% of the emissions were attributed to mobile sources. The sampling site is approximately 80 m from a four-lane road carrying heavy traffic during rush hour, and located 0.5–0.6 km southwest of a major express highway. Accordingly, the emissions from motor vehicles can be an important source of particulate matter observed at the site. Many restaurants are located near the site, and a great deal of meat such as pork, beef, and chicken are grilled with charcoal, kerosene, and natural gas. It has also been reported that concentration levels of particulate matter in the city are being influenced by locally produced emissions and long-range transport of air pollutants from polluted regions of China (Park et al., 2006; Jung et al., 2010; Jung and Kim, 2011; Park and Cho, 2011; Park et al., 2012b).

24-h $PM_{2.5}$ samples were collected every 6th day from September 2010 to August 2011 at the high traffic volume site. Sampling started at approximately 09:00 a.m. Aerosol samples were collected on pre-baked 47 mm quartz-fiber filters (Pall Gellman, Ann Arbor, MI) and 47 mm Teflon filters (Zefluor, 2 μm pore size, Gelman Science) by two URG $PM_{2.5}$ cyclone samplers. The URG samplers were operated at 16.7 L min^{-1}. A carbon impregnated diffusion denuder (Sunset Lab, OR) was placed upstream of the quartz filter pack to minimize a positive artifact due to semi-volatile organic vapors during sampling. A sodium carbonate (Na_2CO_3)-coated annular denuder was also placed upstream of the Teflon filter-pack to remove interferences caused by acid and alkaline gases. Samples collected on the quartz filters were analyzed for organic carbon and elemental carbon (OC and EC), WSOC and two fractionated WSOC components. Field blanks were analyzed to correct for background concentrations. Samples and field blanks collected on the Teflon filters were analyzed for oxalate and eight ionic components as well as $PM_{2.5}$ mass. Black carbon (BC) levels were also measured every 5 min using a seven channel wavelength aethalometer (AE-31 model, Magee Scientific Inc.) which operated at a sampling flow rate of 5 L min^{-1} through a $PM_{2.5}$ sharp-cut cyclone.