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Chemical and light absorption properties of humic-like substances from biomass burning emissions under controlled combustion experiments

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HIGHLIGHTS

- Chemical characteristics of WSOC and HULIS from biomass burning are examined.
- Light absorption of WSOC exhibited strong wavelength dependence.
- AAE and MAE_{365} of WSOC are similar to those from previous studies.
- HULIS is a dominant contributor to light absorption of WSOC.

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ABSTRACT

$PM_{2.5}$ samples from biomass burning (BB) emissions of three types - rice straw (RS), pine needles (PN), and sesame stems (SS) - were collected through laboratory-controlled combustion experiments and analyzed for the mass, organic and elemental carbon (OC and EC), water-soluble organic carbon (WSOC), humic-like substances (HULIS), and water soluble inorganic species (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and oxalate). The combustion experiments were carried out at smoldering conditions. Water-soluble HULIS in BB samples was isolated using a one-step solid phase extraction method, followed by quantification with a total organic carbon analyzer. This study aims to explore chemical and light absorption characteristics of HULIS from BB emissions. The contributions of HULIS (=1.94 × HULIS-C) to $PM_{2.5}$ emissions were observed to be 29.5 ± 2.0, 15.3 ± 3.1, and 25.8 ± 4.0%, respectively, for RS, PN, and SS smoke samples. Contributions of HULIS-C to OC and WSOC for the RS, PN, and SS burning emissions were 0.26 ± 0.03 and 0.63 ± 0.05, 0.15 ± 0.04 and 0.36 ± 0.08, and 0.29 ± 0.08 and 0.51 ± 0.08, respectively. Light absorption by the water extracts from BB aerosols exhibited strong wavelength dependence, which is characteristic of brown carbon spectra with a sharply increasing absorption as wavelength decreases. The average absorption Ångström exponents (AAE) of the water extracts (WSOC) fitted between wavelengths of 300–400 nm were 8.3 (7.4–9.0), 7.4 (6.2–8.5), and 8.0 (7.1–9.3) for the RS, PN, and SS burning samples, which are comparable to the AAE values of BB samples reported in previous publications (e.g., field and laboratory chamber studies). The average mass absorption efficiencies of WSOC measured at 365 nm (MAE_{365}) were 1.37 ± 0.23, 0.86 ± 0.09, and 1.38 ± 0.21 $m^2/g \cdot C$ for RS, PN, and SS burning aerosols, respectively. Correlations of total WSOC, hydrophilic WSOC (= total WSOC −HULIS-C), and HULIS-C concentrations in solution with the light absorption of WSOC at 365 nm indicate that the light absorption of WSOC from BB emissions was strongly associated with HULIS (R^2 = 0.92) - i.e., a hydrophobic component of WSOC, rather than with the hydrophilic WSOC (R^2 = 0.31).

1. Introduction

Carbonaceous aerosols are often divided into organic carbon (OC) and elemental carbon (EC). OC can be categorized into water-insoluble OC (WIOC) and water-soluble OC (WSOC) fractions. The WIOC fraction is mainly from incomplete combustion of both fossil

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and biomass fuels (Simoneit et al., 2004; Park and Cho, 2011), while the WSOC fraction can be emitted directly from combustion sources or produced through atmospheric processes (Weber et al., 2007; Park et al., 2012; Yu et al., 2014). Biomass burning (BB) emission is an important primary source of WSOC (Lin et al., 2010a; Salma et al., 2010; Park et al., 2013a, 2013b, 2015; Zhang et al., 2013; Kuang et al., 2015). The WSOC, which accounts for a significant fraction of atmospheric OC particles, may affect the hygroscopicity of the particles, and hence the ability of the particles to act as cloud condensation nuclei, which contributes to the indirect climate effects of the aerosols (Facchini et al., 1999; Charlson et al., 2001). Furthermore, the WSOC constituents contribute to positive radiative forcing of the climate by absorbing UV and visible light (Andreae and Gelencsér, 2006; Hoffer et al., 2006; Chen and Bond, 2010; Laskin et al., 2015).

WSOC compounds can further be separated into more hydrophilic and more hydrophobic fractions using solid phase extraction methods (Verma et al., 2012; Park et al., 2013b, 2015; Park and Son, 2016). It has been reported that humic-like substances (HULIS), which represent the hydrophobic fraction of the WSOC (Graber and Rudich, 2006), absorb light efficiently in the near UV and visible ranges (Hoffer et al., 2006), affect the aqueous-phase oxidation processes of organic species (Moonshine et al., 2008), and significantly contribute to the oxidative properties of ambient aerosols (Verma et al., 2012). Previous studies have suggested that BB emissions (Hoffer et al., 2006; Lin et al., 2010a; Zhang et al., 2013) and secondary processes (Altieri et al., 2009; El Haddad et al., 2011; Lin et al., 2012; Kuang et al., 2015) are important sources of atmospheric HULIS. The atmospheric HULIS carbon (HULIS-C) fraction contributed 9–72% of the WSOC in $PM_{2.5}$ (Zheng et al., 2013 and references therein). Also the $PM_{2.5}$ HULIS fraction was 15–33% in fresh BB aerosol samples (Mayol-Bracero et al., 2002; Lin et al., 2010a) and 63–76% in tropical BB aerosol samples at a pasture site in Rondonia, Brazil (Salma et al., 2010).

Black carbon has been recognized as the strongest light absorbing aerosol species (Ramanathan and Carmichael, 2008; Bond et al., 2013), especially at the visible and near infrared wavelengths. However, some OC species have also significant light absorption in the near UV (300–400 nm) and visible region, and this kind of organic aerosols is called a "brown carbon" (BrC) (Andreae and Gelencsér, 2006). HULIS has strong wavelength dependence with absorption increasing sharply from the visible to UV ranges (Hecobian et al., 2010; Zhang et al., 2013; Kirillova et al., 2014; Laskin et al., 2015). Noticeable variability in BrC spectral dependence has been reported with absorption Ångström exponent (AAE) values ranging from 2 to 16, due to the chemical variability of BrC constituents. In BB emissions, the relative abundance of BrC and its light-absorption properties are strongly affected by the combustion condition (e.g., smoldering and flaming), the combustion temperature, and moisture content (Duarte et al., 2005; Hoffer et al., 2006; Lukács et al., 2007; Chen and Bond, 2010). The water extract AAE of filter samples from urban and rural sites ranged from approximately 6 to 8, indicating no significant difference between ambient samples without BB emissions and samples dominated by BB, or between urban and rural sites (Hecobian et al., 2010; Cheng et al., 2011, 2016; Liu et al., 2013; Zhang et al., 2013; Du et al., 2014; Kirillova et al., 2014). The AAE for water extract HULIS from Amazon biomass burning aerosols was 7.1 (Hoffer et al., 2006), while AAE values ranging between 8 and 16 were observed in smoke samples from smoldering combustion of two types of wood (oak and pine) in laboratory chamber environments (Chen and Bond, 2010). Also aqueous extracts of fresh SOA produced from the ozonolysis of terpenes had AAE values of ~7 (Bones et al., 2010).

Despite much effort in field and laboratory measurements, our understanding of the relationships between the chemical compositions and optical properties of WSOC remains limited. Chemical and optical properties of organic aerosols from BB are rather variable with biomass type, burning type, combustion efficiency, terrain, and weather (Reid et al., 2005; Rissler et al., 2006; Frey et al., 2009; Chen and Bond, 2010 and references therein; Lin et al., 2010b; Kim Oanh et al., 2011; Park et al., 2013a). However, studies on the light absorption characteristics of organic aerosols from BB in combustion chamber environments are extremely limited (Chen and Bond, 2010; Cheng et al., 2011). In addition, there is little data in literatures addressing the variability of HULIS abundance and its light absorption characteristics for different biomass types. Therefore, in order to improve the understanding of chemical and light absorption properties of organic aerosols in ambient environments, a fundamental understanding of the chemical composition and absorption properties of WSOC from BB emission sources is needed.

In this study, measurements of fine particles from BB emissions were conducted to determine mass, OC, EC, total WSOC, HULIS, and inorganic species. The HULIS was isolated with a solid phase extraction method and then quantified with TOC analyzer. Also light absorption of water extracts in $PM_{2.5}$ between 300 and 400 nm wavelengths was investigated. The variabilities of the relative biomass smoke composition and light absorption linked with biomass type are addressed.

2. Experimental methods

2.1. Collection of $PM_{2.5}$ samples from biomass burning emissions

In this study three types of biomass materials were burned in laboratory combustion environments to examine chemical and light absorption characteristics of organic aerosol particles. Crop residues such as the rice straw, stubbles, and vegetative debris at rural or semi-urban areas in Korea are typically open burned in agricultural fields after harvest and before cultivation. It has also been reported that long-range transport of forest-fire plumes from China could affect fine particulate matter pollution in Korea (Park et al., 2006, 2013b; Cho and Park, 2013, 2015). Thus, the rice straw, pine needles, and sesame stems were chosen as the biomass materials. The rice straw and sesame stem materials were gathered from rural fields, and the pine needles were gathered from a small park adjacent to a two-lane road. Emission rates of fine particles from biomass burning were not measured. The ultimate properties of the three biomass materials are shown in Table 1. On an air-dry basis, moisture content measured for the rice straw, pine needles, and sesame stems was 7.8 ± 0.5, 9.9 ± 0.4, and 10.3 ± 0.4%, respectively. Carbon (C), hydrogen (H), and oxygen (O) contents were found to range from 36.5 to 49.7%, 5.2 to 6.4%, and 21.6 to 24.2%, respectively, depending on the biomass type, with their highest abundances being found in the pine needles. However, there were no significant differences in their weight fractions between the rice straw and sesame stems. The O/C ratio was the

Table 1
Proximate analysis of three biomass types (as air-dry basis) (wt%) (n = 3).

	unit	Rice straw	Pine needles	Sesame stem
H_2O	%	7.8 ± 0.5	9.9 ± 0.4	10.3 ± 0.4
Carbon (C)	%	36.50 ± 0.15	49.67 ± 0.20	39.89 ± 0.15
Hydrogen (H)	%	5.19 ± 0.05	6.37 ± 0.04	5.90 ± 0.15
Oxygen (O)	%	21.73 ± 0.52	24.24 ± 0.11	21.58 ± 1.18
Nitrogen (N)	%	0.60 ± 0.08	0.25 ± 0.11	1.62 ± 0.14
Sulfur (S)	%	0.00 ± 0.00	0.00 ± 0.00	0.03 ± 0.05
O/C ratio	–	0.60 ± 0.02	0.49 ± 0.00	0.54 ± 0.03