Atmospheric Environment 161 (2017) 90–98

Contents lists available at ScienceDirect

Atmospheric Environment

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

The influence of solvent and pH on determination of the light absorption properties of water-soluble brown carbon

Yangzhi Mo [a, d], Jun Li [a, *], Junwen Liu [a], Guangcai Zhong [a], Zhineng Cheng [a], Chongguo Tian [b], Yingjun Chen [c], Gan Zhang [a]

[a] State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China
[b] Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Science, Yantai, 264003, China
[c] College of Environmental Science and Engineering, Tongji University, Shanghai, 200092, China
[d] University of Chinese Academy of Sciences, Beijing, 100049, China

HIGHLIGHTS

- Effects of concentration, pH, and solvent on WSOC optical properties were studied.
- pH and solvent can affect the optical properties of water-soluble brown carbon.
- pH of HULIS should be adjusted for determining contribution to light absorption.
- A particle:water ratio of 0.25 mg/mL is proposed for the extraction of WSOC.

ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form
21 March 2017
Accepted 24 April 2017
Available online 27 April 2017

Keywords:
Brown carbon
Water-soluble carbon
HULIS
pH
Light absorption properties

ABSTRACT

Brown carbon (BrC) is a class of unidentified organic compounds that efficiently absorb solar radiation in the ultraviolet (UV) wavelengths, and its effects on climate are poorly understood. Measurement of the light absorption properties of BrC in liquid extracts is a commonly used BrC analytical method, but the optical characteristics of water-soluble BrC may be affected by pH and solvent. In this work, we investigated the effects of concentration, pH, and solvent on water-soluble BrC from ambient aerosols, biomass burning, diesel exhaust, and a humic substance standard. The results showed that pH can affect the light absorption properties of water-soluble BrC, whereas concentration had little effect, except low concentrations dissolved in methanol. Therefore, the pH of humic-like substances (HULIS) should be adjusted to the same value as water-soluble carbon (WSOC) for calculating the light-absorption contribution of HULIS to WSOC. The light absorptivity of water-soluble BrC dissolved in methanol was higher than that in water. Considering the pH and concentration effects, extraction of WSOC with a particle: water ratio of 0.25 mg/mL is proposed as well as to get a reference pH for light absorption analysis.

1. Introduction

Carbonaceous aerosols account for a large fraction of fine particulate matter in the atmosphere and play an important role in global climate change (Ramanathan and Carmichael, 2008; Tai et al., 2010). Traditionally, black carbon (BC), which exerts a warming effect second to CO_2, is the only light-absorbing carbonaceous aerosol, as organic carbon (OC) is assumed to result in climate cooling due to its scattering effects (Bond et al., 2011). However, recent studies have shown that some organic compounds are also able to absorb radiation, with most absorption in the near-ultraviolet (UV) spectral region. These light-absorbing organic compounds, referred to as brown carbon (BrC), are attracting increasing global attention (Andreae and Gelencsér, 2006; Bahadur et al., 2012; Chung et al., 2012; Feng et al., 2013).

BrC is ubiquitous in the atmosphere. Its source can be primary emissions from fossil fuel and biomass combustion (Chen and Bond, 2010; Zhang et al., 2011) or secondary formation from biogenic or anthropogenic precursors (Liu et al., 2016; Nakayama et al., 2010). Absorption Ångström exponent (AAE) and mass

* Corresponding author.
E-mail address: junli@gig.ac.cn (J. Li).

http://dx.doi.org/10.1016/j.atmosenv.2017.04.037
1352-2310/

absorption efficiency (MAE) are two representative optical parameters that have been widely used to characterize the light absorption properties of BrC, which may vary greatly among sources, formation processes, and measurement techniques (Laskin et al., 2015). Wonaschütz et al. (2009) improved the integrating sphere method to separate BrC from BC and to estimate the concentrations of BrC. Massabò et al. (2016) combined multi-wavelength absorbance analyzer (MWAA) and organic carbon and elemental carbon (OC/EC) analyzer methods to correct the OC/EC split point and obtain an "operative" BrC concentration. Lukács et al. (2007) measured spatial and temporal variations in the concentrations of water-soluble BrC in Europe by relating BrC to HULIS. However, these quantitative methods are highly dependent on the chemical properties of the calibration compounds, which may not represent natural BrC. In contrast, there are various methods for BC quantification, such as thermal/optical, biomarker and chemical oxidation based methods (Hammes et al., 2007), although the uncertainties are still high for these methods. Thus, unlike the case for BC, there is no quantitative reference method for BrC, and therefore most studies report the MAE, AAE, and bulk absorption of BrC at particular wavelengths.

Filter-based (e.g., particle soot absorption photometer, aethalometer and multi-angle absorption photometer) and non-filter-based (e.g., photoacoustic extinctiometer or spectroscope) optical instruments can quantify the light absorption by BrC without time-consuming laboratory analysis. These methods usually assume that $AAE_{BC} = 1.0$; however, encapsulation of BC cores with transparent organic carbon may result in the enhancement of light absorption (Lack and Langridge, 2013; Lack et al., 2012), which introduces uncertainties in the calculated absorption by BrC.

Compared to using optical instruments, measurement of BrC light absorption from different solvent extracts has the benefits of excluding interference from BC and providing complete absorption spectra; thus, it is considered as the better analytical method, and it has been used in many studies (Chen and Bond, 2010; Hecobian et al., 2010; Liu et al., 2013). As an important component of BrC, water-soluble BrC can not only directly absorb light but also has indirect climate effects by enhancing the ability of aerosol particles to act as cloud condensation nuclei. Therefore, the sources, atmospheric processes, and optical properties of water-soluble BrC have been extensively investigated (Kirillova et al., 2013, 2014). Atmospheric humic-like substances (HULIS), a hydrophobic fraction of water-soluble carbon (WSOC) with physicochemical properties similar to humic substances common in soil and aqueous environments, have been treated as an important component of BrC (Andreae and Gelencsér, 2006; Graber and Rudich, 2006; Laskin et al., 2015). However, previous studies have shown that solvent and pH could affect the ultraviolet absorption spectra of natural humic substances (Baes and Bloom, 1990; Pace et al., 2012). Recently, the pH and solvent were shown to affect the absorption properties of water-soluble BrC significantly (Chen et al., 2016; Hinrichs et al., 2016; Lee et al., 2014; Liu et al., 2016; Teich et al., 2016), so it is necessary to study the effects of pH and solvent on the determination of water-soluble BrC.

In this study, two ambient aerosol samples obtained from Guangzhou (GZ) and Beijing (BJ), two typical source samples (biomass burning and diesel exhaust), and Suwannee River Fulvic Acid (SRFA) were studied in detail to investigate the effects of concentration, pH, and solvent on light absorption by water-soluble BrC, especially for MAE_{365} and AAE. Based on the results of this study, we also make some suggestions for optimizing the measurement of BrC absorption.

2. Experimental methods

2.1. Sampling

Ambient samples of particulate matter less than 2.5 μm ($PM_{2.5}$) were collected on quartz fiber filters (8 × 10 inch; Pall, NY, USA) using a high-volume sampler (1 000 L/min; Xintuo Analytical Instruments, Shanghai, China). The samples were collected on 19 December 2013 in Guangzhou (23.08°N, 113.21°E) and 12 December 2014 in Beijing (40.4°N, 116.7°E), China.

Source samples were collected directly using a high-volume sampler as described above without any dilution. We did not consider the humidity, temperature, and combustion state (e.g., smoldering and flaming) during the sampling. The biomass burning sample was collected in a 10 m^3 empty room. To maintain well-ventilated conditions in the room, an exhaust fan was installed in the wall. Sampling was conducted while about 300 g of wheat straws were ignited and burned for 30 min. The diesel exhaust sample was collected directly from the exhaust pipe over 15 min. Before sampling, all filters were baked at 450 °C for 8 h to remove any organic contaminants. After sampling, all filters were folded in half, wrapped in aluminum foil, and stored in a freezer (−20 °C) until analysis.

Another 42 ambient samples were collected from 25 October 2014, to 29 November 2014 in Huairou District, Beijing, China (40.4°N, 116.7°E). But these samples were not studied in detail just like the four samples above, we just showed limited information of water soluble ions, pH and light absorption of WSOC and HULIS in water. The aims of these samples were to (a) compare the light absorption properties of HULIS before and after adjusting the pH; (b) investigate the correlation between water soluble ions and pH (section 3.2).

2.2. Carbon analysis

We determined both OC and EC using an aerosol carbon analyzer (Sunset Laboratory, Inc., USA) following the NIOSH thermal–optical transmittance (TOT) standard method, since the TOT protocol was shown to be more reliable for the split of OC and EC (Cheng et al., 2011). To obtain WSOC, portions of the filter were extracted into 100 mL ultrapure water (resistivity of >18.2 MΩ, Sartorius) for 30 min with sonication at room temperature, and then the filter was drip dried and extracted in 100 mL methanol (OCEANPAK, HPLC-Grade) to obtain solely methanol soluble OC (MSOC). Both the methanol and water extracts were filtered through a 0.22-μm PTFE membrane (Jinteng, China). Before filtration, 10 mL each of methanol and water were used to wash the filter.

HULIS was isolated based on previously published methods (Fan et al., 2012; Lin et al., 2010). Briefly, the water extracts were adjusted to pH 2 with HCl and then passed through a preconditioned soild phase extraction (SPE) cartridge (Oasis HLB, 30 μm, 60 mg/cartridge, Waters, USA). The retained HULIS were eluted with 2% (v/v) ammonia/methanol and evaporated to dryness in a gentle nitrogen stream. Finally, when needed, the HULIS were re-dissolved in a known volume of ultrapure water or methanol.

The carbon content of WSOC and HULIS (in water) were measured by a total organic carbon analyzer (TOC-VCPH, Shimadzu). To measure MSOC, 40 mL MSOC was evaporated to dryness under a nitrogen stream and re-dissolved with 1.0 mL methanol. A 20 μL sample was slowly spiked onto a 1.5 cm^2 precombusted quartz filter. After the methanol evaporated, triplicate OC/EC analysis was conducted for each sample using an aerosol carbon analyzer. The relative standard deviation was within 3%.