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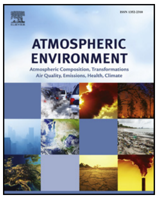

Spectral changes induced by pH variation of aqueous extracts derived from biomass burning aerosols: Under dark and in presence of simulated sunlight irradiation

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ABSTRACT

Water soluble organic carbon (WSOC) can significantly influence the aerosol optical properties and the aqueous phase chemistry in cloudwater, fogwater and aerosol liquid water. Here, we examine how the changing pH (in acidic range) affects the absorption spectra of aqueous extracts from field biomass burning aerosols, under dark conditions and in presence of simulated sunlight illumination. The observation under dark conditions indicates that pH variation from 2 to 5 induces significantly enhanced light absorbance in the wavelength ranges of 235–270 nm and 300–550 nm, whereas the light absorbance decreased in the range of 270–300 nm, which might be partially ascribed to the deprotonation of carboxylic acids and phenols. During the extract photolysis, light absorption exhibits photo-bleaching below 380 nm and photo-enhancement above 380 nm, indicating that at acidic levels (pH = 2–5), the particle extracts could undergo a significant composition evolution leading to a modification of absorptive properties. Meanwhile, after 12 h-photolysis, the acidity ($[H^+]$) normalized by WSOC concentration in aqueous extracts ($[WSOC_{ae}]$) increased with a variation of $\Delta[H^+]/[WSOC_{ae}] = (3.7 \pm 0.7) \times 10^{-7}$ mol mgC^{-1} (mean ± standard deviation), suggesting the formation of new acidic substances. Although these findings were acquired in aqueous solutions more relevant to cloud and fog water, the similar evolution likely occurs in wetted aerosols. This calls more attention to the effect of acidity on the wetted aerosols in order to better estimate the aerosol radiative forcing.

1. Introduction

Biomass burning emits plenty of light-absorbing organic compounds (e.g. phenols, aromatic carbonyls, carboxylic acids and their derivatives produced from lignin pyrolysis) (Graham et al., 2002; Mayol-Bracero et al., 2002; Chang and Thompson, 2010; Net et al., 2010; Gilardoni et al., 2016), contributing an important part of brown carbon (BrC) aerosol (Andreae and Gelencsér, 2006; Chang and Thompson, 2010; Teich et al., 2017). The light-absorbing property of BrC causes a positive radiative forcing on the top of atmosphere (Alexander et al., 2008; Chakrabarty et al., 2010; Feng and Kotamarthi, 2013). Field studies suggest that BrC absorption accounts for about 30% and 28% of the total aerosol absorption at 370 nm (Yang et al., 2009) and 440 nm (Bahadur et al., 2012), respectively. A global model simulation estimates that BrC represents 20% of the global solar absorption by carbonaceous aerosols at 550 nm (Chung et al., 2012). It is thus believed that the negligence of BrC will, to a considerable extent, bias the climate projections based on energy budget (Alexander et al., 2008; Lee et al., 2014; Martinsson et al., 2015).

Aerosol optical characteristics are usually modified by the component of water soluble organic carbon (WSOC), which can experience aqueous photochemical evolution to form new highly oxygenated and light-absorbing products once it dissolves into clouds, fogs, and aerosol liquid water (Lim et al., 2010; Lee et al., 2011; Nguyen et al., 2012; Carlton and Turpin, 2013; McNeill, 2015). Moreover, with the evaporation of liquid water, those low-volatility substances may remain in the particle phase as secondary organic aerosols (SOAs) (Lim et al., 2010; Nguyen et al., 2012; McNeill, 2015). Recently, many laboratory

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studies have investigated the photochemical evolution of water-soluble volatile or semivolatile organic compounds in aqueous media, e.g., low molecular-weight aldehydes (De Haan et al., 2009, 2011; Zhao et al., 2015), polyols (Daumit et al., 2014), organic acids (Griffith et al., 2013), phenols (Sun et al., 2010; Yu et al., 2014), and secondary oxidation products from biogenic volatile organic compounds (VOCs) (Bones et al., 2010; Lee et al., 2011; Ervens et al., 2015; Romonosky et al., 2015). Based on the simulations in a single-precursor system from numerous laboratory investigation, a comprehensive understanding about the photochemical mechanism, product identification and optical characteristics of common water-soluble compounds have been acquired (Sun et al., 2010; Ofner et al., 2011; Smith et al., 2014; Yu et al., 2014; Zhao et al., 2015). However, there is a wide gap between the laboratory-based sample simulations and the WSOC mixture in actual aerosols because the latter contains numerous unidentified organic and inorganic species that can potentially induce more complex spectral changes than the former.

The aqueous acidity (or pH) is a sensitive parameter that can significantly affect the light-absorbing characteristics and the extent of photo (chemical) evolution of organic compounds, e.g., phenols and nitrophenols (Nieto-Gligorovski et al., 2010; Nguyen et al., 2012; Smith et al., 2014; Zhao et al., 2015; Hinrichs et al., 2016). Nguyen et al. (2012) found that low pH could accelerate the formation of colored compounds via acid-catalyzed aldol condensation during evaporation processes. In addition, the absorption spectrum of humic substances or water-soluble fraction of ambient aerosol has also been observed to be sensitive to solution pH (Dryer et al., 2008; Phillips et al., 2017; Teich et al., 2017).

In this study, we investigated the effects of pH on the optical features of aqueous extracts from agricultural biomass burning aerosols. Experiments were conducted under dark conditions and in presence of simulated sunlight irradiation.

2. Experimental section

2.1. Particulate sample collection

Particulate samples were collected in the field of Henan province (Wenxian county and Qinyang county) and Hebei province (Daming county and Handan county) during the summer harvest season of 2013. A portable particulate sampler (MiniVol TAS, AirMetrics, USA), precalibrated with a standard flow meter (Defender 520, BIOS, USA), was used to collect particulate matter (≤ 2.5 μm in diameter, $PM_{2.5}$) in quartz filters (φ47 mm, QMA, Whatman, UK) at a flow rate of 5 L min^{-1}. The sampling time was 30–60 min for each filter. An aethalometer (AE-31, Magee Scientific, USA, with 7 wavelengths: 370, 470, 520, 590, 660, 880 and 950 nm) was employed to measure the light attenuation of aerosol at a flowrate of 5 L min^{-1} and a reading timebase of 3 min.

2.2. Preparation of aqueous extracts from particles

Eleven particulate samples collected from four field sites were chosen for laboratory study (Table S1). The aqueous extraction for particulate samples was conducted in two batches; the first batch of all 11 extract samples (Table S1) were used for the examination of the pH effect on the spectral properties without illumination, and the second batch, for the photolytic experiments and repeatability check. In the first batch, one-eighth of each filter was extracted twice with 5 mL Milli-Q water (≥ 18.2 MΩ cm, Millipore) per time under ultrasonic agitation for 30 min in a brown vial. The two-time extracts were combined and filtered through a PTFE syringe filter (0.2 μm pore size, Thermo Scientific), followed by pH determination with a pH meter (Mettler Toledo SevenEasy™ S20) calibrated at pH 4.00 and 6.86. The extraction for the second batch using a quarter of a particulate filter was carried out in the same manner as described above. Blanks for the filter substrate and extraction process were also prepared during the particle extraction. Prior to analysis or further experiment, the extracts were stored at −20 °C under a light-proof condition. It should be noted that the sonication during the extraction may oxidize some organics, which in turn can induce some changes on the extract absorption properties; however, this is beyond the scope of present study.

2.3. OC/EC quantification, TOC measurement and UV-VIS spectroscopy

Prior to the extraction, all the filter samples and blanks were analyzed for organic carbon (OC) and elemental carbon (EC) (Table S1) using a thermal-optical carbon analyzer (DRI Model, 2001A, Atmoslytic lnc., USA) in accordance to the IMPROVE (interagency monitoring of protected visual environments network) temperature protocol (Zhi et al., 2011).

The WSOC content in each aqueous extract ($WSOC_{ae}$) was determined by a TOC analyzer (vario TOC, Elementar, Germany). The detailed protocol is described in Sun et al. (2013). Briefly, the aqueous extract was firstly acidized with orthophosphoric acid for the elimination of inorganic carbon, and then analyzed by a combustion oxidation-non-dispersive infrared absorption method. The carbon content was quantified by applying a calibration standard curve (with carbon concentration of 0–20 mg L^{-1}) with potassium hydrogen phthalate as standard. In present quantification, 1 ml extract diluted with 9 ml Milli-Q water was measured, and the result was derived from the average of three measurements with a relative standard deviation (RSD) less than 5%.

The UV-VIS spectra for the obtained extracts were measured by applying a Varioskan Flash Spectral Scanning Multimode Reader (Thermo Scientific). Samples were loaded to a 96-well micro-plate (UV-Star, Chimney Well, Greiner bio-one, Germany); each well held a sample amount of 200 μl. The instrument performed the automatic photometric measurement with a scanning wavelength range of 200–1000 nm (spectral resolution, 2 nm). Duplicate measurements of a solution and Milli-Q water were made every ten samples to test the repeatability and stability (RSD < 5%).

2.4. Spectral characterization of aqueous extract at different pH levels

To investigate the effects of pH on the spectral characteristics of particle extracts, each 2.7 ml original extract was mixed with 0.3 ml H_2SO_4 solution of different concentrations (10^{-4}-10^{-1} M), leading to a series of extracts with pH ranging from 2 to 5. The control experiments included blanks for filter and Milli-Q water at different pH levels, and comparison of ionic strength in adjusted solution. For further comparison, we also examined the effects of pH variation (in the range between 2 and 4) on the spectral profile of the Suwannee River Fulvic Acid (SRFA, the International Humic Substances Society) solution (100 mg L^{-1}).

2.5. Photolytic experiments for aqueous extracts

The photolytic experiments were performed in a photo-reactor that was irradiated by a solar simulator (Xe lamp, 1000 W). The lamp was placed into the inner tube of a double-deck quartz condenser, and the outer tube of the condenser was filled with cooling circulation water (18 °C). The comparison of the photon flux emitted from the lamp with the solar actinic flux is shown in Fig. S1. Air-tight quartz tubes (1.5 cm in diameter, 3 ml solution per tube) were equidistantly arranged around the lamp, and 3 tubes of each extract were exposed to the simulated irradiation for 0, 4 and 12 h, respectively.