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Compositional and surface characterization of HULIS by UV-Vis, FTIR, NMR and XPS: Wintertime study in Northern India

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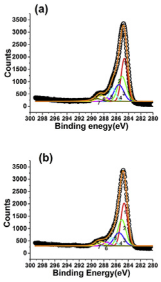
HIGHLIGHTS

- Characterization of HULIS in terms of various functional groups and types of Hydrogens present along the carbon chain by FTIR nd H-NMR spectroscopy.
- Study of the surface composition and oxidation states of various elements present (XPS) on the HULIS molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

This study (first attempt) characterizes HULIS (Humic Like Substances) in wintertime aerosols ($n = 12$ during day and nighttime each) from Indo-Gangetic Plain (IGP, at Kanpur) by using various state-of-the art techniques such as UV-VIS, FTIR, ^{1}H NMR and XPS. Based on UV-Vis analysis the absorption coefficient at 365 nm ($b_{abs\text{-}365}$) of HULIS was found to average at 13.6 and 28.8 Mm^{-1} during day and nighttime, respectively. Relatively high $b_{abs\text{-}365}$ of HULIS during the nighttime is attributed to influence of fog-processing. However, the power fit of UV-Vis spectrum provided near similar AAE (absorption Angstrom exponent) value of HULIS centering at 4.9 ± 1.4 and 5.1 ± 1.3 during daytime and nighttime, respectively. FTIR spectra and its double derivative revealed the presence of various functional groups viz. alcohols, ketones aldehydes, carboxylic acids as well as unsaturated and saturated carbon bonds. ^{1}H NMR spectroscopy was applied to quantify relative percentage of various types of hydrogen atoms contained in HULIS, whereas XPS technique provided information on surface composition and oxidation states of various elements present. A significantly high abundance of H–C–O group has been observed in HULIS (based on ^{1}H NMR); 41.4± 2.7% and 30.9± 2.4% in day and nighttime, respectively. However, aromatic protons (Ar-H) were higher in nighttime samples (19.3± 1.8%) as compared to that in daytime samples (7.5 ± 1.9). XPS studies revealed presence of various species on the surface of HULIS samples. Carbon existed in 7 different chemical states while total nitrogen and sulfur exhibited 3 and 2 different oxidation states (respectively) on the surface of HULIS. This study reports structural information and absorption properties of HULIS which has implications to their role as cloud condensation nuclei and atmospheric direct radiative forcing.

1. Introduction

HULIS in aerosols widely refers to a group of compounds having similar structure and properties to those with the Humic substances ubiquitously present in terrestrial environments

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(Graber and Rudich, 2006; Zheng et al., 2013). They are comprised of macromolecular substances and exhibit potential light-absorption and cloud-condensation nuclei (CCN) activity (Sun and Ariya, 2006). Currently a limited knowledge on molecular characterization and composition of these substances exists due to the fact that they are composed of a very large number of different molecules, very difficult to characterize individually. Many studies have suggested that HULIS form a major part of WSOC and originate from biomass burning emission, sea-salt spray (marine aerosols) and fossil-fuel combustion (Decesari et al., 2007; Fan et al., 2012; Lin et al., 2010; Salma et al., 2007; Song et al., 2012; Zheng et al., 2013). Rigorous attempts have been made to study the abundance and properties of HULIS from several locations in US, European countries, China and New Zealand (Kiss et al., 2002; Salma et al., 2007, 2010; Song et al., 2012; Zheng et al., 2013). Indo-Gangetic Plain (IGP) has a large stretch in India from north to east region in India and experiences high aerosol loading and haze and fog episodes (Pawar et al., 2015; Rajput et al., 2014; Singh et al., 2014). In view of aforementioned properties and its significant contribution to WSOC, it is utmost important to assess atmospheric abundance, sources and properties (base on surface characterization and absorption properties) of HULIS. However, these informations on HULIS are hitherto unknown for the entire IGP.

The complex molecular characteristics of HULIS have been studied previously elsewhere (Duarte and Duarte, 2005; Duarte et al., 2007; Kiss et al., 2002; Krivácsy et al., 2001; Varga et al., 2001). The complex nature of atmospheric HULIS has been studied previously with techniques such as UV-Vis and ^{1}H NMR (Chen et al., 2016; Duarte and Duarte, 2005; Fan et al., 2016; Song et al., 2012). There are several studies in Indian subcontinent particularly from IGP pertaining to atmospheric aerosol characterization, for example (Chakraborty et al., 2015; Rajput et al., 2014; Ram and Sarin, 2015), but none of previous studies have assessed HULIS from the region. In this context, our study represents first comprehensive attempt to characterize HULIS from IGP region. Details on analytical extraction, matrix purification and day-night abundance of HULIS in ambient aerosols from IGP has been reported elsewhere (Kumar et al., 2017).

This study assesses absorption and molecular properties of HULIS. We reiterate that analytically it is challenging to characterize HULIS on an individual molecular level owing to their complex composition. However, the state-of-the art technologies can be applied to infer their integrated molecular properties and structure viz. elemental composition, functional groups, chemical state of elements and types of hydrogen atoms and their relative abundance. In this study, HULIS has been characterized using spectroscopic techniques namely UV-VIS, FTIR, ^{1}H NMR and XPS. HULIS absorbs primarily in the UV region (Pavlovic and Hopke, 2012; Samburova et al., 2005; Zappoli et al., 1999), and hence it is important to study their absorption property in this region. Second derivative FTIR spectroscopy was used to identify the type of functional groups present in the HULIS. It is important to mention here that an FTIR spectrum of HULIS is complex and unresolved. However, on differentiation it shows hidden peak characteristics. XPS technique is a powerful tool to assess the surface composition and chemical states of various elements in the matter, and thus, can be utilized to infer about possible sources, chemical reactivity, hygroscopicity etc. of the HULIS. ^{1}H NMR technique helps us to identify the types of hydrogen atoms present in the HULIS. This information can be linked to sources and various properties of HULIS. Utilization of all such techniques allowed us to look deeply into the molecular properties and structure of HULIS in IGP and helped us to gain an insight into its possible sources.

2. Methodology

2.1. Aerosol sampling and isolation of HULIS from aerosol aqueous extract

Filter sampling of ambient aerosols was carried out in the months of December 2015 and January 2016 on the roof-top of CESE Building inside IIT Kanpur campus (26.30 °N, 80.14 °E and 142 m above mean sea level). Kanpur area (district) has a large population of 4.5 million and is located centrally to the most densely populated and polluted region (IGP) in India. IIT Kanpur campus is located nearly 15 km upwind of nearby city and is a fully residential and educational institution. In the close vicinity there are some villages and agricultural lands where in biomass burning activity goes on. PM_{10} (particulate matter of aerodynamic diameter $\leq$ 10 μm) sampling onto pre-combusted quartz fiber filters was achieved using a high-volume air-sampler (Envirotech Instruments Pvt. Ltd., New Delhi, India; Model no: APM460 NL; flowrate: $\approx$ 1 m^3/min). Samples were collected on a day-night basis by running the sampler continuously for 10 h; from 8 a.m. to 6 p.m. during daytime and from 8 p.m. to 6 a.m. during nighttime. Sampling was systematically conducted on almost every fourth day. A total of 24 (12 daytime and 12 nighttime) PM_{10} samples were collected during wintertime between 19th December 2015 and 1st February 2016. Soon after retrieval, each sample was wrapped gently into aluminum foil and stored at −20 °C until chemical analysis.

Organic and elemental carbon (OC-EC) have been measured following NIOSH (National Institute for Occupational Safety and Health) protocol on an EC-OC analyzer (Birch and Cary, 1996). For quantification of WSOC and carbon associated with HULIS (HULIS-C), aerosol samples (1/8th of the aerosol laden filter) were pre-soaked overnight and then extracted three times (sonication) with 45 (= 20 + 15 + 10) mL of Milli-Q (resistivity: 18.2 MΩ cm). The extracts were filtered through a syringe filter (pore-size: 0.22 μm) (Rajput and Sarin, 2014; Varga et al., 2001). Aerosol aqueous extract (20 mL) maintained at pH $\approx$ 2 was loaded onto pre-conditioned (with methanol) HLB cartridge (Hydrophilic-Lipophilic Balanced polymer: Oasis HLB, waters, USA; 3 cc, 60 mg) (Varga et al., 2001). Elution of HULIS was carried out with 20 mL of methanol: acetonitrile (1: 1; v/v) in this study. A 500 μL solution of the eluted HULIS (for each sample) was deposited onto pre-baked and weighed 47 mm quartz filter. Subsequent to drying under nitrogen atmosphere, these deposited filters were first used for the gravimetric determination of HULIS-organic mass (HULIS-OM) on an analytical microbalance (accuracy: 0.01 mg). The remaining eluted fraction of HULIS was evaporated under gentle stream of nitrogen gas and the residue was redissolved with Milli-Q for quantification of HULIS-C on TOC analyzer (Shimadzu; LCPH). Relevant details on analytical protocol (solvent selection, accuracy, quality assurance and quality control) of the data on HULIS has been reported elsewhere (Kumar et al., 2017).

2.2. UV-VIS spectral analysis of HULIS

Absorption properties viz. absorption coefficient ($b_{abs\text{-}\lambda}$) and absorption Angstrom exponent (AAE) of HULIS in PM_{10} samples have been reported herein. Absorbance signal (A) has been measured in all 20 samples (10 daytime and 10 nighttime) from 200 to 700 nm on a dual-channel UV-VIS spectrophotometer (Agilent Cary 60 spectrophotometer) (Baduel et al., 2009; Duarte and Duarte, 2005; Fan et al., 2012; Havers et al., 1998; Krivácsy et al., 2008; Varga et al., 2001). The measured “A” signal was utilized to determine b_{abs} at different wavelengths. For example, mathematical expression for calculating b_{abs} at 365 nm is given below:

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