Diurnal Variability in Secondary Organic Aerosol Formation over the Indo-Gangetic Plain during Winter Using Online Measurement of Water-Soluble Organic Carbon

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ABSTRACT

Understanding the secondary organic aerosol (SOA) formation is among most important topics in the field of aerosol research because its poor understanding leads to large uncertainty in the assessment of aerosol effects on air quality and climate. This study reports the diurnal and temporal variability in SOA formation over a site (Patiala: 30.2°N, 76.3°E, 249 m amsl) located in the Indo-Gangetic Plain (IGP) during winter using the first online measurements of water-soluble organic carbon (WSOC) over India. Online WSOC, measured with particle-into-liquid sampler (PILS) connected to total organic carbon (TOC) analyzer, ranged from 0.1 to 99 µg m^{-3} (avg: 15.6, sd: 9.4) with a considerable day-to-day and within the day variability, and attributed to meteorological conditions and regional sources. Diurnal trends of online WSOC suggest significant SOA formation during 7:00 to 22:00 hrs when sources of SOA precursors are active; and loss of SOA occurs during afternoon when ambient air temperature is at its peak. In parallel to online measurements, filter-based particulate matter smaller than 2.5 µm (PM$_{2.5}$) samples were also collected and analyzed for major cations, anions and carbonaceous aerosols. Filter-based PM$_{2.5}$ composition suggests that the emissions from biomass burning contribute more to carbonaceous aerosols than those from fossil fuel burning. In spite of this, average primary WSOC was only ~20% whereas secondary WSOC (or SOA) dominated the total WSOC concentration with ~80% contribution. A strong linear relationship between PM$_1$ and WSOC (R^2 = 0.83, slope = 0.113, intercept = 4.7), suggests that a significant fraction of fine particles are SOA.

Keywords: Biomass burning; SOA; Carbonaceous aerosols: WSOC; India.

INTRODUCTION

Organic material contributes 20–50% to the total fine aerosol mass at continental mid-latitudes and as high as 90% in tropical forested areas (Kanakidou *et al.*, 2005 and references therein). Organic compounds that are emitted directly in particulate form are referred to as Primary Organic Aerosol (POA); whereas, those formed in the atmosphere through different physico-chemical transformation processes are called as Secondary Organic Aerosols (SOA). Volatile organic carbon (VOCs) emit from variety of natural and anthropogenic sources including biomass burning (BB), fossil fuel burning (FFB) and biogenic emissions and subsequently, are oxidized by different atmospheric oxidants such as O$_3$, OH and NO$_3$ radicals and form semi-volatile VOCs (SVOCs). The SVOCs get further oxidized and form SOA, which are usually oxidized water-soluble species. Therefore, WSOC in ambient aerosols is often considered as a measure of SOA (Weber *et al.*, 2007; Ervens *et al.*, 2011). However, a part of water-insoluble OC can also be SOA. Further, all WSOC may not be SOA as BB can also contribute to primary WSOC (usually highly oxidized low volatile HULIS, Paglione *et al.*, 2014 and references therein). In addition to primary WSOC, BB also emits large quantity of VOCs that can also lead to SOA formation (WSOC) i.e., BB can contribute both primary as well as secondary WSOC. Given the above mentioned complexity, the primary and secondary fractions of WSOC in atmospheric aerosols are still poorly constrained. Poor understanding on SOA formation on temporal and spatial scale leads to measurement-modeling mismatch (Heald *et al.*, 2011), and among major causes of large uncertainty in the assessment of aerosol effects on air quality and climate.

The Indo-Gangetic Plain (IGP) receives large amount of primary particles and precursors of secondary particles due

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to emissions from vehicles, industries, biomass and bio-fuel burning during winter (Lawrence and Leliveld, 2010 and references therein). Further, severe fog with the visibility of less than a few tens of meters and often daytime hazy atmosphere is a common phenomenon over the IGP during winter. Enhanced SOA formation is reported during foggy days over the IGP (Kaul *et al.*, 2011). The particulate chemical composition over the IGP is dominated by organic aerosols and, WSOC is a large component of the total OC (Rajput *et al.*, 2011; Rastogi *et al.*, 2014); however, understanding on WSOC (SOA) formation is meager. Online measurements of WSOC offer greater insights in understanding the processes forming SOA during different time of the day (Sullivan *et al.*, 2004). Present study attempts to understand SOA formation through online WSOC measurements, and quantifies primary vis-à-vis secondary fraction of WSOC over the IGP during winter.

EXPERIMENT

Site Description

The study site Patiala (30.2°N, 76.3°E; 250 m asl) is located in the Punjab province in the IGP. This study was carried out during the January 9th to February 5th 2014, which represents the peak of winter season with average daytime and nighttime temperature and relative humidity as 18 and 10°C, and 63 and 91%, respectively. Winds are usually westerly during winter. Usually winter remains dry but there are a few spells of rain due to western disturbances, which also brings moisture over the study region. The term 'western disturbance' is used in South Asian countries (e.g., India, Pakistan, Bangladesh and Nepal) to describe an extra tropical storm originating in the Mediterranean that brings sudden winter rain to the northwestern parts of the Indian subcontinent. This is a non-monsoonal precipitation pattern driven by the westerly winds.

The winter months are prevailed by the emissions from fossil fuel burning including power plants, from bio-fuel burning, and from the burning of dry woods by local people to keep themselves and livestock warm. Detailed site description has been reported elsewhere (Rastogi *et al.*, 2014).

Semi-Continuous Measurements

Particle-into-liquid sampler (PILS, Model ADI 2081, Applicon Analytical) was coupled to total organic carbon (TOC, Sievers 900 Portable with Turbo, GE Analytical Instruments) analyzer for semi-continuous analyses of ambient water-soluble organic carbon (WSOC), for the first time in India, with 4 min integration time during January 9th to Feb 5th 2014. PILS-TOC was installed in a clean room at third floor (~12 m above the ground) of the Physics department building in Punjabi University, Patiala. The stainless steel (ss) tubing (10 mm outer diameter) with cyclone inlet (URG-2000-30EH, 16.7 L min^{-1}, 2.5 µm) was used for drawing the ambient air through PILS using diaphragm vacuum pump (Part No: N840.3FT.40.18 KNF, flow rate 16.7 L min^{-1}). The air inlet was ~2 m away from the window of the room with open atmosphere outside. The Ecoline VC-MS/CA 8-6 multi 8 channel 6-roller

peristaltic pump was used for supplying Milli-Q water to and from PILS. The water-extract of ambient aerosols coming out of PILS was filtered through in-line syringe filter (25 mm diameter, 0.45 µm porosity) and directed to TOC analyzer for measuring the concentration of WSOC. Subsequently, the liquid concentration of WSOC was converted into ambient air concentration as per the method reported elsewhere (Rastogi *et al.*, 2009). Ambient air was also drawn through Teflon filter (47 mm diameter, 0.45 µm pore size) everyday for about an hour (at different time on different days) and corresponding average WSOC concentration has been considered as ambient air WSOC blank, which was subtracted from corresponding WSOC data of that particular day. Potassium hydrogen phthalate (KHP) standards with the concentrations ranging between 250 and 1000 mg L^{-1} were also run as sample on TOC analyzer on every alternate day for keeping the track of data quality of WSOC and found to be accurate within ± 3%. Overall uncertainty on WSOC measurement is estimated to be within ± 10% based on the combined uncertainties associated with the sampling air flow rate and liquid flows.

In parallel to WSOC, black carbon (BC) with Aethalometer (MG Scientific) and mass concentrations of particulate matter smaller than 1.0, 2.5 and 10 µm aerodynamic diameter (PM$_1$, PM$_{2.5}$, and PM$_{10}$) using Aerosol Spectrometer (Grimm, model 1.108), were also measured with 5 min integration time (details are given in Singh *et al.*, 2015), and meteorological parameters were measured with automatic weather station installed at the same site. Mixing height data was procured through NOAA-Hysplit model.

Filter Sample Analyses

For supporting data, high volume filter samples were also collected in parallel during the study period. Towards this, high volume sampler (Thermo Scientific, USA, flow rate: 1.13 m^3 min^{-1}) was installed at the terrace of Department of Physics, Punjabi University, Patiala, ~20 m above ground level. Day/night pairs of PM$_{2.5}$ samples were collected on large tissuquartz filter (PALLFLEX, 2500QAT-UP, 20 cm × 25 cm). Sampling time was about 09:00 to 17:00 and 22:00 to 06:00 hours for daytime and nighttime samples, respectively. A total of 25 day/night pairs samples (total 50) were collected during January 9th to February 5th, 2014. After collection, filters were packed and stored in deep freezer (–20°C) until analysis.

The PM$_{2.5}$ mass was determined gravimetrically. The concentrations of elemental carbon (EC) and organic carbon (OC) were measured on EC-OC analyzer (Model 2000, Sunset Laboratory, USA) using National Institute of Occupational Health and Security 5040 (NIOSH-5040) protocol (Birch and Cary, 1996). The concentration of inorganic cations (NH$_4^+$, Na$^+$, K$^+$, Mg^{2+}, and Ca^{2+}) and anions (Cl$^-$, NO$_3^-$, and SO$_4^{2-}$) were measured by ion chromatography (Dionex-500). Several blank filters were analyzed for all the measured species and species concentrations in each sample were corrected for their respective average blank concentrations. Details of chemical analyses has been reported in our earlier work (Rastogi and Sarin, 2007; Rajput *et al.*, 2011; Rastogi *et al.*, 2014).

RESULTS AND DISCUSSIONS

Filter-Based Chemical Composition of PM$_{2.5}$

Filter-based PM$_{2.5}$ mass concentration ranged from 33 to 313 µg m^{-3} (avg: 145; sd: 56) during the study period with the highest concentration during Lohiri and Makar Sankranti festivals (January 14) and lowest concentration during the rain events (January 18 and 22, Fig. 2(a)) with the considerable rainfall (~32 mm). The Lohri and Makar Sankranti are big festivals in Punjab when people perform singing and dancing programs whole night around bonfires, which explains the corresponding high PM$_{2.5}$ mass concentrations. The chemical composition of ambient PM$_{2.5}$ was also assessed in terms of percentage contributions of water-soluble inorganic species (WSIS, estimated by adding the concentrations of all the measured cations and anions), carbonaceous aerosols (sum of organic matter (OM) and elemental carbon (EC)), and unidentified fraction (termed as 'Others') to PM$_{2.5}$ for each sample. It is presented in the form of a ternary plot (Fig. 1). Here, the OM was estimated as 2.1 times the measured concentration of OC based on Rajput *et al.* (2013), which has documented OM/OC ratio upto 2.5 for polar organic compounds for the samples collected from the same site in previous years over the IGP. The average WSOC/OC ratio during this study was 0.80 (discussed later), which indicates that the majority of organics would be of polar nature and therefore, OC-to-OM conversion factor was chosen as 2.1. On average, the PM$_{2.5}$ were composed of ~31% WSIS, 31% OM, 5% EC and remaining fraction was unidentified (given as 'Others'). These observations suggest that the composition of PM$_{2.5}$ was dominated by carbonaceous aerosols (OM + EC) with comparable contribution from WSIS during the study period. Fig. 2(b) presents the temporal variability in OC and EC concentrations during the study period, which were more or less similar to the variability in PM$_{2.5}$ mass concentrations (Fig. 2(a)). Further, a large fraction of OC could be SOA, as suggested by the regression parameters (R^2 = 0.86, slope = 0.80) of a strong linear relationship between filter-based OC and online WSOC averaged over filter integration time (discussed in detail in latter sections).

The WSIS were dominated by salts of SO$_4^{2-}$ and NO$_3^-$ with NH$_4^+$ and K$^+$, as evident by a strong linear relationship (R^2 = 0.97, figure not shown) between (NH$_4^+$ + K$^+$) and SO$_4^{2-}$ + NO$_3^-$). The concentrations of other inorganic species were relatively very low and can be ignored. Further, the NO$_3^-$ was a significant anion as compared to SO$_4^{2-}$ with average NO$_3^-$/SO$_4^{2-}$ weight ratio of 0.83 ± 0.30, which also indicates the significant abundance of secondary nitrate precursors over the study region. The NH$_4^+$ was a dominant cation followed by K$^+$, whereas other cations were insignificant. A strong linear relationship between K$^+$ and OC (R^2 = 0.87) attests that the dominant source of K$^+$ is BB over the study region and it can be used as proxy for emissions from BB. The observed chemical composition of PM$_{2.5}$ in this study is somewhat similar to that documented in detail by Rastogi *et al.* (2014) using the samples collected from the same site during winter in previous years.

Temporal Variability in Semi-Continuous WSOC

Temporal variability in semi-continuously measured WSOC concentrations reveals that there was a large day-to-day and within the day variability (Fig. 2(c)). It ranged from 0.1 to 99 µg m^{-3} (median: 14.1, average: 15.6, sd: 9.4) during the study period, however, mostly it was between 5.0 to 40 µg m^{-3} (Fig. 2(c)). Highest WSOC concentrations were observed during January 13th and 14th. These dates correspond to a big celebration of the Lohri and Makar Sankranti festivals in Punjab (as mentioned earlier). Large amount of wood burning for bonfires with wintertime meteorological conditions suggest that the observed high WSOC concentration on these dates could be both primary and secondary (discussed later). Lowest concentrations were observed on January 18th and 23rd due to significant rainfall (~32 mm) on these days (Fig. 2(c)). The Fig. 2(c) also suggests that the ambient WSOC attains its average value within a couple of hours even after an event when atmosphere was cleaned by significant rainfall. Such an observation also indicates that the sources (primary/secondary) of WSOC are of local/regional origin during winter. Further, the large variability in WSOC concentration within a day and day-
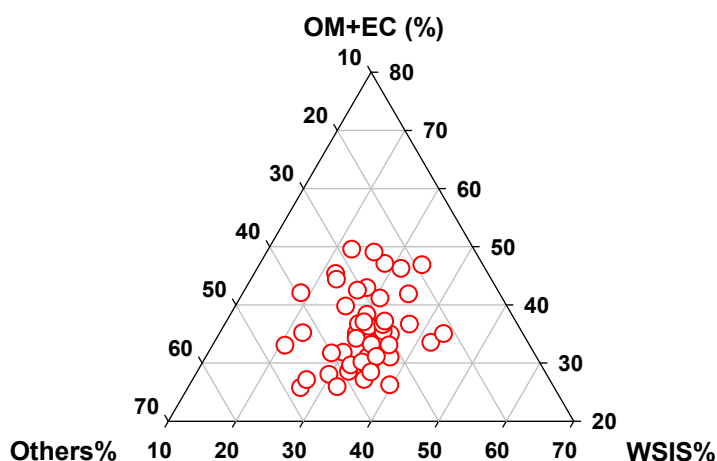

Fig. 1. A ternary plot depicting the composition of individual aerosol filter sample. Here, OM is organic matter, EC is elemental carbon, WSIS is water-soluble inorganic species, and others correspond to unidentified fraction.
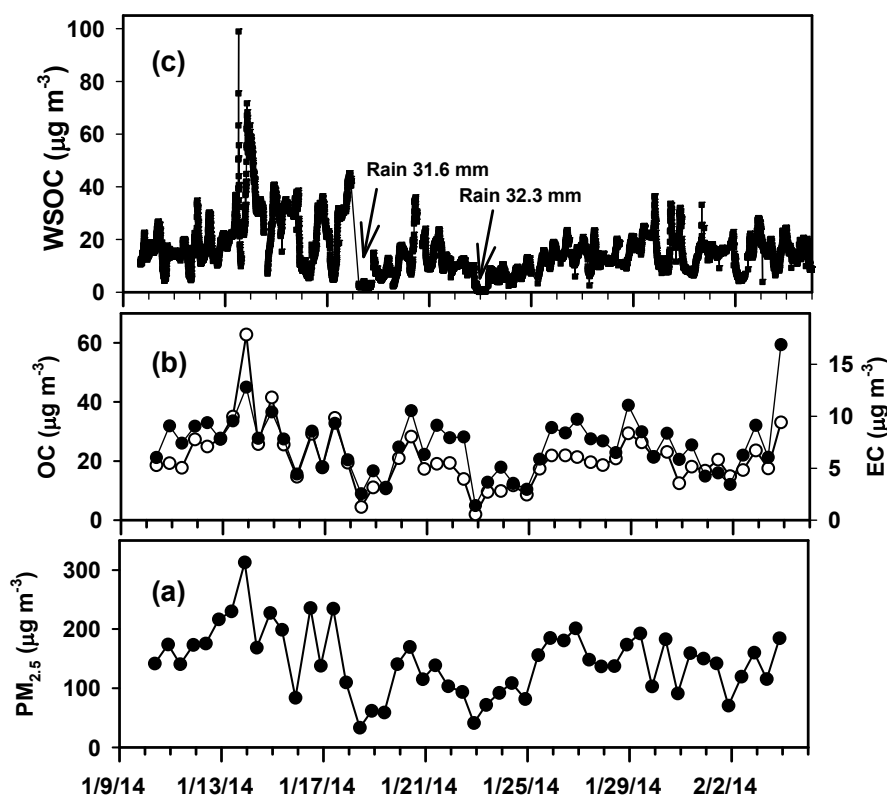
Fig. 2. Temporal variability in (a) filter based $PM_{2.5}$ mass, and (b) OC (open circle) and EC (closed circle), and (c) online WSOC concentrations during the study period.

to-day could be due to several factors such as variability in source (s), source (s) strength, meteorological conditions, and SOA formation. Here, it is important to mention that although WSOC is often considered as a measure of SOA, emissions from BB can also contribute primary WSOC (usually highly oxidized low volatile humic like substances (HULIS), Paglione *et al.*, ACP, 2014 and references therein). In addition to primary WSOC, BB also emits large quantity of VOCs that would lead to SOA formation (WSOC) i.e., emissions from BB can contribute both primary as well as secondary WSOC.

To investigate the major sources of carbonaceous aerosols (and precursors) over a study region, OC/EC and K^+/EC ratios are often used as a tracers in literature with the understanding that the higher OC/EC and K^+/EC ratios indicate the dominance of emissions from BB and lower ratios suggest prevalence of emissions from FFB (Andreae *et al.*, 1983; Wang *et al.*, 2005; Ram and Sarin, 2011). The observed OC/EC (range: 1.4 to 4.9; average: 2.9; sd: 0.7) and K^+/EC (range: 0.08 to 0.44; average: 0.28; sd: 0.06) ratios suggest that the contributions of emissions from both BB and FFB to carbonaceous aerosols were considerable, however, BB contributes relatively more than FFB during winter. The observed OC/EC and K^+/EC ratios also imply that the observed WSOC could be of both primary (from BB) and secondary origin (from both BB and FFB). The comparison of the diurnal variability in the concentrations of WSOC (can be both primary and/or secondary particles) and BC (essentially primary particles) suggests that a

considerable fraction of WSOC is secondary (Fig. 3). However, the question remains that what is the relative fraction of primary and secondary WSOC?

Presuming K^+ as a tracer for primary particles from BB emissions (as discussed earlier), the primary WSOC from BB, and secondary WSOC from any other source (s) such as fossil fuel burning, biogenic emissions etc. were estimated. Online WSOC was averaged over filter integration time for this purpose. Here, we have used a methodology for primary and secondary WSOC estimation using WSOC/K^+ ratio (range: 1.4 to 15.6; avg: 7.9, sd: 2.5), similar to that suggested by Lim and Turpin (2001) for the estimation of primary and secondary OC using OC/EC ratio. Similar methodology has been used in literature to assess the contribution of BB emissions to different chemical species (Feng *et al.*, 2012).

Primary WSOC i.e., $[WSOC]_{primary} = [K^+] \times (WSOC/K^+)_{minimum}$ (1)

Secondary WSOC i.e., $[WSOC]_{secondary} = [WSOC]_{total} - [WSOC]_{primary}$ (2)

Primary WSOC concentration varied from 0.30 to 8.0 $\mu g\ m^{-3}$ (avg: 2.7, sd: 1.2) and secondary WSOC ranged from 0.0 to 40 $\mu g\ m^{-3}$ (avg: 12.8, sd: 7.5). On average, primary WSOC was only ~20% whereas secondary WSOC dominated the total WSOC concentration with ~80% contribution, in spite of the fact that the emissions from BB
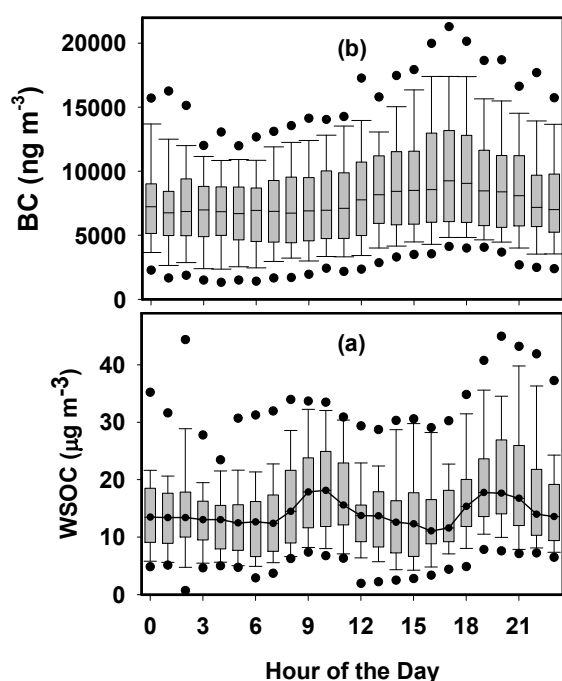
Fig. 3. Comparison of diurnal variability in (a) WSOC (can be both primary and secondary particle) and (b) BC (primary particle only) during the study period suggests that a considerable fraction of WSOC is secondary. Each bin of this whisker plot represents ~400 data points.

contributed relatively more than those from FFB to total carbonaceous aerosol abundance over the IGP during winter. The scatter plot between filter-based OC and online WSOC averaged over filter time (Fig. 4), with data points colored with respect to WSOC/K$^+$ ratio in corresponding sample, in a way presents secondary fraction of WSOC in the individual samples. Further, Figs. 2(b), 2(c) and Fig. 4 also indicate that the highest WSOC observed on Jan 13th and 14th were composed of both primary and secondary fractions.

Diurnal Variability in SOA Formation

The diurnal variability of WSOC in the atmosphere is expected to be driven by emission sources, physico-chemical transformations, transport and deposition processes (Sullivan *et al.*, 2004; Zhang *et al.*, 2012). There is no study from India and limited studies in the world which have documented diurnal trends of WSOC in ambient aerosols. Fig. 3(a) depicts the diurnal variability in WSOC (SOA) concentration over the study site during winter. The concentration levels and diurnal trends of WSOC were considerably different over Patiala than those documented by Zhang *et al.* (2012) over Los Angeles and Atlanta, and can be attributed to different sources, processes and meteorological conditions prevailing over corresponding sites. WSOC concentrations were more or less uniform (~13 µg m^{-3}) during late night/ early morning (22:00 to 5:00 hrs) and afternoon hours (13:00 to 17:00 hrs) whereas peaked with almost 1.5 times higher concentrations (~18 µg m^{-3}) during the morning (08:00 to 12:00) and late evening (18:00 to 22:00) hours. These peak hours of WSOC concentration corresponds to the time when

variety of local/regional sources such as wood and bio-fuel burning for cooking and other daily routine work, vehicular emissions etc are used at their maximum, suggesting them as major sources of the precursors of observed WSOC. There was a decrease in WSOC concentration during afternoon hours, which can be attributed to several factors such as increase in the mixing layer height (Fig. 5), and/or, there may be a volatile loss of semi-volatile WSOC as ambient air temperature increases to its maximum during afternoon hours. The effect of mixing layer height compression or expansion is expected to be experienced by all the particles present in the atmosphere, irrespective of their primary and/or secondary origin. Atmospheric WSOC can come from both primary and secondary sources, as discussed earlier, however, BC comes only from primary sources. It implicates that the diurnal variation in WSOC/BC ratio would minimize the effect of change in mixing layer height. Diurnal behavior of WSOC/BC suggests a significant SOA formation during 7:00 to 12:00 and 18:00 to 24:00 hrs. Decrease in WSOC/BC ratio during afternoon hours coincides with increasing temperature and decreasing RH (Fig. 5), indicating that a significant part of observed WSOC could be semi-volatile which remains in particulate phase under lower temperature/higher humidity conditions in the morning and evening hours, and lost to gas phase with increasing temperature during afternoon hours.

Further, the process of SOA formation during 08:00 to 12:00 hours is expectedly different (oxidation of VOCs by daytime oxidants such as OH, O$_3$) than that during 18:00 to 22:00 hours (oxidation of VOCs by nighttime oxidants like NO$_3$ radical). However, firm conclusions cannot be drawn on formation processes because direct measurements of various oxidants were missing in this study and suggested for future work.

Nevertheless, WSOC (or SOA) was always a significant contributor to ambient PM$_{2.5}$, as their concentrations vary in same fashion (Figs. 2(a) and 2(c)). A strong correlation between semi-continuously measured PM$_1$ and WSOC (R^2 = 0.83; slope = 0.113, intercept = 4.7, figure not shown) was also observed, which further suggests that SOA was a significant contributor to PM$_1$ over the IGP during winter. Interestingly, the slope observed over Patiala is similar to that documented over southeast USA (Zhang *et al.*, 2012), however, diurnal trends and WSOC concentration levels were considerably different over these sites, as discussed earlier.

CONCLUSIONS

The online measurements of WSOC along with BC, PM mass and meteorological parameters were performed over a site (Patiala: 30.2°N, 76.3°E, 249 m asl) located in the IGP during winter to understand the role of sources and meteorological conditions in SOA formation. In parallel, filter samples (n = 50) were also collected in day/night pair. The major conclusions of this study are:
- Filter-based PM$_{2.5}$ composition was dominated by ~31% water-soluble inorganic species (WSIS), 31% organic matter (OM), 5% elemental carbon (EC), while remaining fraction was unidentified.
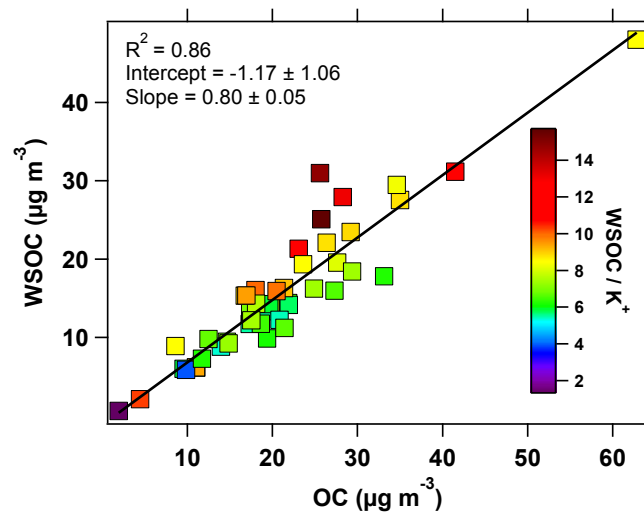
Fig. 4. Regression parameters of a strong linear relationship between filter-based OC and online WSOC averaged over filter integration time suggest that a considerable fraction of OC is secondary.
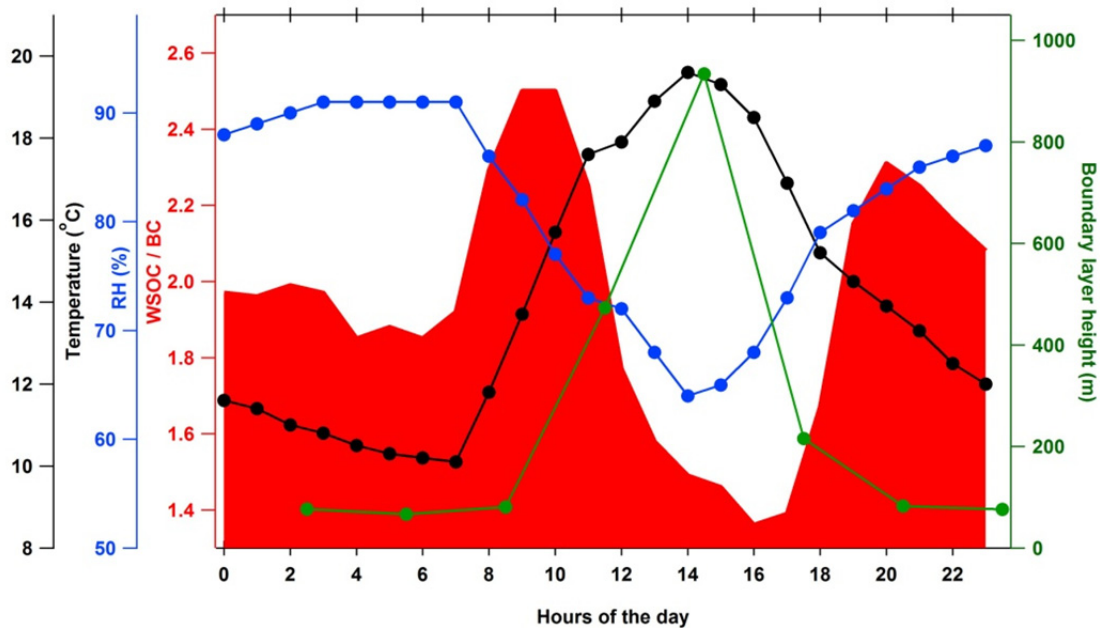

Fig. 5. Diurnal trends of WSOC/BC, ambient air temperature, relative humidity (RH) and boundary layer height at the study site during the study period.

- Temporal variability in online WSOC concentrations indicates that WSOC is largely produced by local/regional sources.
- The contribution of BB emissions to carbonaceous aerosols is relatively more than those from FFB, suggesting that the observed WSOC can be of both primary and secondary origin.
- On average, primary WSOC was only ~20% whereas secondary WSOC (or SOA) dominated the total WSOC concentration with ~80% contribution.
- Diurnal trends of online WSOC suggest considerable SOA formation during ~7:00 to 22:00 hrs when sources of SOA precursors are active. Afternoon decrease is attributed to volatile loss of SVOC compounds present in WSOC.

- Relationship between PM_1 and WSOC concentrations suggests that a significant fraction of fine particles is SOA over the IGP.

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