Aerosol Chemical Characterization and Contribution of Biomass Burning to Particulate Matter at a Residential Site in Islamabad, Pakistan

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ABSTRACT

Air pollution creates a very serious problem in developing countries, and scarce information is available about the nature of pollutants. This study describes the chemical composition of particulate matter (TSP and PM₁₀), including marker compounds pointing to pollution sources, and estimates the contribution of biomass smoke to organic carbon (OC) and particulate matter (PM) at a residential site in Islamabad during the winter period in December 2007. Levoglucosan and its relationship with other anhydrosaccharides were used to estimate the biomass burning contribution, and polyols and primary and secondary saccharides were investigated regarding biological aerosol. Polyols and primary saccharides contribute a small fraction of the total PM₁₀ and TSP mass, whereas anhydrosaccharides contribute more than 90% in both the PM₁₀ and TSP. A significant contribution from biomass smoke has also been found in Islamabad, forming 10% of the TSP and 18% of the PM₁₀ mass. The analysis of the distributions of saccharide concentrations between the TSP and PM₁₀ fractions shows that anhydrosaccharides, viz., levoglucosan, mannosan and galactosan, all of which are directly related to the combustion of biomass, are mainly present in the PM₁₀. The concentration of TSP varied from 218 $\mu\text{g m}^{-3}$ to 468 $\mu\text{g m}^{-3}$ (mean: 343 $\mu\text{g m}^{-3}$), and PM₁₀ concentrations were in the range of 89–304 $\mu\text{g m}^{-3}$ (mean: 194 $\mu\text{g m}^{-3}$). A good correlation was observed between PM₁₀, TSP and Ca²⁺, which implies that mineral/road dust may be a major contributor to the PM in Islamabad.

Keywords: Particulate matter; Urban air pollution; Biomass burning aerosol; Saccharides.

INTRODUCTION

Atmospheric pollution is increasing day by day all over world due to rapid urbanization, industrialization and environmental degradation especially in developing countries like Pakistan, India and China. High levels of pollutants which are not only damaging the cultural heritage but also very harmful to human health especially in urban areas, where these concentrations are so high that it's very difficult to breathe. Ghude *et al.* (2016) established association of premature mortality in India due to PM_{2.5} and ozone exposure while Chate *et al.* (2010) and Kaushar *et al.* (2013) assessed the population exposure to environmental pollutants during Commonwealth Games in India while Beig *et al.* (2013) examined the population exposure during Deepavali Festival in India. All these studies reported higher risk of human health due to air pollution. Atmospheric aerosol or particulate matter (PM) is chemically complex and a dynamic mixture

of solid and liquid particles. The major sources of these particles are combustion generated particles, sea salt spray, dust, vehicles exhaust, industrial stacks, construction activities, fossil fuel combustion and biomass burning (Dutkiewicz *et al.*, 2009). There are limited studies available regarding chemical nature of atmospheric aerosol in Pakistan region (Alam *et al.*, 2014; Bibi *et al.*, 2015; Shahid *et al.*, 2015a, b, 2016; Alvi *et al.*, 2018; Shahid *et al.*, 2018). There are limited data available like Stone *et al.* (2010) on chemical characterization and source apportionment of coarse particulate matter in Lahore; Kamal *et al.* (2015) has reported risk related to PAH during traditional cooking in Pakistan and Singh *et al.* (2017) has reported organic aerosol over Indo-Gangetic Plain and sources and climate implications. Ghauri *et al.* (2007) reported TSP and PM₁₀ level in different cities of Pakistan, the maximum particulate matter (TSP and PM₁₀) concentrations were observed at Lahore (996 $\mu\text{g m}^{-3}$ and 368 $\mu\text{g m}^{-3}$ respectively) followed by Quetta (778 $\mu\text{g m}^{-3}$, 298 $\mu\text{g m}^{-3}$) and in Karachi (410 $\mu\text{g m}^{-3}$, 302 $\mu\text{g m}^{-3}$).

There is limited information available on the comprehensive characterization of particulate matter in Islamabad. The heavy metals concentration and their sources in Islamabad atmosphere have been reported many

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times in previous studies (Parekh *et al.*, 2000; Shah *et al.*, 2004; Rajput *et al.*, 2005; Shah *et al.*, 2006, 2007, 2010). Parekh *et al.* (2001) reported TSP concentration at Islamabad and Karachi, at Islamabad daily TSP concentrations varied in the range of 428–998 $\mu\text{g m}^{-3}$ (mean: 691 $\mu\text{g m}^{-3}$); even at a relatively remote site of the city Saidpur TSP loading was high as 145–448 $\mu\text{g m}^{-3}$. Rajput *et al.* (2005) reported the TSP and elemental concentrations in the area around the industrial sector (I-9), TSP concentration was found to be double (279 $\mu\text{g m}^{-3}$) than in the sector F-7 (133 $\mu\text{g m}^{-3}$). Shah and Shaheen (2010) has reported seasonal behaviors in elemental composition of atmospheric aerosols collected in Islamabad, and found good correlation between TSP and metal in Islamabad atmosphere. Saddique *et al.* (2012) discussed the air quality in Islamabad using metal concentration by X-ray fluorescence spectrometry. The metal concentration was found less than from megacities of Pakistan, i.e., Karachi, Lahore, and Faisalabad. Qadir *et al.* (2012) reported evaluation of trace elemental composition of aerosols in the atmosphere of Rawalpindi and Islamabad using radio analytical methods. While A. Rasheed discussed the air quality of Islamabad by reporting concentrations of $\text{PM}_{2.5}$ and gaseous species and found that $\text{PM}_{2.5}$ and NO concentrations exceeded WHO limits. Bulbul *et al.* (2018) reported the PM_{10} concentrations and their structure morphology in Islamabad during winter fog period (December–March). Awais *et al.* (2018) assessed the aerosol optical properties using remote sensing over twin cities of Pakistan, i.e., Islamabad and Rawalpindi. There is exponential growth in vehicle population in city since 2007. However, introduction of new technologies and emission standard has reduced emission but their volume is still huge. Shah and Zeeshan (2016) reported estimation of light-duty vehicle emissions in Islamabad and climate co-benefits of improved emission standards implementation and observed that highest overall emissions (59%) were on arterials, followed by residential roads (24%) and highways (17%) with higher emissions during morning (8–10 a.m.) and evening (4–6 p.m.) rush hours.

All these studies over Islamabad has reported continuous degradation of air quality in the city, no study has given the comprehensive characterization of atmospheric aerosol and most of these studies are short-term. Unfortunately, no continuous air quality data is available for Pakistan cities and scientific studies are also short-term due to lack of facilities. This study is an attempt to characterize particulate matter, i.e., carbonaceous species, soluble ions, anhydrosugars and sugar alcohols in both TSP and PM_{10} size fraction at a residential site in Islamabad, Pakistan.

EXPERIMENTAL

Site Description

Islamabad is the capital of Pakistan and is situated at an elevation about 500 m above sea level (latitude: 33.7294°N and longitude: 73.0931°E) with a population of about two million and an area about 906 km². The climate is subtropical with four distinct seasons, summer (June–August), autumn (September–November), winter (December–February) and

spring (March–May). The average wind magnitude and wind vectors at 2 meter height, average over 2007 to 2017 has been shown in Fig. 1. The average annual rainfall is 1143 mm. The city is divided into residential, commercial, industrial and diplomatic zones; some of them are shown in the map of Islamabad (Fig. 2). The sampling was done in F-11 Sector Islamabad. This site is a residential area and away from commercial and traffic zone of the city. There are small villages close to sampling sites that mostly burn biomass for cooking and heating purposes. There is no industry and heavy traffic zone in proximity of the sampling site. The site location represented here in Fig. 2 is recent of 2018. In 2007 when the sampling was done the Sector E-11 (the upper left side in Figure) was not developed. In last 10 years there is increase in city population and lot of deforestation in lieu of housing societies and urbanization. The city is expanding in all directions and suburbs are now part of the city.

Sampling

Daily 24 hours' samples of TSP and PM_{10} were collected on Whatman filters using Thermo-Electron Cooperation high-volume sampler at flow rate of 1.018 $\text{m}^3 \text{min}^{-1}$ for TSP and 0.962 $\text{m}^3 \text{min}^{-1}$ for PM_{10} . Filters was pre-conditioned at 550°C and humidity room for 24 hours before and after sampling in order to avoid artefacts. Filters were weighed on site and store at 4°C. Twelve samples for TSP and PM_{10} , starting from 3 December 2007 to 16 December 2007 (no sampling on 8 and 15 December), were collected. After collection, these samples were stored in a freezer and transported to Vienna, Austria, by air luggage for analysis.

Experimental Methods

Carbonaceous Species

TC (total carbon) was determined by a combustion method, where all material on the filter is combusted in pure oxygen at 1000°C and the resulting CO_2 is measured by non-dispersive IR photometry (NDIR, Mairhak). The calibration procedure was done using tartaric acid dyed in aluminum foil. The elemental carbon (EC) was determined by a two-step combustion method described by Cachier *et al.* (1989). In the first step filters were heated for 2 hours at 340°C in an oxygen atmosphere to remove organic carbon (OC). In a subsequent second step (high-temperature step) filters was heated at 1000°C, in O_2 atmosphere, EC (and carbonate carbon, IC) is oxidized. CO_2 originating in this step is detected by an NDIR analyzer. The two major factors affecting the uncertainty of EC and OC measurements are the sampling artefacts related to OC, and the analytical challenge of separating EC from OC. Due to glass fiber filter samples thermal-optical methods were not used for EC measurement. Carbonate carbon (CC) was determined by two-step combustion method described by Jankowski *et al.* (2008). In first step filter samples was kept in an oven at 480°C in oxygen atmosphere and in second step filters are combusted at 1000°C and emitted CO_2 was determined by non-dispersive NDIR, resulting values are reported as CC. While the organic carbon was calculated using following relationship $\text{OC} = \text{TC} - \text{EC} - \text{CC}$.

Fig. 1. Wind Magnitude and Wind vectors at 2 meter height, average over 2007 to 2017 (Merra 2 satellite data).

Fig. 2. Sampling site in Islamabad (This figure is taken from openstreetmap.org).

Saccharides

The determination of saccharides was performed with an improved high-performance anion-exchange chromatography with pulsed amperometric detection (HP AEC-PAD) according to method described by Iinuma *et al.* (2009). The method uses NaOH gradient (480–650 mM) which allows a good separation of levoglucosan and arabitol, both relevant constituents of atmospheric aerosols in Pakistan (Shahid *et al.*, 2016). Circular filter aliquots (1.6 cm²) were extracted with 3 mL of ultra-pure water (Milli-Q, Milipore, 18.2 MΩ) under ultrasonic agitation for 30 min. The extracts were centrifuged and filtered through PET syringe filters (0.45 μm, Chromafil, Macherey-Nagel) to remove insoluble material. Analytical procedure was carried out using Dionex ICS-3000 system consisting of a gradient pump, Carbopac MA1 column and electrochemical detector with working gold electrode. For quantification, an external calibration based upon mixed standards prepared from frozen 1000 ppm stock solutions (self-prepared once a year by weighing of pure solids supplied by Fluka or Sigma-Aldrich) was used. Five mixed standard solutions containing xylitol, levoglucosan, arabitol, mannosan, trehalose (mycose), mannitol, galactosan, glucose, galactose, fructose and sucrose in the concentration range of 0.05–10 ppm were prepared each week and were stored aliquoted in a freezer. A five-point calibration curve was run at the beginning and end of each measurement sequence to assure the accuracy of calibration with relation to measurement conditions. Blank filters were prepared in the same way as samples and measured to correct the possible contaminations related to extraction or to filter material itself, as glass fibers are known to contain relatively high amount of adsorbed organic carbon.

The detection limits (calculated as threefold standard deviation of multiple analysis of the lowest standard) were at 0.008 μg m⁻³ for arabitol and levoglucosan and 0.003 μg m⁻³ for the other determined saccharides. The method uncertainty based upon multiple analyses of distinctly extracted samples is 9%. All measured blanks were free of saccharides chosen for determination (mostly no visible peaks at all or if observed then under the detection limit).

Inorganic Ions

Anions (Cl⁻, NO₃⁻, SO₄²⁻) were eluted from glass fiber filter aliquots by washing with high-purity water (Millipore Milli-Q plus 185). After sonicating and centrifuging, the extract was analyzed on an AS12A anion-exchange column, with an ASRS Ultra II auto-regenerating suppressor, and a model CD20 conductivity cell detector (the whole system from Dionex). Cations (Na⁺, K⁺, NH₄⁺, Mg²⁺ and Ca²⁺) were eluted with 0.1% v v⁻¹ methane sulphonic acid, which is the chromatography eluent. After sonication and centrifugation, the extract was analyzed by isocratic ion chromatography: a system consisting of CS12A cation-exchange column, self-regenerating CSRS suppressor and a conductivity detector (Dionex, ICS3000). Blanks prepared in the same method as samples were measured and all results were corrected by blank values. Quantification was done based upon external standards measured along with the samples. For

ions, all blanks were either in the same order of magnitude as the detection limit only Cl⁻ was a bit higher (5 times) and Na⁺ was 10 times higher, which is a typical observation for this kind of filter material. The detection limits were 0.03 μg m⁻³ for chloride and sodium and 0.007 μg m⁻³ for other ions. The method uncertainty based upon multiple analyses of distinctly extracted samples is 12%. Quality assurance comprised reference solution measurements (Thermo Scientific) and regular ring measurements (World Meteorological Organization).

RESULT AND DISCUSSION

PM₁₀ and TSP Concentrations and Main Aerosol Components

The average concentration of PM₁₀ and TSP for measured within the study period was 194 ± 60 μg m⁻³ and 343 ± 87.8 μg m⁻³ which are comparable with other cities of the region like TSP in Delhi is 416.34 ± 223 μg m⁻³ (Khillare *et al.*, 2004). Sandilya *et al.* (2007) have reported higher TSP for Delhi, i.e., 687 ± 117.4 μg m⁻³ and PM₁₀ in Delhi 268 ± 39 μg m⁻³. Bhaskar and Mehta have reported PM₁₀ concentrations in Ahmadabad, India, ranging from 17–327 μg m⁻³ respectively. The PM₁₀ makes about 50–60% of the TSP. The difference between TSP and PM₁₀ varies from 78 μg m⁻³ to 196 μg m⁻³ with an average of 148 μg m⁻³. The main constituent of the coarse (TSP-PM₁₀) fraction is water-soluble calcium. Ca²⁺ concentrations in TSP is 42.6 μg m⁻³ of which 50% contributes to the coarse fraction. A good correlation between water-soluble calcium in TSP and PM₁₀ with $r^2 = 0.94$ and $r^2 = 0.83$ respectively as shown in Fig. 3 indicates the mineral dust is major contributor to both PM₁₀ and TSP fractions in Islamabad.

Total carbonaceous fraction (EC, OC and CC) was the main contributor to PM₁₀ mass and no significant difference was found between total carbon concentration in TSP and PM₁₀ (63.2 μg m⁻³ and 60.2 μg m⁻³). The average EC concentrations were 17.8 μg m⁻³ for TSP and 16.5 μg m⁻³ for PM₁₀ which is given in Table 1. EC concentration were not reported for Islamabad before, however, compared to other cities, e.g., Karachi, Lahore, Mumbai, Allahabad, Ahmedabad, Dhaka, Hangzhou and Beijing. The concentrations are comparable even if artefacts in the range of 10% resulting from the thermal EC determination method are considered. EC was used as tracer for traffic emissions (Turpin and Huntzicker, 1995; Salma *et al.*, 2004). Some studies have reported higher EC and BC concentrations in South Asian cities, e.g., for Dhaka OC and BC varied from 5–96 μg m⁻³ and 4–48 μg m⁻³ respectively (Begum *et al.*, 2012) while average OC and BC concentration reported by Salam *et al.* (2003) was 45.9 μg m⁻³ and 22.0 μg m⁻³ respectively. High EC shares in Islamabad in this study (30% of the total carbon fraction) can be related to the significant influence of traffic, including two-stroke vehicles and diesel engines. Such situation was also shown previously for another Pakistani city, Lahore (Zhang *et al.*, 2008b). The correlation between EC and nitrate ions (Table S1) underlines that a large part of EC may be related to the regional traffic and fossil fuel combustion and biomass

Fig. 3. Linear regression plot between PM₁₀ and TSP with water soluble Ca⁺⁺.

burning are significant sources of EC, which is alike given by the correlation with suitable tracers: K⁺, levoglucosan and Cl⁻. The OC concentration at Islamabad was 38 µg m⁻³ and 40 µg m⁻³ for TSP and PM₁₀ respectively.

Also, the ratio OC/EC can also be used as an indicator for sources of carbonaceous species (Schauer et al., 1999; Andreae et al., 2001; Schauer et al., 2001; Sudheer et al., 2008; Sandradewi et al., 2008; Rastogi et al., 2009; Ram et al., 2010). Low OC/EC ratio (1–4.2) indicates fresh aerosols, like the diesel and gasoline exhaust influences (Schauer et al., 1999, 2001) while for biomass burning a OC/EC = 7.7 has been reported by Zhang et al. (2007) and very high OC/EC ratio greater than 14 have been reported for forest fire, where also a large impact of secondary organic aerosol formation is expected (Gray et al., 1986; Turpin et al., 1990; Hidemann et al., 1991; Chow et al., 1996).

In the present study, OC/EC ratio varies from 2.2 to 3.3 with an average of 2.5 for PM₁₀ and 2.1 for TSP. This implies that fresh combustion aerosol, e.g., diesel and gasoline exhaust, as indicated by high EC concentrations itself is an important source of PM at Islamabad. A strong correlation between EC and OC in both fractions with $r^2 = 0.94$ for PM₁₀ and $r^2 = 0.84$ for TSP has been observed which indicates that they have common sources. The OC/EC ratio in Islamabad is comparable with other cities of region like Mumbai (India) and Dhaka, Bangladesh (Salam et al., 2003), while it lower than in Ahmedabad, India (Rastogi et al., 2009), where biomass combustion is found to be major source of carbonaceous species.

Water Soluble Ions

Water soluble inorganic ions: calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), ammonium (NH₄⁺), potassium (K⁺), sulphate (SO₄²⁻), nitrate (NO₃⁻), and chloride (Cl⁻) were found in atmospheric aerosol samples collected in Islamabad during winter period. The average concentrations of soluble

ions are given in Table 1. The Ca²⁺, SO₄²⁻ and NO₃⁻ concentrations were found major quantity in Islamabad. The Ca²⁺ concentration in Islamabad varied from 8–32 µg m⁻³ with an average of 22 µg m⁻³ for PM₁₀ and for TSP it varied from 21–66 µg m⁻³ with an average of 42 µg m⁻³. The high Ca²⁺ concentration has also been reported by Shahid et al. (2016) in Karachi and Ghude et al. (2017) in Delhi. The contribution of Ca²⁺ to total PM mass was 12.5% in Islamabad while Ghude et al. (2017) reported Ca²⁺ contribution to PM was 14%. Thus, high Ca²⁺ concentration in Islamabad is not an anomaly. Khawaja et al. (2009) also reported a strong correlation between TSP, PM₁₀ and Ca²⁺ indicated mineral dust contributions. The average concentration of the secondary inorganic constituents NH₄⁺, NO₃⁻ and SO₄²⁻ were 1.3 µg m⁻³, 12 µg m⁻³ and 7.8 µg m⁻³ respectively for TSP and 1.3 µg m⁻³, 11 µg m⁻³ and 6.7 µg m⁻³ for PM₁₀. NO₃⁻ was correlating with ammonium, as well with elemental carbon and the concentrations of nitrate are comparable with Hangzhou (China) and Beijing (China) but higher, if compared to Mumbai (India), Ahmedabad (India), Allahabad (India) and Dhaka (Bangladesh). The SO₄²⁻ concentrations in Islamabad were found to be comparable with concentration in Mumbai but less than other Asian cities like Dhaka, Beijing, Hangzhou and Karachi. The SO₄²⁻ has only correlation with NH₄⁺ indicating that it can be present as ammonium sulphate and thus should be rather seen as component of trans-regional pollution transport, formed with ammonia resulting from agricultural activities outside the city (Rastogi et al., 2009). Cl⁻/Na⁺ ratio of 1.8 has been reported for sea water, while at Islamabad Cl⁻/Na⁺ was 0.6–0.73 in TSP and PM₁₀ indicating the Cl⁻ depletion during long-range transport. The comparison between the sum of cations and anions in equivalent values have been shown in Fig. 4, a linear relationship is present if carbonates, calculated out of CC are added to anions.

Table 1. Concentrations of carbonaceous species, ions, sugars ($\mu\text{g m}^{-3}$).

Component	Pakistan				India			Bangladesh		China	
	Islamabad ^a	Lahore ^b	Karachi ^c	Mumbai ^d	Allahabad ^e	Ahmedabad ^f	Dhaka ^g	Hangzhou ^h	Beijing ⁱ		
	TSP	PM ₁₀	TSP-PM ₁₀	PM ₁₀	TSP	TSP	TSP	PM ₁₀	PM ₁₀		
PM	343.5 ± 87.8	194.5 ± 60	149	128	300	156	n.d	157	154		
TC	63.2 ± 17.8	60.2 ± 17.2	3	39.1	n.d	n.d	67.8	n.d	26.9		
EC	17.8 ± 4.9	16.5 ± 5.4	1.3	12.6	6.2	2.1	22	4.43	6.6		
CC	9.1 ± 3.6	3.4 ± 1.8	5.7	1.2	n.d	1.5	n.d	n.d	n.d		
OC	37.9 ± 10.5	40.2 ± 0.4	--	25.3	49	12.8	45.7	23.8	20.4		
Na ⁺	4.4 ± 0.4	4.8 ± 0.4	--	2.2	n.d	n.d	1.3	n.d	n.d		
NH ₄ ⁺	1.3 ± 0.7	1.26 ± 0.8	--	n.d	n.d	n.d	1.8	9.3	6.67		
K ⁺	2.5 ± 0.5	2.6 ± 0.6	--	8.9	n.d	n.d	1.5	n.d	n.d		
Mg ⁺	0.8 ± 0.3	0.45 ± 0.2	0.39	2.2	n.d	n.d	0.41	n.d	n.d		
Ca ²⁺	42.6 ± 15.4	22.4 ± 7.6	20.2	6.2	n.d	n.d	6.8	n.d	9.78		
Cl ⁻	3.2 ± 0.8	2.9 ± 0.7	0.3	2.6	n.d	n.d	2	1.8	n.d		
NO ₃ ⁻	11.9 ± 5.9	11 ± 5.3	0.9	6	n.d	1.43	3.6	11.2	10.8		
SO ₄ ²⁻	7.8 ± 2	6.7 ± 2.1	1.1	6.2	n.d	4.35	11.3	21.6	30.8		
Levogluconan	1.7 ± 0.5	1.7 ± 0.5	--	n.d	n.d	n.d	n.d	n.d	n.d		
Mannosan	0.19 ± 0.1	0.19 ± 0.7	--	n.d	n.d	n.d	n.d	n.d	n.d		
OC/EC	2.2	2.4	--	0.5	8.1	8.3	2.1	5.4	3		

n.d implies not determined, ^a This study, ^b Stone et al., 2007, ^c Shahid et al., 2016, ^d Venkatraman et al., 2002, ^e Ram et al., 2010, ^f Rastogi et al., 2009, ^g Salam et al., 2003, ^h Cao et al., 2009, ⁱ Duan et al., 2003, 2005.

Fig. 4. Correlation between sum of cations and anions.

Size Distribution and Relations between Determined Saccharides

Total concentrations of analyzed saccharides account to $2.2 \mu\text{g m}^{-3}$ for TSP and $2.1 \mu\text{g m}^{-3}$ for PM₁₀, which makes around 1% of the total particulate matter (TSP and PM₁₀). Although saccharides are not a main mass contributor the wide spread of those compounds in the living and burned biomass enhances their relevance in terms of source attribution or particles.

The analysis of the distributions of saccharide concentrations between the TSP and PM₁₀ fractions shows that anhydrosaccharides, i.e., levoglucosan, mannosan and galactosan, all directly related to combustion of biomass are present mainly in PM₁₀, which is in line with expectations for the combustion aerosol sizes (Hosseini *et al.*, 2010). The coarse fraction of saccharides consists of a small share of polyols, as well as primary and secondary saccharides as shown in Fig. 5.

Average levoglucosan concentrations were the same in both fractions ($1.70 \mu\text{g m}^{-3}$) and contribute with 78% and 83% to total saccharides in TSP and PM₁₀ respectively. The concentrations of levoglucosan in atmosphere varied from $0.79 \mu\text{g m}^{-3}$ to $2.58 \mu\text{g m}^{-3}$ during the whole study period, whereas the relation to PM₁₀ was in stable range of 0.8–1% in all samples. Levoglucosan showed a strong correlation with mannosan and galactosan, both related to PM₁₀ fraction only (Fig. 6). Their concentrations are respectively one or two orders of magnitude lower than those of levoglucosan, but still higher than the concentration of other determined sugars. Average levoglucosan to mannosan ratio in PM₁₀ was 10, which is lower than reported for burning of typical Pakistani wood species (20) and typical Asian biomass types (> 30), but rather in the range of European residential hardwood burning (Shahid *et al.*, 2015, and references therein). On the other hand, the ratio of levoglucosan to galactosan of 24 is perfectly in line with what was reported for Asian biomass and most probably this anhydrosaccharidic patterns must be explained

by co-firing of wood and other biomass types (e.g., leaves, grasses).

Further components, which were related merely to PM₁₀ were xylitol and glucose. The average concentrations of those compounds in PM₁₀ were much lower than those of anhydrosugars: $0.01 \mu\text{g m}^{-3}$ for xylitol and $0.03 \mu\text{g m}^{-3}$ for glucose. Both compounds showed a strong correlation with levoglucosan with slopes (ratio of each compound to levoglucosan) 0.004 and 0.014 for xylitol and glucose respectively. This suggests that both sugars originate from biomass combustion but are respectively 60 and 200 times lower concentrated. Both xylitol and glucose are mainly associated with living biomass, e.g., fungal spores and soil biota, but were reported alike as minor constituents of biomass smoke (Caseiro *et al.*, 2007). The previously proposed co-firing of different biomass types, also wet, non-seasoned wood or green wastes can explain the correlation of xylitol and glucose with levoglucosan in the aerosols from Islamabad. Furthermore, anthropogenic open fires or simple fireplaces placed in the backyards of houses in which firing is linked to the resuspension of soil dust, as it was reported for wildfires (Pio *et al.*, 2008; Ma *et al.*, 2009) are not atypical as well.

Arabitol, mannitol and trehalose were spread among both fractions, whereas on average 77–79% of arabitol and mannitol contributed to PM₁₀ with variations among single samples reaching 25%. PM₁₀ fractions of both polyols correlated well with levoglucosan, which points to impact from burning of moldy biomass, as arabitol and mannitol are common fungal spore tracers (Bauer *et al.*, 2008). Trehalose was in 36% related to PM₁₀ but the contribution varies considerably on different days. Further secondary saccharide, sucrose, was detected only in TSP fraction.

Trehalose was proposed as tracers for soil dust (Simoneit *et al.*, 2004). Also sucrose can be expected in natural soil dust, as significant amount of those secondary saccharides are present in plant debris, which form soils. In the present study, it was observed that only trehalose correlates with

Fig. 5. Share of different saccharide groups in the total saccharide mass in TSP and PM₁₀ fractions.

Fig. 6. Correlation between levoglucosan (Lev) and other saccharides detected in the ambient aerosols in Islamabad.

levoglucosan, as expected for prescribed- or open fires. This correlation is driven by concentrations in coarse particles and disappears in PM₁₀ (Fig. 6). Sucrose shows absolutely no correlation with levoglucosan, which points to another source than combustion of biomass and related soil dust

resuspension. Most probably it depicts a presence of larger biological particles, i.e., fragments of plants or insects in the atmosphere. Along with TSP-related fraction of arabinol and mannitol, sucrose is not expected to have a long-standing impact on atmospheric aerosols. The occurrence of those

sugars in TSP has most probably a local and periodic character and thus shows no distinct relations with other measured TSP constituents. However, also large biological particles in the atmosphere should not be neglected in the discussions, because they can be relevant allergenic factor with high short-time impact.

Galactosan and fructose were either not detected in the samples or were under the detection limits, which points to the fact that non-intensive vegetation influence can be expected in Islamabad during winter period.

Until now saccharide concentrations were not discussed in relation to the region of Islamabad. The measurements done within the study in Karachi during pre-monsoon period (Shahid *et al.*, 2016) showed much lower levoglucosan concentrations ($0.21 \mu\text{g m}^{-3}$) by higher total PM_{10} levels. Regarding the discrepancies in climate conditions it can be expected that this contribution is related to cooking stoves used in the residential kitchens and the enrichment seen during winter in Islamabad can be attributed mainly to heating purposes. Recent measurements reported for Nepal (Wan *et al.*, 2017) showed very similar distributions of anhydrosugars during the seasons with levoglucosan concentration of $1.16 \mu\text{g m}^{-3}$ during wintertime and $0.77 \mu\text{g m}^{-3}$ during pre-monsoon season. Also the ratios between anhydrosaccharides were in the similar range as those reported here and in previous work conducted in Karachi, which shows that a certain stability of biomass burning constituents can be assumed in the large region of Indo-Gangetic Plain in the line from north until the coastal zones.

Contribution of Biomass Smoke to Ambient Aerosol

Levoglucosan and mannosan were shown to be the main saccharides in the aerosols from Islamabad, which points to significant contribution of biomass burning to particulate matter, specifically to its PM_{10} fraction. The levoglucosan has been used as a tracer for biomass burning (Wang *et al.*, 2007; Lanz *et al.*, 2008; Schmidl *et al.*, 2008; Caseiro *et al.*, 2009; Shahid *et al.*, 2015; Shahid *et al.*, 2016; Wan *et al.*, 2017). Also further components can be seen as indications of biomass burning. Among here analyzed components the water-soluble potassium (K^+) poses an alternative (e.g., Duan *et al.*, 2004). K^+ was similarly to levoglucosan found mainly in the PM_{10} fraction and showed a good correlation with levoglucosan if TSP concentrations are considered (Table S1). Nevertheless, K^+ is less unique than levoglucosan as wood burning marker and since it was reported also as constituent of soil dust and sea spray (Pachon *et al.*, 2013) it might be burdened with high uncertainty as tracer for biomass burning. In order to calculate contribution of biomass smoke to ambient aerosol a simplified method has been used, i.e., by using a source specific tracer and OC concentrations (Zhang *et al.*, 2008a; Zhang *et al.*, 2010). The emission factors of levoglucosan, expressed as a fraction of OC on carbon/carbon basis $\mu\text{gC} (\mu\text{gC})^{-1}$, from previous biomass studies in Asia and USA are given in Table S2. For commonly used South Asian biofuels, such as rice straw, dried cow dung patties, leaves and briquettes, an average emission factor of $12.6 [0.079 \mu\text{g levoglucosan} (\mu\text{g OC})^{-1}]$ has been reported (Sheesley *et al.*, 2003). Sullivan *et al.*

(2008) reported approximately the same emission factor in a chamber studies in Taiwan and USA. While in China an average emission factor of 3.7% has been reported in a chamber experiment for burning of rice straw (Zhang *et al.*, 2007). In a recent study Zhang *et al.* (2010) have used an average emission factor 3.6% [$0.080 \mu\text{g levoglucosan} (\mu\text{g OC})^{-1}$] to calculate the contribution of biomass to OC in China. Higher emission factor has been reported in fireplace experiments for hard wood and soft wood by Fine *et al.* (2001, 2002) in USA. All these values are given in Table 2. In this study contribution of biomass burning (BB) to OC and PM have been calculated using the factors elaborated previously for Karachi (Shahid *et al.*, 2016), as these are based upon a robust average build for burning of mixed biomass fuels.

$$\text{BB-EC} = \text{Levoglucosan} \times 2.7 \quad (1)$$

$$\text{BB-OC} = \text{Levoglucosan} \times 10.2$$

$$\text{BB-PM} = \text{Levoglucosan} \times 20 \quad (2)$$

These relationships have been derived from South Asian biomass source studies comprised in the Table S2. Emission ratios in relation to levoglucosan were calculated for a 53/47% mix of wood and other biomass using wood smoke data from Shahid *et al.* (2015) and biomass emission data from Sheesley *et al.* (2003) (Sy) and Zhang *et al.* (2007) (Z), resulting factors indicated as “Mix” in Table S2. Mix (Sd/Sy) is calculated for using other biomass data from Sheesley *et al.* (2003); Mix (Sd/Z) uses Zhang *et al.* (2007) data.

The shares of levoglucosan in OC has been reported in the literature are comprised in Table S2. Calculation of biomass burning contribution is burdened with certain uncertainty, which is primarily related to data used for calculation. As a wide variety of biofuels is used and biomass combustion in Asia seem to have an inter-regional character, e.g., as reported for Indo-Gangetic Plain (Wan *et al.*, 2017), constructing of average values from possibly high number of source studies and regional reports may keep the uncertainty within a limit of a few percent and seem more adequate than strict selection of locally used fuels.

The calculated relative contributions from biomass burning to EC, OC and particulate matter PM_{10} and TSP have been given in Table 3. Significant contribution of biomass burning (BB) to OC and PM has been found in both PM_{10} and TSP in Islamabad. In PM_{10} , BB-OC contribution to average OC was found in the range from 20–60% with an average of 44% while for BB-PM contribution to average PM_{10} mass was found in the range from 8–27% with an average of 18%. For TSP the BB contribution to the total mass was smaller (10% in average), but nearly the same for organic carbon, which underlines the fact that both biomass burning aerosols and organic aerosols are mainly consisting of particles with low aerodynamic diameters.

Biomass burning related elemental carbon made on average 26% of PM_{10} related EC, which points that previously mentioned traffic is a stronger EC contributor. The BB-EC might be however underestimated, as also after subtraction of BB-EC from the total EC still a good

Table 2. Ratios of levoglucosan (Lev) to organic carbon (Lev/OC) from different combustion studies and averages used in calculation of biomass burning contribution in Asian ambient studies.

Biomass type	Experiment type	Source location (measured PM type)	Emission factor Avg Lev/OC	Referenc
Hardwood (Pakistan)	Open Burning	Pakistan	11.4 %	Shahid <i>et al.</i> , 2015
Cereal straw	Dilution Chamber	China (PM _{2.5})	8.2%	Zhang <i>et al.</i> , 2007
Rice straw, cowdung, briquettes, leaves and jackfruit branches	Wood stove	South Asia (PM _{2.5})	7.9%	Sheesley <i>et al.</i> , 2003
Rice straw	Chamber	Taiwan (PM _{2.5})	3.5%	Sullivan <i>et al.</i> , 2008
Branches, grasses, duffs, needles, straw, leaves	Chamber or stack	USA (PM _{2.5})	3.1%	Sullivan <i>et al.</i> , 2008
Residential and agricultural sources	Fireplace	USA (PM _{2.5})	1.9%	Mazzoleni <i>et al.</i> , 2007
Wildland fuels	Controlled room	USA (PM _{2.5})	5.5%	Mazzoleni <i>et al.</i> , 2007
Hardwood	Fireplace	USA (PM _{2.5})	6.4%	Fine <i>et al.</i> , 2001, 2002, 2004
Softwood	Fireplace	USA (PM _{2.5})	4.0%	Fine <i>et al.</i> , 2001, 2002, 2004
Spruce, beach, briquettes	Wood stove	Austria PM ₁₀	5.5%	Schmidl <i>et al.</i> , 2008
Asian Biomass	Literature average	Lumbini, Nepal, Northern Indo-Gangetic Plain	8.1%	Wan <i>et al.</i> , 2017
Asian Biomass	Literature average	Pakistan, Karachi and Islamabad	9.8%	This study

linear relation between EC and levoglucosan is observed. If underestimation is a case it would point to the fact that residential biomass combustion in Islamabad is conducted in higher percentage with wood than with other biomass types (Shahid *et al.*, 2015).

Identified Particle Sources/Types and their Contribution to PM₁₀ and TSP

Mass closure of PM₁₀ and TSP has been given in Fig. 7 that indicates that organic matter and calcareous substances contributes a large fraction followed by soluble ions in both PM₁₀ and TSP. OM contributes 18% in TSP and 34% in PM₁₀ while carbonates 31% and 28% in TSP and PM₁₀ respectively. Shahid *et al.* (2016) has reported contribution of OM to PM₁₀ as 34.9% and carbonates 68% in Karachi. The unidentified portion in PM₁₀ is less than 2% as mineral dust and crustal elements are considered to be part of the calcareous substances while for TSP unidentified components are 24% that might be crustal matter OR mineral dust as trace metals like Al are missing.

Biomass burning (BB) also contributes to OC in Islamabad and its contribution to OC mass both in TSP and PM₁₀ has been given in Fig. 8. BB contribution is 45% of OC-TSP mass and 44% of OC-PM₁₀ mass. Anhydrosugars including levoglucosan and mannosan contributes to 5% and 6% respectively to OC-PM₁₀ and OC-TSP respectively. Thus, major fraction of organic carbon comes from biomass burning.

CONCLUSION

The PM₁₀, TSP mass, water-soluble ionic species, anhydrosugars, sugar alcohols and carbonaceous fractions were measured in atmospheric aerosol samples collected during wintertime at a residential site in Islamabad. The particulate matter concentrations were found to be very high for both PM₁₀ and TSP, exceeding WHO guidelines (150 µg m⁻³ for Target I, 100 µg m⁻³ for Target II and 75 µg m⁻³ for Target III). During the study period of 12 days, PM₁₀ concentrations exceeded the WHO Target I limit on 9 days, the Target II limit on 11 days and the Target III limit on all days. The mass closure of PM₁₀ and TSP indicates that CaCO₃ contributes 28% and 31%, respectively. OM contributes the largest share of the PM₁₀ mass (34%) but only 18% of the TSP. The mass closure of OC in both these fractions indicates about a 45% contribution from biomass to OC in the PM₁₀ and TSP. EC forms 5% of the TSP and 8% of the PM₁₀ mass in Islamabad. Biomass smoke, which may originate in residential heating and cooking in the vicinity of the city, forms a major fraction of the organic carbon.

It is evident from the above results that OM, soluble ions and calcareous species are the main components in PM₁₀, while calcareous species, followed by soluble ions and OM, contribute the largest fraction in TSP. However, in order to develop mitigation strategies, comprehensive long-term measurements are required for assessing the source of these pollutants.

Table 3. PM, OC, Levoglucosan concentrations and contribution of biomass burning (BB) to PM and carbonaceous fraction in Islamabad.

	TSP			PM ₁₀		
	Min	Max	Average	Min	Max	Average
PM ($\mu\text{g m}^{-3}$)	219	468	343	90	305	194
OC ($\mu\text{g m}^{-3}$)	28	57	38	20	56	40
EC ($\mu\text{g m}^{-3}$)	12	26	18	6	24	16
Levoglucosan ($\mu\text{g m}^{-3}$)	1.0	2.7	1.7	0.8	2.6	1.7
BB-EC ($\mu\text{g m}^{-3}$)	2.8	7.5	4.6	2.1	7.0	4.6
BB-OC ($\mu\text{g m}^{-3}$)	11	29	17	8.0	26	18
BB-PM ($\mu\text{g m}^{-3}$)	21	56	34	16	52	34
Contribution of BB-EC to average EC (%)	16	42	26	13	42	28
Contribution of BB-OC to average OC (%)	28	75	45	20	66	44
Contribution of BB to average PM (%)	6	16	10	8	27	18
Contribution of BB to PM (%) Karachi, Pakistan, pre-monsoon (Shahid <i>et al.</i> , 2016)	-	-	-	0.41	1.8	0.96
Contribution of BB to PM (%) Lumbini, Nepal, winter (Wan <i>et al.</i> , 2017)	0.01	1.3	0.47	-	-	-

Fig. 7. Mass closure of PM₁₀ and TSP. **Fig. 8.** Mass closure of organic carbon in PM₁₀ and TSP.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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