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 poses 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 winter period in December 2007. Levoglucosan and its relationship with further anhnydrosaccharides were used for estimating of biomass burning contribution while polyols, primary and secondary saccharides were discussed regarding biological aerosol. Polyols and primary saccharides makes small contribution toward total PM10 and TSP mass while anyhrosaccharides contributes more than 90% in both PM10 and TSP. Significant contribution of biomass smoke has been found in Islamabad and it makes 10% of TSP and 18 % of the PM10 mass. The analysis of the distributions of saccharide concentrations between the TSP and PM10 fractions shows that anhydrosaccharides i.e. levoglucosan, mannosan and glactosan, all directly related to combustion of biomass are present mainly in PM10. The concentration of TSP varied from 218 µg m$^{-3}$ to 468 µg m$^{-3}$ (mean 343 µg m$^{-3}$) and for PM10 concentrations were in the range of 89 – 304 µg m$^{-3}$ (mean 194 µg m$^{-3}$). A good correlation was observed between PM10, TSP and Ca$^{2+}$ which implies that mineral / road dust may be major contributor to PM in Islamabad.

Key Words: Particulate matter, urban air pollution, biomass burning aerosol, saccharides

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1 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 breath. Ghude et al., (2016) established association of Premature mortality in India due to PM2.5 and ozone exposure while Chatte et al., (2010) assessed the population exposure to environmental pollutants during common wealth games in India while Beig et al., (2013) examined the population exposure during Deepawali 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 (Bibi H et al., 2015; M. Z. Shahid et al., (2015a, 2015b), Alam K et. al., 2014; Shahid et al., 2015; 2016; 2017a, 2017b). 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 plains and sources and climate implications. Ghauri et al 2007, reported TSP and PM$_{10}$ level in different cities of Pakistan, the maximum particulate matter (TSP and PM$_{10}$) concentrations were observed at Lahore (996 µg m$^{-3}$ and 368 µg m$^{-3}$ respectively) followed by Quetta (778 µg m$^{-3}$, 298 µg m$^{-3}$) and in Karachi (410 µg/m$^3$, 302 µg/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 time in previous studies (Shah M.H. et al., (2004; 2006; 2007; 2010; Parekh et al., 2000; Rajput et al., 2005). Parekh et al., (2000), reported TSP concentration at Islamabad and Karachi, at Islamabad daily TSP concentrations varied in the range of 428 µg m$^{-3}$ – 998 µg m$^{-3}$ (mean 691 µg m$^{-3}$) even at a relatively remote site of the city Saidpur TSP loading was high as 145µg m$^{-3}$ - 448 µg 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 µg m$^{-3}$) than in the sector F-7 (133 µg m$^{-3}$). M. H. Shah & N. 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. N. 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 mega cities of Pakistan i.e. Karachi, Lahore, and Faisalabad. M.A. 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 PM$_{2.5}$ and gaseous species and found that PM$_{2.5}$ and NO concentrations exceeded WHO limits. Bulbul et al., (2018) reported the PM10 concentrations and their structure morphology in Islamabad during winter fog period (December – March). M. 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. I.H Shah & M. 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 am) and evening (4–6 pm) 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, there is 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.

2 Experimental

2.1 Site Description

Islamabad is the capital of Pakistan and is situated at an elevation about 500 m above sea level (latitudes 33.7294° N and longitudes 73.0931° E) with a population of about two million and an area about 906 km$^2$. 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 Figure-1a. The average annual rainfall is 1143mm. The city is divided into residential, commercial, industrial and diplomatic zones; some of them are shown in the map of Islamabad (Figure-1). 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 Figure-1 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.

**Figure -1 Sampling site in Islamabad** (This figure is taken from openstreetmap.org)

### 2.2 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 m$^3$ min$^{-1}$ for TSP and 0.962 m$^3$ min$^{-1}$ for PM$_{10}$. Filters were pre-conditioned at 550 ºC and humidity room for 24hours 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 3rd December 2007 to 16th December 2007 (no sampling on 8th and 15th December), were collected. After collection, these samples were stored in a freezer and transported to Vienna, Austria by Air luggage for analysis.

Figure: -2-a Wind Magnitude and Wind vectors at 2 meter height, average over 2007 to 2017 (Merra 2 satellite data)

2.3 Experimental Methods

2.3.1 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, Maihak). The calibration procedure was done using tartaric acid died 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 O₂ atmosphere, EC (and carbonate carbon,
IC) is oxidized. CO₂ originating in this step is detected by a 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 fibre filter
samples Thermal - Optical methods were not used for EC measurement. Carbonate carbon
(CC) – carbonate carbon 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 CO₂ was
determined by non-dispersive NDIR, resulting values are reported as CC. While the organic
carbon was measured calculated using following relationship OC = TC- EC-CC.

2.3.2 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 mM – 650
mM) which allows a good separation of levoglucosan and arabitol, both relevant constituents
of atmospheric aerosols in Pakistan Shahid I. 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
(0.45µm, 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-
Alrich) 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 than under the detection limit).

### 2.3.3 Inorganic ions

Anions (Cl\(^-\), NO\(_3\)\(^-\), SO\(_4\)\(^{2-}\)) 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\(^+\), NH\(_4\)\(^+\), Mg\(^{2+}\) and Ca\(^{2+}\)) 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 time 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).

### 3 Result and Discussion

#### 3.1 PM\(_{10}\) and TSP concentrations and main aerosol components

The average concentration of PM\(_{10}\) 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 PM\(_{10}\) in Delhi 268 ± 39 µg m\(^{-3}\).

Bhaskar and Mehta have reported PM\(_{10}\) concentrations in Ahmadabad India ranging from 17 - 327 µg m\(^{-3}\) respectively. The PM\(_{10}\) makes about 50 – 60 % of the TSP. The difference between TSP and PM\(_{10}\) 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 - PM$_{10}$) fraction is water soluble Calcium. Ca$^{2+}$ 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 PM$_{10}$ with $r^2 = 0.94$ and $r^2 = 0.83$ respectively as shown in Figure-2 indicates the mineral dust is major contributor to both PM$_{10}$ and TSP fractions in Islamabad.

**Figure-2 Linear regression plot between PM$_{10}$ and TSP with water soluble Ca$^{2+}$**

Total carbonaceous fraction (EC, OC and CC) was the main contributor to PM$_{10}$ mass and no significant difference was found between total carbon concentration in TSP and PM$_{10}$ (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 PM$_{10}$ 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 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., 2008). The correlation between EC and nitrate ions (Table S-1 a,b) underlines that a large part of EC may be related to the regional traffic and fossil fuel combustion and biomass 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.
<table>
<thead>
<tr>
<th>Component</th>
<th>Pakistan</th>
<th></th>
<th></th>
<th>India</th>
<th>Bangladesh</th>
<th>China</th>
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<tr>
<td></td>
<td>Islamabad&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Lahore&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Karachi&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Mumbai&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Allahabad&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Ahmedabad&lt;sup&gt;f&lt;/sup&gt;</td>
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<td>TSP</td>
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<td>194.5±60</td>
<td>149</td>
<td>150</td>
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<td>63.2±17.8</td>
<td>60.2±17.2</td>
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<td>n.d</td>
<td>40</td>
<td>39.1</td>
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<td>17.8±4.9</td>
<td>16.5±5.4</td>
<td>1.3</td>
<td>6</td>
<td>4.7</td>
<td>12.6</td>
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<td>PM&lt;sub&gt;2.5&lt;/sub&gt;</td>
<td>9.1±3.6</td>
<td>3.4±1.8</td>
<td>5.7</td>
<td>n.d</td>
<td>13.7</td>
<td>1.2</td>
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<td>37.9±10.5</td>
<td>40.2±0.4</td>
<td>--</td>
<td>3.1</td>
<td>21.8</td>
<td>25.3</td>
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<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>4.4±0.4</td>
<td>4.8±0.4</td>
<td>--</td>
<td>n.d</td>
<td>3.7</td>
<td>2.2</td>
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<tr>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>1.3±0.7</td>
<td>1.26±0.8</td>
<td>--</td>
<td>n.d</td>
<td>1.0</td>
<td>n.d</td>
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<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
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<td>2.6±0.6</td>
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<td>n.d</td>
<td>1.2</td>
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<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
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<td>0.45±0.2</td>
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<td>n.d</td>
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<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
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<td>22.4±7.6</td>
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<td>n.d</td>
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<td>2.9±0.7</td>
<td>0.3</td>
<td>3.8</td>
<td>6.6</td>
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<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;−&lt;/sup&gt;</td>
<td>11.9±5.9</td>
<td>11±5.3</td>
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<td>2.7</td>
<td>5.7</td>
<td>6</td>
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<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2−&lt;/sup&gt;</td>
<td>7.8±2</td>
<td>6.7±2.1</td>
<td>1.1</td>
<td>3</td>
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<td>n.d</td>
<td>0.21</td>
<td>n.d</td>
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<tr>
<td>Mannosan</td>
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<td>0.19±0.07</td>
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<td>n.d</td>
<td>0.1</td>
<td>n.d</td>
</tr>
<tr>
<td>OC/EC</td>
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<td>2.4</td>
<td>--</td>
<td>0.5</td>
<td>4.6</td>
<td>2.01</td>
</tr>
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</table>

n.d implies not determined, <sup>a</sup>This study, <sup>b</sup>E Stone et al., 2007, <sup>c</sup>Shahid I. et al., 2016, <sup>d</sup>Venkatraman et al., 2002, <sup>e</sup>Ram et al., 2010, <sup>f</sup>Rastogi et al., 2009, <sup>g</sup>Salam et al 2003, <sup>h</sup>Cao et al 2009, <sup>i</sup>Duan et al. 2003, 2005.
Also, the ratio $OC / EC$ can also be used as an indicator for sources of carbonaceous species (Ram et al., 2010; Rastogi et al, 2009; Sudheer et al, 2008; Sandradewi et al., 2008; Schauer et al, 1999, 2001; Andreae et al, 2001). 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 and 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 PM$_{10}$ 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 PM$_{10}$ 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.

### 3.2 Water Soluble Ions

Water soluble inorganic ions: calcium (Ca$^{++}$), magnesium (Mg$^{2+}$), sodium (Na$^+$), ammonium (NH$^+_4$), potassium (K$^+$), sulphate (SO$_4^{2-}$), nitrate (NO$_3^-$), and chloride (Cl$^-$) were found in atmospheric aerosol sample collected in Islamabad during winter period. The average concentrations of soluble ions are given in Table-1. The Ca$^{2+}$, SO$_4^{2-}$ and NO$_3^-$ concentrations were found major quantity in Islamabad. The Ca$^{++}$ concentration in Islamabad varied from 8 – 32 µg/m$^3$ with an average of 22µg/m$^3$ for PM$_{10}$ and for TSP it varied form 21 - 66 µg/m$^3$ with an average of 42µg/m$^3$. The high Ca$^{++}$ concentration has also been reported by Shahid et al., (2016) in Karachi and Ghude et al., (2017) in Delhi. The contribution of Ca$^{++}$ to total PM mass was 12.3% Islamabad while Ghude et al., (2017) reported Ca$^{++}$ contribution to PM was 14%. Thus, high Ca$^{++}$ concentration in Islamabad in not an anomaly. Khawaja et al., (2009) also reported a strong correlation between TSP, PM$_{10}$ and Ca$^{++}$ indicated mineral dust contributions. The average concentration of the secondary inorganic constituents NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ were 1.3µg/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\textsuperscript{−3} for PM\textsubscript{10}. NO\textsubscript{3}\textsuperscript{−} 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 SO\textsubscript{4}\textsuperscript{2−} 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 SO\textsubscript{4}\textsuperscript{2−} has only correlation with NH\textsubscript{4}\textsuperscript{+} 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\textsuperscript{−}/Na\textsuperscript{+} ratio of 1.8 has been reported for sea water, while at Islamabad Cl\textsuperscript{−} / Na\textsuperscript{+} was 0.73 – 0.6 in TSP and PM\textsubscript{10} indicating the Cl\textsuperscript{−} depletion during long range transport. The comparison between the sum of cations and anions in equivalent values have been shown in Figure-3, a linear relationship is present if carbonates, calculated out of CC are added to anions.

![Figure -3 Correlation between sum of cations and anions](image)

#### 3.3 Size distribution and relations between determined saccharides

Total concentrations of analysed saccharides account to 2.2 µg m\textsuperscript{−3} for TSP and 2.1 µg m\textsuperscript{−3} for PM\textsubscript{10}, which makes around 1% of the total particulate matter (TSP and PM\textsubscript{10}). 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 PM<sub>10</sub> fractions shows that anhydrosaccharides i.e. levoglucosan, mannosan and glactosan, all directly related to combustion of biomass are present mainly in PM<sub>10</sub>, 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 Figure-4.

![Figure - 4: Share of different saccharide groups in the total saccharide mass in TSP and PM<sub>10</sub> fractions.](image)

Average levoglucosan concentrations were the same in both fractions (1.70 µg m<sup>-3</sup>) and contribute with 78% and 83% to total saccharides in TSP and PM<sub>10</sub> respectively. The concentrations of levoglucosan in atmosphere varied from 0.79 µg m<sup>-3</sup> to 2.58 µg m<sup>-3</sup> during the whole study period, whereas the relation to PM<sub>10</sub> was in stable range of 0.8-1% in all samples. Levoglucosan showed a strong correlation with mannosan and galactosan, both related to PM<sub>10</sub> fraction only (Figure - 5). 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 PM<sub>10</sub> 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 cited 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 PM$_{10}$ were xylitol and glucose. The average
concentrations of those compounds in PM$_{10}$ were much lower than those of anhydro sugars: 0.01
µg m$^{-3}$ for xylitol and 0.03 µg 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 untypical as well.

Arabitol, mannitol and trehalose were spread among both fractions, whereas on average 77 - 79
% of arabitol and mannitol contributed to PM$_{10}$ with variations among single samples reaching
25 %. PM$_{10}$ 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 PM$_{10}$ 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 levoglucosan, as expected for prescribed- or open fires. This correlation is driven by
concentrations in coarse particles and disappears in PM$_{10}$ (Figure - 5). 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.

Figure - 5. Correlation between levoglucosan (Lev) and other saccharides detected in the ambient aerosols in Islamabad

Glaetosan 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 µg 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 µg m$^{-3}$ during winter time and 0.77 µg 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.

3.4 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 (Schmidl et al., 2008, Puxbaum et al., 2007; Wang et al., 2007; Lanz 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 watersoluble 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-2). Nevertheless, K$^+$ is less unique than levoglucosan as wood burning marker, and since it was reported also as constituent of soil dust and seas 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 T. et al., 2008; Zhang Z. et al., 2010). The emission factors of levoglucosan, expressed as a fraction of OC on carbon / carbon basis µgC (µgC)$^{-1}$, from previous biomass studies in Asia and US are given in Table S-2. For commonly used South Asian biofuels, (such as rice straw, dried cowdung patties, leaves and briquettes), an average emission factor of 12.6 {(0.079 µg levoglucosan (µg 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 µg levoglucosan (µg 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, 2004 in USA. 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.

$$BB-EC = \text{Levoglucosan} \times 2.7$$

$$BB-OC = \text{Levoglucosan} \times 10.2 \quad (1)$$

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

These relationships have been derived from South Asian biomass source studies comprised in the Table S-2. Emission ratios in relation to levoglucosan were calculated for a 53/47 % mix of wood and other biomass using wood smoke data from Shahid I. 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 S-2. Mix (Sd/Sy) is calculated for using other biomass data from Sheesley et al., 2003; Mix (Sd/Z) using Zhang et al. 2007 data.

The shares of levoglucosan in OC has been reported in the literature are comprised in Table-3. 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, as reported for e.g. 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.

### Table-4 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

<table>
<thead>
<tr>
<th>Biomass type</th>
<th>Experiment type</th>
<th>Source location</th>
<th>Emission</th>
<th>Reference</th>
</tr>
</thead>
</table>


<table>
<thead>
<tr>
<th>Fuel Type Description</th>
<th>Measured PM Type</th>
<th>Factor</th>
<th>Avg Lev / OC</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardwood (Pakistan) Open Burning</td>
<td></td>
<td>11.4%</td>
<td>Shahid et al., 2015</td>
<td></td>
</tr>
<tr>
<td>Cereal straw Dilution Chamber</td>
<td></td>
<td>8.2%</td>
<td>Zhang et al., 2007</td>
<td></td>
</tr>
<tr>
<td>Rice straw, cowdung, briquettes, leaves and jackfruit branches</td>
<td></td>
<td>7.9%</td>
<td>Sheesley et al., 2003</td>
<td></td>
</tr>
<tr>
<td>Rice straw Chamber</td>
<td></td>
<td>3.1%</td>
<td>Sullivan et al., 2008</td>
<td></td>
</tr>
<tr>
<td>Branches, grasses, duffs, needles, straw, leaves</td>
<td>Chamber or stack</td>
<td>3.1%</td>
<td>Sullivan et al., 2008</td>
<td></td>
</tr>
<tr>
<td>Residential and agricultural sources</td>
<td>Fireplace</td>
<td>1.9%</td>
<td>Mazzoleni et al., 2007</td>
<td></td>
</tr>
<tr>
<td>Wildland fuels Controlled room</td>
<td>USA (PM2.5)</td>
<td>5.5%</td>
<td>Mazzoleni et al., 2007</td>
<td></td>
</tr>
<tr>
<td>Hardwood Fireplace</td>
<td>USA (PM2.5)</td>
<td>6.4%</td>
<td>Fine et al., 2001, 2002, 2004</td>
<td></td>
</tr>
<tr>
<td>Softwood Fireplace</td>
<td>USA (PM2.5)</td>
<td>4.0%</td>
<td>Fine et al., 2001, 2002, 2004</td>
<td></td>
</tr>
<tr>
<td>Spruce, beach, briquettes Wood stove</td>
<td>Austria PM10</td>
<td>5.5%</td>
<td>Schmidl et al, 2008</td>
<td></td>
</tr>
<tr>
<td>Asian Biomass Literature average</td>
<td>Lumbini, Nepal, Northern Indo-Gangetic Plain</td>
<td>8.1%</td>
<td>Wan et al., 2017</td>
<td></td>
</tr>
<tr>
<td>Asian Biomass Literature average</td>
<td>Pakistan, Karachi and Islamabad</td>
<td>9.8%</td>
<td>This study</td>
<td></td>
</tr>
</tbody>
</table>
The calculated relative contributions from biomass burning to EC, OC and particulate matter $\text{PM}_{10}$ and TSP) have been given Table -5. Significant contribution of biomass burning (BB) to OC and PM has been found in both $\text{PM}_{10}$ and TSP in Islamabad. In $\text{PM}_{10}$, 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 $\text{PM}_{10}$ 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 $\text{PM}_{10}$ 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 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).

Table -5 PM, OC, Levoglucosan concentrations and contribution of biomass burning (BB) to PM and carbonaceous fraction in Islamabad

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

### 3.5 Identified particle sources/types and their contribution to PM$_{10}$ and TSP

Mass closure of PM$_{10}$ and TSP has been given in Figure-6 that indicates that organic matter and calcereous substances contributes a large fraction followed by soluble ions in both PM$_{10}$ and TSP. OM contributes 18% in TSP and 34% in PM$_{10}$ while carbonates 31% and 28% in TSP and PM$_{10}$ respectively. I. Shahid et al., (2016) has reported contribution of OM to PM$_{10}$ 34.9% and carbonates 68% in Karachi. The unidentified portion in PM$_{10}$ is less than 2% as mineral dust and crustal elements are considered to part of the calcereous 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 PM$_{10}$ has been given in Figure-7. BB contribution is 45% of OC - TSP mass and 44% of OC - PM$_{10}$ mass. Anhydro-sugars including levoglucosan and mannosan contributes to 5% and 6% respectively to OC - PM$_{10}$ and OC - TSP respectively. Thus, major fraction of organic carbon comes from biomass burning.
Figure 6. Mass closure of PM$_{10}$ and TSP

Figure 7: Mass closure of organic carbon in PM$_{10}$ and TSP
Conclusion

PM$_{10}$, TSP mass, water soluble ionic species, anhydrosugars, sugar alcohols and carbonaceous fractions were measured in atmospheric aerosol samples collected during winter time at a residential site in Islamabad. The particulate matter concentrations were found to be very high in both PM$_{10}$ 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 these study period PM$_{10}$ concentrations from 12 days exceeds WHO Target I limit, 11 days’ Target II limits while all exceed Target III limits. The mass closure of PM$_{10}$ and TSP indicates that CaCO$_3$ makes contribution of 28% and 31% respectively. In OM makes the biggest contribution to PM$_{10}$ mass i.e. 34% while in TSP OM contributes only 18%. The mass closure of OC in both fractions indicates about 45% contributions of biomass to OC in PM$_{10}$ and TSP. The EC make 5% of TSP and 8% of PM$_{10}$ mass at Islamabad. Biomass smoke makes major part of organic carbon in fractions, residential heating and cooking in the vicinity of Islamabad city might be possible source of biomass smoke.

It is evident from the above results that OM, soluble ions and Calcerous species are main components in PM$_{10}$ while in TSP Calcerous species makes largest contribution followed by soluble ions and OM. However, a comprehensive long-term measurement are required to assess the source of the pollutants to develop mitigation strategies.

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References:


