Seasonality of carbonaceous aerosol composition and light absorption properties in Karachi, Pakistan

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ABSTRACT

Characteristics of carbonaceous aerosol (CA) and its light absorption properties are limited in Karachi, which is one of the most polluted metropolitan cities in South Asia. This study presents a comprehensive measurement of seasonality of CA compositions and mass absorption cross-section (MAC) of elemental carbon (EC) and water-soluble organic carbon (WSOC) in total suspended particles (TSP) collected from February 2015 to March 2017 in the southwest part of Karachi. The average TSP, organic carbon (OC), and EC concentrations were extremely high with values as 391.0 ± 217.0, 37.2 ± 28.0, and 8.53 ± 6.97 μg/m³, respectively. These components showed clear seasonal variations with high concentrations occurring during fall and winter followed by spring and summer. SO₄²⁻, NO₃⁻, K⁺, and NH₄⁺ showed similar variations with CA, implying the significant influence on atmospheric pollutants from anthropogenic activities. Relatively lower OC/EC ratio (4.20 ± 2.50) compared with remote regions further indicates fossil fuel combustion as a primary source of CA. Meanwhile, sea salt and soil dust are important contribution sources for TSP. The average MAC of EC (632 nm) and WSOC (365 nm) were 6.56 ± 2.70 and 0.97 ± 0.37 m²/g, respectively. MAC_EC is comparable to that in urban areas but lower than that in remote regions, indicating the significant influence of local emissions. MAC_WSOC showed opposite distribution with EC, further suggesting that OC was significantly affected by local fossil fuel combustion. In addition, dust might be an important factor increasing MAC_WSOC particularly during spring and summer.

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Introduction

Karachi, one of the largest metropolitan regions located on the Arabian Sea, has been experiencing severe air pollution over recent decades (Colbeck et al., 2010; Shahid et al., 2016; Ifthikhar et al., 2018). Rapid industrialization, large population and heavy traffic are responsible for bad air quality in this city due to elevated levels of gaseous and particulate pollutants (Gurjar et al., 2008, 2010). Karachi has a rapid urbanization rate of approximately 2.81%, and the population currently stands around 27.51 million people, which is 38.8% of Pakistan’s total population (Central Intelligence Agency, 2016). According to the WHO (2014), there were more than 9.08 million vehicles registered in Pakistan in 2011 and Karachi has the largest number of vehicles (>3.6 million) (Khan et al., 2018). Studies have pointed out that local residents in Karachi face a fairly high health risks from elevated levels of particulate matter (PM) (Parekh et al., 2001; Gurjar et al., 2010).

Carbonaceous aerosol (CA), consisted of organic carbon (OC) and elemental carbon (EC), contributed large fractions to the PM in urban atmospheres (Cao et al., 2007; Bond et al., 2013; Li et al., 2016a). CA significantly affects the radiation budget as well as the hydrological cycle and weather by absorbing and scattering incoming solar radiation and indirectly by altering cloud microphysical properties (Bond et al., 2013; Bond and Bergstrom, 2006; Gustafsson and Ramanathan, 2016; Kang et al., 2019; Ramanathan et al., 2001). In general, EC absorbs solar radiation in the visible and infrared wavelengths (Chung et al., 2012; Bond et al., 2013; Rap et al., 2013; Hodnebrog et al., 2014). In addition, water-soluble OC (WSOC) has been proved having a positive direct radiative effect due to its strong light absorption for the blue to ultraviolet spectral range (Sun et al., 2007; Bahadur et al., 2012; Bosch et al., 2014; Kirillova et al., 2014, 2016; Li et al., 2016b, 2016c; Wu et al., 2019). Therefore, both components contribute to regional and global radiative forcing and climate change to some extent (Alexander et al., 2008; Bond et al., 2013; Rap et al., 2013). The mass absorption cross-section (MAC) is generally used to evaluate the radiative forcing of light absorbing particles. It is therefore essential to study MAC of both EC and WSOC together to quantify their relative light absorption contribution to climate change which is rather lacking in Pakistan.

A few studies have reported measurements of CA in Karachi (Bibi et al., 2017a, 2017b; Dutkiewicz et al., 2009; Lurie et al., 2019; Shahid et al., 2016). For instance, the temporal including diurnal, monthly, and seasonal variation of black carbon (BC) was measured using Aethalometer in Karachi during the period of March 2006 to December 2008. High BC concentrations (2.2–12.5 μg/m³) were observed particularly in November, January, and February (Bibi et al., 2017a, 2017b; Dutkiewicz et al., 2009). OC and EC concentrations in PM10 during spring (March–April 2009) were 21.8 and 4.7 μg/m³, respectively, at an urban site of Karachi. The PM is considered to be mainly affected by mineral dust, a mixture of combustion and bioaerosol, and sea salt (Shahid et al., 2016). Furthermore, the composition and source of PM2.5 differed significantly at two sites of Karachi, reflecting the crucial role of local emissions to ambient PM2.5 (Lurie et al., 2019). However, none of these studies presented the light absorption characteristics of CA, which is essential for a better understanding of CA effects on radiative forcing and climate change over this region.

This present study reports on the seasonality of light absorption characteristics of EC and WSOC, along with measurements of mass concentration of OC, EC, and 8 water-soluble ions (WSIs) in total suspended particles (TSP) collected during a time span of 2 years (from February 2015 to March 2017) in Shershah colony of Karachi city. The main objectives of this study are to (1) investigate the ambient OC, EC, WSOC, and WSIs concentrations in the atmosphere and compare the data with those in other regions; (2) to assess the seasonal variations of all components and identify their potential sources; (3) to calculate MAC of EC and WSOC.

1. Sampling and analysis

1.1. Sampling site description

Karachi, the capital city of Sindh province located on the coast of the Arabian Sea (24°51’ N; 67°02’ E; 8 m a.s.l.), is the most urbanized and industrialized megacity in Pakistan. It is composed by 18 urban/sub-urban towns with a population currently stands around 27.51 million (Central Intelligence Agency, 2016). The population density varies from the central city (33,014 persons/km²) to the outskirts (433 persons/km²). Being the largest port city of Pakistan, Karachi has a large industrial base in and around the city including oil-fired power plants, cement factories, steel mills, scrap metal recycling plants, shipping, railroad yards, foundries, oil refineries, heavy petrochemical industries, automobile assembly plants, printing and publishing plants, food processing plants, tanneries, brick kilns, and several light industries. There is also solid waste incineration and open burning of municipal wastes (Parekh et al., 2001; Shahid et al., 2016).

There are two industrial zones in Karachi namely, Korangi industrial area and Singh Industrial Trading Estates (SITE) industrial area. The sampling site in Shershah colony is located nearby SITE industrial area. Shershah colony itself is a commercial and industrial area having several plastic, textile, and other kind of small, medium and large industries. Solid waste management system in the colony is in worse condition since last few years. People of the colony are frequently burning the plastic bags and other solid waste (municipal wastes) in the streets and road side causing to increase the concentration of CA and other pollutants in the atmosphere.

Karachi’s climate is subtropical and semi-arid with scanty rainfall. The mean annual rainfall in Karachi is around 200 mm, which occurs primarily (80%) during the July to August. The region has four distinct seasons: winter (January–March), spring (April–June), summer (July–September), and fall (October–December). The average monthly temperature ranges from 13°C to 34°C with annual mean temperature is about 26°C. During the summer, there is a strong west and southwesterly airflow and brisk wind as Karachi is dominated by marine air off the Arabian Sea. Winds are relatively calm during the winter, but there is a strong northeasterly influence of continental air (Dutkiewicz et al., 2009).
1.2. TSP sample collection

TSP sampling was conducted at the extreme southwest portion, just few km away from the Arabian Sea (Fig. 1). A total of 133 TSP samples were collected by one sampler fitted with TSP cyclone at a flow rate of 100 L/min (T2034, Qingdao Laoying Environmental Technology Co., Ltd., China) in this study. Detailed information on the filter pre- and after-treatment was presented in supporting information file (Text S1).

1.3. OC, EC, WSOC and WSIs analysis

The OC and EC concentrations were analyzed using IMPROVE-A thermal/optical reflectance (TOR) protocol at 632 nm by using a Thermal/Optical Carbon Analyzer (Desert Research Institute Model 2001, Atmoslytic Inc., Calabasas, CA, USA) (Chow et al., 2007; Chen et al., 2015). The WSOC concentration was measured with a total organic carbon (TOC) analyzer (Model 5000A, Shimadzu Corp, Kyoto, Japan). Average field blank values for OC, EC and WSOC were 0.2 μg/m^3, 0.06 μg/m^3 and 0.17 μg/m^3, respectively. All of these values are much lower than those of collected samples. The light absorption of the WSOC was measured with a spectrophotometer (SpectraMax M5, USA) from 200 to 800 nm (Li et al., 2016b, 2016c). Each spectrum was determined relative to that of blank filter treated by the same amount of Milli-Q water. WSIs including Cl^−/C0, NO3^−/C0, SO4^2−/C0, Na^+, NH4^+, K^+, Mg^2+, and Ca^2+ were measured with an ion chromatograph (DIONEX, ICS-90, USA). The detection limits of the methods for 8 ions were 0.01 μg/m^3 with overall uncertainty was less than 5% for the reproducibility test (Wan et al., 2016). Detailed information on the measurement method of OC, EC, WSOC, and WSIs is presented in the supporting information file (Text S2).

1.4. MAC of EC and WSOC calculation

The MAC_{raw} of EC was calculated as:

\[ \text{MAC}_{\text{raw}} = \frac{\text{ATN}}{\text{EC}_s} \times 10^2 \]  

where EC_s is EC loading (in μg/cm^2). ATN = ln(I/I_0), I and I_0 are the intensities of the transmittance signal measured at the beginning and end of thermal-optical analysis, respectively. (Cheng et al., 2011). Furthermore, an empirical correction factor 3.6 was adopted to correct the multiple scattering effects when using Thermal-optical carbon analyzer (Ram and Sarin, 2009; Cheng et al., 2011). Therefore Eq. (1) is described as:

\[ \text{MAC}_{\text{corrected}} = \frac{\text{ATN}}{\text{EC}_s} \times \frac{1}{3.6} \]  

The value of MAC_{WSOC} can be calculated from following equation:

\[ \text{MAC}_{\text{WSOC}} = \frac{A}{C} \times \ln(10) \]  

where A (absorbance) is derived directly from the spectrophotometer at 365 nm, L is absorbing path length, and C is WSOC concentration.

2. Results and discussion

2.1. Concentration and variation of TSP, OC, and EC

The TSP concentrations for the sampling period ranged from 60.7 to 1505 μg/m^3 with extremely high concentrations occurring from November to February of next year, gradually decreasing from March to the minimum around July and...
August (Fig. 2a). The daily OC and EC concentrations showed the same seasonal variation as TSP with daily concentrations ranged from 7.68 to 125.5 \( \mu g/m^3 \) and 1.95 to 42.1 \( \mu g/m^3 \), respectively, during the sampling period (Fig. 2b and 2c). The seasonal variation is consistent with previous researches on other primary pollutants such as BC, PM2.5 and PM10 at Karachi (Bibi et al., 2017; Dutkiewicz et al., 2009; Lurie et al., 2019; Mansha et al., 2012). Extremely high OC and EC concentrations during the period of November to February can be associated with stable meteorological conditions and increased emission sources. During these months, the atmospheric boundary layer is generally closer to the surface and become more stable, often resulting in higher pollutants concentrations when they become trapped and accumulate (Mues et al., 2017; Lurie et al., 2019). In addition, burning activities due to indoor heating, industrial and vehicular emissions also contributed to high CA concentrations (Bibi et al., 2017a). On the other hand, the washout during summer is responsible for lower OC and EC concentrations (Dutkiewicz et al., 2009). Furthermore, airflow during the summer is directly off the Arabian Sea and coastal areas to the east and northeast of Karachi, which could also lead to low OC and EC concentrations.

The TSP in Karachi (391.0 ± 217.0 \( \mu g/m^3 \)) was higher than that in heavily polluted urban areas in northern India and Nepal such as Delhi and Kathmandu (Kumar and Yadav, 2016; Tripathee et al., 2017), suggesting that Karachi is among the most polluted cities worldwide. Parekh et al. (2001) reported a higher TSP concentration (668 \( \mu g/m^3 \)) at a road site in Karachi, whereas PM10 concentrations were observed differing significantly at different regions (Ghauri et al., 2007; Shahid et al., 2016). The disparity of PM concentrations indicates the great influence of local emissions on the spatial distribution of pollutants.

A comparison of the OC, EC concentrations in aerosols from Karachi and those from other sites are presented in Fig. 3a, b. The levels of these species (OC: 37.2 ± 28.0 \( \mu g/m^3 \), EC: 8.53 ± 6.97 \( \mu g/m^3 \)) were comparable to those recorded at urban or rural areas such as Kathmandu, Lumbini (Chen et al., 2019) and 14 Chinese cities during winter (Cao et al., 2007). However, they were slightly higher than other urban areas such as Delhi (Sharma et al., 2014) and Kanpur (Ram and Sarin, 2010) in South Asia. Furthermore, both OC and EC concentrations were significantly higher than those recorded in remote regions such as Manora Peak in India (Ram et al., 2010), QOMS on the northern side of the Himalayas (Cong et al., 2015) and Nam Co inland of the Tibetan Plateau (Chen et al., 2019). Extremely high ambient OC and EC concentrations can pose severe environmental and health concerns to the residents of Karachi.

The OC/EC ratio is generally used to identify the emission type and strength, secondary organic aerosol formation, and different removal rates (Turpin and Lim, 2001; Pio et al., 2011). Biomass burning usually leads to a high OC/EC ratio (Chen et al., 2015; Srinivas et al., 2016), whereas fossil fuel combustion is one of the main reasons for low OC/EC ratio particularly in urban areas (Cao et al., 2007). In the present study, the OC/EC ratios varied from 1.96 to 11.4 during the sampling period. The average ratio (4.20 ± 2.50) was similar to those reported in Kathmandu (Chen et al., 2019); Delhi (Sharma et al., 2014) and some Chinese cities (Cao et al., 2007), suggesting that CA in
Karachi was mainly emitted from fossil fuel combustion. However, the value was lower than that reported in remote regions over the central Himalayas such as NCO-e (Decesari et al., 2010), Manora Peak (Ram et al., 2010), and QOMS (Cong et al., 2015). Low OC/EC ratios in Karachi suggested that these components were mainly affected by local emission whereas those remote regions were influenced by long-range transport pollutants which undergo more secondary organic aerosol formation (Wan et al., 2015). In addition, biomass burning is another factor causing higher OC/EC ratios in those remote regions (Chen et al., 2015, 2019).

2.2. Water-soluble ions

The annual average concentrations of WSIs in TSP have been presented in Table 1. WSIs ranged from 34.2 to 106.7 µg/m³ with an average of 57.3 µg/m³. The dominant anion was SO₄²⁻ followed by Cl⁻ and NO₃⁻ with average concentrations of 14.0, 11.0, and 6.95 µg/m³, respectively. The cations were observed to be in the order Ca²⁺ > Na⁺ > K⁺ > Mg²⁺ > NH₄⁺ in the sampling site. Ca²⁺ and Na⁺ had higher concentrations with an average of 14.6 and 7.54 µg/m³ which accounted for 25.3% and 13.1%, respectively, of total WSIs. The rest of the cations (K⁺, Mg²⁺, and NH₄⁺) accounted for 5.62% of the total ions.

WSIs concentrations in Karachi were comparable to those in urban areas such as Delhi (Chelani et al., 2010) and Beijing (Wang et al., 2006) but slightly higher than those in Kathmandu (Tripathee et al., 2016) and Agra (Satsangi et al., 2013). In addition, the total ion concentrations were significantly higher than those in remote regions over the central Himalayas (Decesari et al., 2010; Cong et al., 2015). In detail, concentrations of Cl⁻, Na⁺, and Ca²⁺ in Karachi were the highest among all sites presented in Table 1, suggesting that the atmosphere of Karachi was significantly affected by sea salt and higher loadings of calcium-rich dust particles. Anthropogenic WSIs such as SO₄²⁻ and NO₃⁻ in Karachi were lower than that in Beijing but comparable to that in Delhi and Kathmandu. Such a result suggests heavy air pollution in Karachi. The concentration of NH₄⁺ was slightly higher than in remote regions but significantly lower than in other cities in India and China. Moreover, K⁺ concentration in Karachi was comparable to Beijing and Pokhara but was slightly lower than that at other cities from Indo-Gangetic Plain (IGP) where biomass burning is common.

The seasonal variations of CA and WSIs are presented in Fig. 4. Similar variations in SO₄²⁻, NO₃⁻, K⁺, and NH₄⁺ with CA were observed with higher concentrations occurring during fall and winter whereas relatively lower values occurring during spring and summer, implying that these pollutants might have common sources mainly from anthropogenic activities. However, Cl⁻, Na⁺, and Mg²⁺ had opposite seasonal variations with CA, suggesting that the atmosphere of Karachi was somewhat affected by sea salt. Ca²⁺ had relatively higher concentrations during fall and spring, which clearly reflects the influence of crustal ions in dry periods.
The contribution of WSIs to TSP at different seasons has been presented in Fig. 5. SO$_4^{2-}$ is the biggest anion contributor, followed by Cl$^-$ and NO$_3^-$. The proportions of Cl$^-$ and SO$_4^{2-}$ during spring and summer were higher than those in fall and winter whereas NO$_3^-$ had similar contributions among four seasons. Ca$^{2+}$ was the highest of all the measured ions in TSP during all seasons, with higher values during spring (5.5%) and summer (4.74%) (Fig. 5a and 5b). The same variation with Ca$^{2+}$ was observed for Mg$^{2+}$, suggesting higher dust loadings during this period. Na$^+$ had similar seasonal variation with Cl$^-$ with values approximately 2 times higher during spring and summer than that in other seasons, reflecting the prevalent air mass from the Arabian Sea. K$^+$ and NH$_4^+$ showed similar seasonal variations with slightly higher contributions during winter (Fig. 5d), probably because the increased burning of biomass, plastics and municipal wastes.

Table 1 — Annual statistics of water-soluble inorganic ions concentration ($\mu g/m^3$) between February 2015 and March 2017 in Karachi, Pakistan.

<table>
<thead>
<tr>
<th>Components</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>SO$_4^{2-}$</th>
<th>Na$^+$</th>
<th>NH$_4^+$</th>
<th>K$^+$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Anions</th>
<th>Cations</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>11.0</td>
<td>6.95</td>
<td>14.0</td>
<td>7.54</td>
<td>0.55</td>
<td>1.65</td>
<td>1.03</td>
<td>14.6</td>
<td>32.0</td>
<td>25.4</td>
<td>57.3</td>
</tr>
<tr>
<td>SD</td>
<td>4.35</td>
<td>4.57</td>
<td>4.60</td>
<td>2.65</td>
<td>0.65</td>
<td>1.29</td>
<td>0.33</td>
<td>4.00</td>
<td>9.10</td>
<td>5.96</td>
<td>14.7</td>
</tr>
<tr>
<td>Min</td>
<td>3.91</td>
<td>1.70</td>
<td>5.35</td>
<td>3.40</td>
<td>0.02</td>
<td>0.58</td>
<td>0.45</td>
<td>7.71</td>
<td>17.8</td>
<td>16.3</td>
<td>34.2</td>
</tr>
<tr>
<td>Max</td>
<td>20.6</td>
<td>22.8</td>
<td>29.9</td>
<td>13.5</td>
<td>3.29</td>
<td>6.21</td>
<td>1.79</td>
<td>29.9</td>
<td>61.9</td>
<td>44.8</td>
<td>106.7</td>
</tr>
<tr>
<td>Percentage (%)</td>
<td>19.1</td>
<td>12.1</td>
<td>24.3</td>
<td>13.1</td>
<td>0.96</td>
<td>2.87</td>
<td>1.79</td>
<td>25.3</td>
<td>55.7</td>
<td>44.3</td>
<td></td>
</tr>
</tbody>
</table>

Kathmandua | 2.17 | 5.38 | 10.96 | 3.36 | 6.17 | 2.62 | 0.65 | 8.19 | 18.51 | 20.99 | 39.5 |
Delhi | 8.23 | 15.13 | 16.74 | 5.76 | 6.06 | 4.11 | 1.30 | 6.82 | 40.1 | 24.05 | 64.15 |
Agra | 4.6 | 6.7 | 5.9 | 4.0 | 2.7 | 3.5 | 1.4 | 6.7 | 17.2 | 18.3 | 35.5 |
Beijing | 8.22 | 22.76 | 27.25 | 2.05 | 12.4 | 1.84 | 0.8 | 12.16 | 58.23 | 29.25 | 87.48 |
Pokhara | 0.51 | 1.94 | 4.23 | 1.87 | 1.17 | 1.05 | 0.33 | 8.39 | 6.99 | 12.84 | 19.54 |
Jomsom | 0.27 | 1.64 | 3.79 | 2.59 | 0.96 | 0.58 | 0.31 | 7.35 | 5.7 | 11.79 | 17.49 |
NCO-P | 0.01 | 0.31 | 0.59 | 0.07 | 0.21 | 0.03 | 0.01 | 0.14 | 0.91 | 1.37 | 2.28 |
QOMS | 0.02 | 0.20 | 0.43 | 0.07 | 0.03 | 0.04 | 0.08 | 0.65 | 1.69 | 2.34 |       |

SD: standard deviation; a: TSP samples (Tripathee et al., 2016); b: PM$_{10}$ samples (Chelani et al., 2010); c: TSP samples (Satsangi et al., 2013); d: TSP samples (Wang et al., 2006); e: TSP samples (Tripathee et al., 2017); f: NCO–P (Nepal Climate Observatory-Pyramid) PM$_{10}$ samples (Decesari et al., 2010); g: TSP samples (Cong et al., 2015).
2.3. Optical properties of EC

The relationship between optical attenuation (ATN at 632 nm) and EC loading (ECS) can be used to study the absorption characteristics of EC. In the present study, the ATN were significantly correlated to those of ECS below 15 μg/cm² (Fig. 6). However, this relationship ceases when ECS were higher than 15 μg/cm². This result differs from those of the previous studies conducted in Beijing and Lhasa which reported the ECS limit is 7 μg/cm² (Cheng et al., 2011; Li et al., 2016b). The deviations at higher concentrations indicate the influence of the shadowing effect gradually becoming more evident as the number of particles on the filter increase.

The calculated MACEC at 632 nm ranged from 1.5 to 11.5 m²/g for the entire sampling period. The average value (6.56 ± 2.70 m²/g) is comparable to that of freshly emitted EC (6.5 m²/g), implying that EC in the atmosphere of Karachi was mainly affected by local emissions and experienced minor aging process (Bond and Bergstrom, 2006). In addition, it was similar to those in urban and rural areas in South Asia such as Kanpur (Choudhary et al., 2018), Kathmandu, Mardan, and Lumbini (Chen et al., 2019) where are significantly affected by local emissions particularly fossil fuel combustion (Fig. 7a). However, the value was lower than that in remote mountain regions such as Everest and Hunza (Chen et al., 2019) due to EC particles can change their structure and morphology by aging, coating, and other chemical processes during long-range transport (Wang et al., 2017; Dong et al., 2019).

The seasonal variation of MACEC was presented in Fig. 8a with similar values during all seasons except fall. This is different from other regions such as Beijing (Cheng et al., 2011) and Manora Peak (Ram et al., 2010), where had higher MACEC in summer compared with other seasons. In general, emission source and coating enhancement are key factors influencing the variability of MACEC (Cozic et al., 2008; Chen and Bond, 2019).
However, the climate of Karachi is subtropical without evident change of monthly temperature, thus leading to similar coating level for the whole year. In addition, dust is prevalent during spring and summer as indicated by Ca\(^{2+}\) contribution to total TSP (Fig. 5a and 5b). A negative correlation between Ca\(^{2+}\) and MACEC was observed during the sampling period (Fig. S1), suggesting that dust can decrease the MACEC value. Thus, similar MACEC values in summer were observed with other seasons.

2.4. Optical properties of WSOC

The WSOC demonstrated seasonal variations similar to those of OC with concentration ranged from 2.04 to 42.1 \(\mu g/m^3\) with an average of 7.35 \(\mu g/m^3\). The average WSOC/OC ratio is 0.16 ± 0.04, which is significantly lower than that reported in other urban areas such as Kanpur, Allahabad (ratio: 0.35, Ram and Sarin, 2010), Tokyo (ratio: 0.35, Kondo et al., 2007), and Nanjing (ratio: 0.30, Yang et al., 2005) and remote mountains like Manora Peak (ratio: 0.55, Ram et al., 2010) and QOMS (ratio: 0.58, Cong et al., 2015). The relatively low WSOC/OC ratios suggested poor aging, a dominant contribution from primary emission sources of WSOC in Karachi. Previous researches also observed high WSOC/OC ratios (>0.6) for photochemical haze in suburban and rural environment (Kumagai et al., 2009) as well as for biomass burning aerosols (Decesari et al., 2006). In addition, the low ratio might reflect the influence of dust on aerosols in Karachi.

A significant relationship existed between absorption coefficient (\(b_{abs}\)) at 365 nm and WSOC concentrations (\(R^2 = 0.92, p < 0.01;\) Fig. S2), indicating a similar light absorption ability of WSOC in Karachi throughout the year. The annual average MAC\(_{WSOC}\) at 365 nm in Karachi was 0.97 ± 0.37 \(m^2/g\), which is slightly lower than those in urban areas inland of the IGP and East Asia (Fig. 7b). In addition, the MAC\(_{WSOC}\) values were higher than the data recorded at remote sites, such as the NCO-P and downwind regions of IGP (Srinivas and Sarin, 2013; Bosch et al., 2014; Kirillova et al., 2016). Karachi has a larger primary and anthropogenic contribution for WSOC than those in remote regions. Previous studies have reported that primary emitted WSOC is more light absorptive than secondary aerosols. In addition, secondary organic aerosols (SOAs) with higher aromaticity (mainly from anthropogenic sources) also show a higher light-absorbing efficiency than terrestrial-biogenic SOA (Lambe et al., 2013). By contrast, photochemical aging of WSOC during long-range transport leads to less absorptive chemical compounds (Zhong and Jang, 2014). Furthermore, WSOC mixture with non-absorbing components and drift to water-insoluble forms during transport also contribute some parts to the lower MAC\(_{WSOC}\) at remote regions (Bosch et al., 2014).

Slightly higher MAC\(_{WSOC}\) values were observed during spring and summer, suggesting that photobleaching plays a minor role in seasonality of MAC\(_{WSOC}\) (Fig. 8b). In contrast to EC, dust can increase the MAC of WSOC as indicated by the positive correlation between Ca\(^{2+}\) and MAC\(_{WSOC}\) (Fig. S1).
Correspondingly, increased more absorbing components (e.g., from biomass burning) resulting in relatively higher MAC\textsubscript{WSOC} values in winter (Hecobian et al., 2010; Cheng et al., 2011; Hu et al., 2017).

3. Conclusions

In this study, TSP samples were collected from February 2015 to March 2017 in Karachi to analyze OC, EC, and WSOC, and their respective light absorption characteristics. The average TSP, OC, EC, and WSOC concentrations were 391.0 ± 217.0, 37.2 ± 28.0, 8.53 ± 6.97, and 7.35 ± 7.55 mg/m\textsuperscript{3}, respectively, for the entire period. Ca\textsuperscript{2+} (14.6 ± 4.0 µg/m\textsuperscript{3}) and SO\textsubscript{4}\textsuperscript{2-} (14.0 ± 4.6 µg/m\textsuperscript{3}) were the most dominant cation and anion in TSP. These values were similar to those observed over urban areas in South and East Asia but much higher than those in remote regions over the Himalayas and Tibetan Plateau, suggesting severe air pollution in the study region. All the carbonaceous components exhibit a clear seasonal variation with maximum concentrations observed in fall, followed by winter, spring, and summer in decreasing order; this pattern in the concentrations is most likely caused by the combination of meteorological condition and emission source. SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}\textsuperscript{-}, K\textsuperscript{+}, and NH\textsubscript{4}\textsuperscript{+} showed similar variations with CA, implying the significant influence on atmospheric pollutants from anthropogenic activities. Meanwhile, sea salt and soil dust also contributed to some extent. The relatively low OC/EC ratio (4.20 ± 2.50) suggested that fossil fuel combustion is the primary source of these pollutants. The annual average MAC\textsubscript{EC} was 6.56 ± 2.70 m\textsuperscript{2}/g, indicating that the study site was mainly affected by local emissions. Similar MAC\textsubscript{EC} values among four seasons reflecting combined influence of less coating enhancement and increased dust. The average MAC\textsubscript{WSOC} was 0.97 ± 0.37 m\textsuperscript{2}/g, further indicating the significant contribution of local emissions to OC. In contrast to EC, dust can increase MAC\textsubscript{WSOC} particularly during spring and summer. The results showed a large spatial and temporal variability in CA concentrations and MAC values for different geographical locations in South Asia. Using site-specific MAC values is thus preferable to the constant value conventionally assigned to reduce the uncertainty in the estimation of atmospheric radiative forcing due to CA.

Fig. 8 – Seasonal variations in MAC value (m\textsuperscript{2}/g) of EC (a) and WSOC (b) in Karachi.

Correspondingly, increased more absorbing components (e.g., from biomass burning) resulting in relatively higher MAC\textsubscript{WSOC} values in winter (Hecobian et al., 2010; Cheng et al., 2011; Hu et al., 2017).

Declaration of Competing Interest

We declare that we have no financial and personal relationships with other people or organizations that can appropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in/or the review of the manuscript entitled “Seasonality of carbonaceous aerosol composition and light absorption properties in Karachi, Pakistan”.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.12.006.

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