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RESEARCH ARTICLE

Seasonal variation of chemical composition and source apportionment of $PM_{2.5}$ in Pune, India

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Abstract Particulate matter with size less than or equal to 2.5 μm ($PM_{2.5}$) samples were collected from an urban site Pune, India, during April 2015 to April 2016. The samples were analyzed for various chemical constituents, including water soluble inorganic ions, organic carbon (OC), and elemental carbon (EC). The yearly mean total mass concentration of $PM_{2.5}$ at Pune was 37.3 $\mu g/m^3$, which is almost four times higher than the annual WHO standard (10 $\mu g/m^3$), and almost equal to that recommended by the Central Pollution Control Board, India (40 $\mu g/m^3$). Measured (OC, EC) and estimated organic matter (OM) were the dominant component (56 ± 11%) in the total particulate matter which play major role in the regional atmospheric chemistry. Total measured inorganic components formed about 35% of $PM_{2.5}$. Major chemical contributors to $PM_{2.5}$ mass were OC (30%), SO_4^{2-} (13%), and Cl^- and EC (9% each). The high ratios of OC/EC demonstrated the existence of secondary organic carbon. The air mass origin and correlations between the various components indicate that long range transport of pollutants from Indo-Gangetic Plain (IGP) and Southern part of the Arabian Peninsula might have contributed to the high aerosol mass during the dry and winter seasons. To our knowledge, this is the first systematic study that comprehensively explores the chemical characterization and source apportionment of $PM_{2.5}$ aerosol speciation in Pune by applying multiple approaches based on a seasonal perspective. This study is broadly applicable to understanding the differences in anthropogenic and natural sources in the urban environment of particle air pollution over this region.

Keywords Air pollution · $PM_{2.5}$ · Chemical composition · Biomass burning · Long range transport

Introduction

The aerosols affect air quality and, in turn, human and ecosystem well-being (IPCC 2013; WHO 2014; Forouzanfar et al. 2015; Atkinson et al. 2015). South Asia, due to its large population density involved in a wide range of human activities, is considered to be one of the hotspots of particulate pollutants like black carbon (BC) (Bond et al. 2007, 2013; Ramanathan and Carmichael 2008). Cities act as sources of aerosol and are likely to be important on a regional scale (Kumar et al. 2007). In South Asia, a city like Pune is facing serious threat from air pollution due to its rapid economic and industrial developments, urbanization, and increasing number of motor vehicles (Budhavant et al. 2011; Ali et al. 2012; Safai et al. 2013; Rao et al. 2016).

The chemical composition of fine particles gives us a better idea about their sources, which helps to make strategies for controlling particle emissions. The carbonaceous aerosol is one of the most important, ubiquitous materials in the atmosphere and comprises OC and EC, contributing up to 70% of the fine particulate mass (Jimenez et al. 2009). EC is used as a tracer of primary OC in $PM_{2.5}$, emitted from anthropogenic

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combustion sources, e.g., traffic, industrial, or biomass burning, and does not undergo chemical transformations. In addition to incomplete combustion processes, OC is also emitted from biogenic sources or formed within the atmosphere through gas-to-particle conversion of volatile organic compounds through photochemical reactions (Jacobson et al. 2000; Tsigaridis et al. 2006).

The present paper describes a data set on fine aerosol mass with major organic and inorganic chemical constituents collected in Pune for a period of 1 year during April 2015 to April 2016. The main objectives of the present study were to provide a comprehensive perspective on the physical (mass) and chemical (mass concentration of constituents) properties of fine aerosols with respect to seasonal change. The study also investigates the possible major sources that may be responsible for the variation in the concentrations of $PM_{2.5}$ in the urban atmosphere of Pune. The results of these data sets are likely to be of significant interest to both the process-modeling community and the large-scale modeling community.

Materials and methods

Sampling site and meteorological aspects

Pune (18°32′N, 73°51′E, 559 m amsl) is one of the rapidly growing cities in India in terms of industrial installations as well as vehicular population and also urbanization. Observations of $PM_{2.5}$ filter sampling were carried out at the roof top of the Indian Institute of Tropical Meteorology (IITM), at about 15 m height above the ground in Pashan which is located about 7 km from the center of Pune city. Pune is situated in the southwest part of India, at about 100 km from the adjoining Arabian Sea. It is the 9th most populated (3.115 million, in 2011) city in India and the 101st largest city in the world, by population.

Pune has a hot semi-arid climate bordering with three seasons: summer, monsoon, and winter. The summer (February–May) season is very hot with daytime maximum temperature reaching around 40 °C and surface winds are mostly gusty. During monsoon (June to September), westerly/south westerly winds, rich in marine air masses from the Indian Ocean and Arabian Sea, prevail over this region. The transition phases, the pre- (~May) and post- (~October) monsoon periods, are characterized by shifting wind directions. The normal annual rainfall of Pune is about 750 mm and about 80% of it is received during the monsoon season. During the winter (October–January) seasons, winds change direction from westerly to easterly, covering a landmass to the NE/E of sampling location.

Instrumentation

Sampling of $PM_{2.5}$ was carried out using a fine dust sampler (NPM-FDS 2.5 μ (A), NETEL India Pvt. Ltd) with a WINS Impactor. Sample duration was set ~24 h with a flow rate of 16.7 LPM. A total of 103 samples were collected using preweighed and pre-combusted (at 450 °C for 5 h) 47 mm diameter high-purity quartz microfiber filters. All the filter handling and chemical analysis of the aerosols followed the quality-controlled analytical protocols described earlier (e.g., Safai et al. 2010; Ali et al. 2012; Budhavant et al. 2016). Collected samples were stored in a freezer till the gravimetric and chemical characterization was conducted.

Gravimetric and chemical analysis of water-soluble ions

Each filter was then weighed twice, before and after sample collection. The difference of the two measurements corresponded to total $PM_{2.5}$ particle mass. Uncertainty of particulate matter mass concentrations was estimated to be 5% of the total measurement. The $PM_{2.5}$ mass concentrations were determined using an electronic balance with a detection limit of 1 μg after stabilizing at a constant temperature (20 ± 2 °C) and relative humidity (40 ± 4%) for 24 h. For chemical analysis, samples were extracted with ultrapure water (40 ml) using ultrasonic bath and were analyzed for major water soluble ions like Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and NH_4^+. The anions were analyzed by using ion chromatograph, IC (Dionex DX-100); the cations were analyzed by using atomic absorption spectrophotometer (AAS) (Perkin Elmer, AAnalyst 400), whereas the NH_4^+ ion was measured by colorimetric method (Weatherburn 1967) using a double beam spectrophotometer (Spectronic 20D, Milton Roy Company, USA). The detailed description of the extraction procedure and the detection limits for IC and AAS analysis are given in Budhavant et al. (2016).

EC and OC measurements

The OC and EC contents were measured with the use of a Semi continuous OC-EC Aerosol Analyzer (Sunset Laboratory, USA) by selecting the National Institute for Occupational Safety and Health (NIOSH) 5040 protocol (Birch and Cary 1996). The analyzer was calibrated periodically (weekly once) for quality control purposes by using a blank punch of pre-heated quartz fiber filter and standard sucrose solutions. OC and EC concentration values were blank corrected by subtracting an average of the field blanks. The average relative standard deviation of triplicate analysis was 5% for EC and 7% for OC. The overall blank concentrations from the quartz filters for OC were 0.12 ± 0.1 $\mu g/cm^2$ whereas no EC was detected in the blanks. The total carbon (TC) content on a filter is obtained by adding EC and OC. Details of this analysis are mentioned elsewhere (Safai et al. 2014).

Atmospheric transport

Air mass back trajectories have been recognized as a valuable tool to investigate the origin of air pollutants. The NOAA HYSPLIT model was used to calculate three-dimensional 5-day receptor oriented trajectories of the air reaching the measurement site at the end of the each sampling time at 559 m altitude (Draxler and Rolph 2013). Back trajectories were categorized according to seasons as shown in Fig. 1.

Summer: This category represents trajectories originated mainly from the west coast of India, North-eastern Africa, and Arabian Peninsula and then transported over the Arabian Sea before reaching to the sampling site. Monsoon: The predominant wind direction during this season from the Arabian Sea and Indian Ocean. This category is represented by clear air mostly transported from sea regions to the sampling site with very limited contact with anthropogenic sources. Most of the cases recorded low mass concentrations, about 50% less than that observed during polluted winter season. Winter: This group represents air with likely influence of anthropogenic and other continental sources. This category is represented by air transported mainly from IGP, parts of Central India and Bay of Bengal to the sampling site.

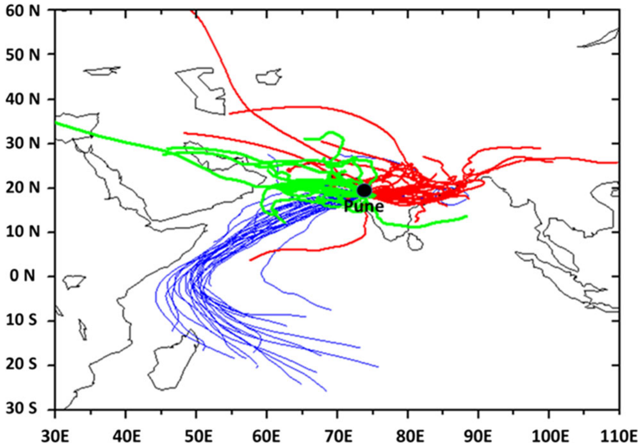

Fig. 1 Air mass backward trajectories at 559 m for 5 days ending at Pune, India, in different seasons during April 2015 to April 2016. *Colored line* indicates the back trajectories for three different seasons: winter (*red*), summer (*green*), and monsoon (*blue*)

Result and discussion

Fine particulate mass

Table 1 provides a statistical summary of the obtained data on atmospheric concentrations for $PM_{2.5}$, water-soluble ions, OC, and EC during the sampling period. The annual mean total mass concentration of $PM_{2.5}$ at Pune was 37.3 $\mu g/m^3$, which is almost equal to that recommended by the Central Pollution Control Board, India (40 $\mu g/m^3$). The annual threshold limit for $PM_{2.5}$ recommended by the European commission is 25 $\mu g/m^3$. The present study shows significant seasonal variation in the mass of $PM_{2.5}$ (Fig. 2). The highest 24-h concentration (76 $\mu g/m^3$) was observed in winter season and the lowest in monsoon (19.2 $\mu g/m^3$) season. The particle mass concentrations showed significant seasonal variation with elevated concentrations during the winter (43.9 $\mu g/m^3$) season followed by summer (41.7 $\mu g/m^3$) and lowest concentration during the monsoon (26.4 $\mu g/m^3$). Variations in mass concentration of $PM_{2.5}$ were observed due to seasonal variation of different emission sources in Pune as well as seasonal differences in local meteorological conditions at the sampling site. The low aerosol mass in monsoon season could be the result of scavenging of aerosol particles by rainfall. From all the filters collected, approximately 91 ± 7% of the ionic and carbon contents were detected, with the remaining balance 9% attributed to the contribution from undetected organic matter, trace metals, and other components. The present results are also compared with other studies reported in India and other part of Asia. The concentrations of $PM_{2.5}$ mass in the present study are low compared to earlier studies (Table 2) reported from Delhi (Pant et al. 2015), Durg (Deshmukh et al. 2011), Kharagpur (Srinivas and Sarina 2014), Taiyuan (He et al. 2017), Lahore (Raja et al. 2009), Dhaka (Begum et al. 2012), Kuala Lumpur (Rahman et al. 2015), and Male (Budhavant et al. 2015a).

Carbonaceous aerosols

We observe a clear seasonality of carbonaceous species (EC and OC) and other anthropogenic major water-soluble inorganic ions (Fig. 3). The overall percentage contribution of EC (3.26 $\mu g/m^3$) was found to be 9% in $PM_{2.5}$. Dominant seasonal average concentration of EC was found in winter 5.06 $\mu g/m^3$ (12%) and less during monsoon 1.18 $\mu g/m^3$ (5%). The mean concentration of OC (11 $\mu g/m^3$) was found to be 30% of total $PM_{2.5}$ mass. OC was the predominant contributor to the total carbon (OC + EC), contributing on an average 77% of the measured total carbon in $PM_{2.5}$. A strong correlation was observed between OC and EC (Table 3, $R = 0.81$). Almost similar OC concentration of the total mass of $PM_{2.5}$, was reported at Kharagpur (33%) during winter by Srinivas and Sarina (2014).

OC/EC ratio

The mass ratio of OC to EC reflects multiple processes in the atmosphere: (1) the ratio is higher from biomass burning than from fossil sources, (2) the ratio is elevated by biogenic secondary organic carbon contributions, (3) the atmospheric lifetime for OC is shorter due to higher chemical reactivity, and (4) the ratio is affected by atmospheric processing of organic chemicals (Saarikoski et al. 2008; Ram and Sarin 2010; Kroll

Table 1 Statistical details of carbonaceous species and various ionic concentrations (μg/m^3) in $PM_{2.5}$ at Pune, India

Season		$PM_{2.5}$	EC	OC	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	NO_3^-	SO_4^{2-}	nss-SO_4^{2-}	nss-Ca^{2+}	nss-Mg^{2+}	nss-K^+
Total avg. *N* = 103	Avg.	37.3	3.26	11.0	0.51	1.98	0.47	0.51	0.28	3.42	0.98	4.80	4.31	0.43	0.04	0.40
	Min.	19.2	0.52	3.71	0.01	1.14	0.07	0.05	0.16	1.17	0.09	0.46	0.16	0.01	0.01	0.01
	Max.	76.0	9.90	25.0	5.77	5.04	3.79	2.79	0.67	9.90	3.89	22.1	21.61	2.71	0.33	3.72
	S.D.	12.2	2.17	4.39	0.80	0.53	0.53	0.40	0.08	1.59	0.78	3.16	3.15	0.40	0.05	0.53
Summer 31	Avg.	41.7	3.45	12.7	1.07	2.05	0.42	0.71	0.30	3.20	1.45	4.90	4.38	0.63	0.05	0.35
	Min.	24.9	1.23	7.28	0.01	1.14	0.08	0.05	0.16	1.17	0.21	2.23	1.72	0.01	0.01	0.04
	Max.	70.1	7.70	20.5	5.77	5.04	0.93	2.79	0.67	9.90	3.89	10.9	10.3	2.71	0.20	0.85
	S.D.	10.8	1.46	2.95	1.16	0.73	0.18	0.59	0.10	2.09	0.86	2.10	2.01	0.58	0.05	0.18
Monsoon 35	Avg.	26.4	1.18	6.85	0.16	2.04	0.13	0.52	0.29	3.98	0.46	2.22	1.71	0.44	0.05	0.05
	Min.	19.2	0.52	3.71	0.01	1.15	0.07	0.21	0.16	1.48	0.09	0.46	0.12	0.13	0.01	0.01
	Max.	42.4	4.12	12.2	1.41	3.12	0.43	1.41	0.47	6.89	1.28	6.15	5.62	1.30	0.15	0.35
	S.D.	4.8	0.68	1.90	0.33	0.49	0.06	0.28	0.07	1.28	0.31	1.29	1.28	0.28	0.03	0.06
Winter 37	Avg.	43.9	5.06	13.5	0.38	1.87	0.79	0.33	0.25	3.09	1.08	7.16	6.69	0.26	0.03	0.72
	Min.	21.5	1.60	6.55	0.01	1.19	0.15	0.09	0.20	1.26	0.09	2.92	2.57	0.01	0.01	0.10
	Max.	76.0	9.90	25.0	1.33	2.54	3.79	0.60	0.55	5.49	3.12	22.1	21.6	0.52	0.33	3.72
	S.D.	11.1	1.89	4.26	0.38	0.28	0.73	0.11	0.06	1.17	0.72	3.28	3.28	0.11	0.05	0.72

et al. 2011; Budhavant et al. 2015a). A strong correlation was observed between OC and EC, which reflects similar sources of emission contributing to fine ambient carbonaceous particles and also indicating day-to-day fluctuations of emissions along with SOA formation in Pune. The OC/EC ratios at Pune during the study period ranged from 1.8 to 14.8 with an average of 4.6 ± 2.7. These values were found higher in monsoon than in summer and winter seasons. Different sources have been assigned to the OC/EC ratios by various studies, e.g., OC/EC value between 1 and 4 is reported to be corresponding to diesel- and gasoline-powered vehicle exhaust, whereas that between16. 8 and 40 for wood combustion (Schauer et al. 1999, 2002). Feng et al. (2009) showed biomass burning as a source for OC/EC ratio of 7.7. Saarikoski et al. (2008) reported that if this ratio is around 12, it corresponds to long range transport. The wide range of OC/EC ratio observed at Pune during this period indicates towards contribution from multiple sources for a carbonaceous fraction of $PM_{2.5}$. Generally, if the OC/EC ratios exceed 2.0, it suggests secondary organic aerosol formation in addition to primary emission sources (Chow et al. 1993). The MODIS active fire counts' data shows higher incidences of fires over India and Bangladesh during summer and winter, and this might have influenced high emissions of combustion aerosols during these seasons (Budhavant et al. 2015a). The estimated emission from the agricultural waste burning on an IGP scale is predicted to contribute ~22% of primary OC and 21% of EC (Rajput et al. 2014). Earlier studies reported that the dominant source of particulate matter during the winter in the northern part of India and IGP is attributed to emissions from biofuel/biomass burning (Ram et al. 2008, 2010; Ram and Sarin 2010; Satsangi et al. 2012; Rajput et al. 2011, 2014; Kumar and Attri

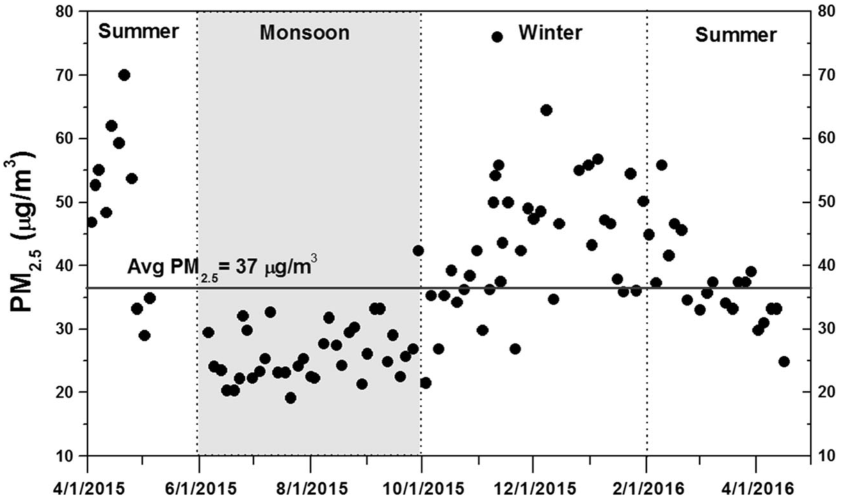

Fig. 2 Time series of $PM_{2.5}$ mass measured at Pune during April 2015 to April 2015. The *horizontal line* denotes the yearly average value. *Vertical gray shaded bar* indicates the monsoon season

Table 2 Comparison of $PM_{2.5}$ mass, carbonaceous species, and inorganic ions in Asian region

Location	Period	$PM_{2.5}$	EC	OC	OC/EC	Nss SO_4^{2-}	NO_3^-	nss-K^+	Reference
Pune, India	Apr 15–Apr 16	37	3.3	11	4.6	4.3	0.98	0.40	Present study
Delhi, India	Nov 10–Feb 11	277	46.3	104.4	2.3	25.9	32.8	3.81	Pant et al. (2015)
Kharagpur, India	Nov 09–Mar 10	90	4.5	30.7	7.0	17.6	na	2.20	Srinivas and Sarina (2014)
Durg, India	Jul 09–Jun 10	135	na	na	na	6.5	3.16	0.83	Deshmukh et al. (2011)
Lahore, Pakistan	Nov 05–Jan 06	190	14.7	76	5.2	12.7	20	3.96	Raja et al. (2009)
Taiyuan, China	Aug 09–Apr 10.	210	na	na	na	28.7	11.6	1.52	He et al. (2017)
Dhaka, Bangladesh	Feb 10–Feb 11	83	22.8	23.9	1.0	na	na	na	Begum et al. (2012)
Kuala Lumpur, Malaysia	2002–2011	25	na	na	na	8.7	na	0.4	Rahman et al. (2015)
Male, Maldives	Jan 13–Apr 13, Nov 13–Dec 13	21	0.76	1.9	2.3	na	na	na	Budhavant et al. (2015a)

The concentrations are given in $\mu g/m^3$

2016). On the other hand, at other places like Mumbai (Venkataraman et al. 2002), Delhi (Pant et al. 2015), Chennai (Pavuluri et al. 2011), Dhaka (Begum et al. 2012), and Male' (Budhavant et al. 2015b), dominance of fossil fuel sources is reported with low OC/EC ratio.

Total carbonaceous aerosol contribution

To estimate the contribution of organic matter (OM) to fine particulate mass concentration, a conversion factor of 1.6 has been suggested for urban aerosols by Turpin and Lim (2001). Based on this information, the total carbonaceous material (TCM = EC + OM) was 56 ± 11% of $PM_{2.5}$. This clearly indicates that TCM is a dominant component of total fine particles. TCM was typically a more dominant constituent in $PM_{2.5}$ during winter (61%) and lower during monsoon (46%). The seasonal variability of total carbon concentration over Pune is a result of prevailing meteorology and different emission sources. The low air circulation (lower boundary layer height and low wind speed) during winter results in more efficient trapping of carbonaceous aerosols and, thus, contributes to their enhanced atmospheric abundances over Pune. Alternatively, an increase in insolation during summer season results in the dispersal of ground level emissions to much higher heights and, therefore, explains the lower concentrations of carbonaceous aerosols over Pune in summer. OC is high during the summer indicating a high contribution of biogenic OC as the EC is clearly lower in summer than in winter. Furthermore, the frequent heavy rain events in monsoon result in efficient washout of particles from the ambient air leading to minimum concentrations of both OC and EC.

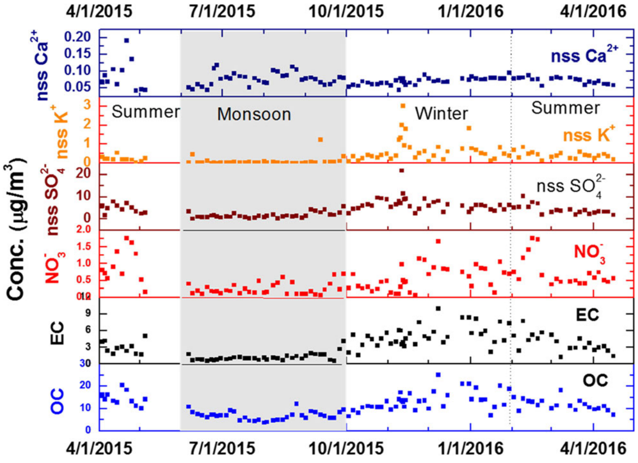

Fig. 3 Temporal variability of nss-Ca^{2+}, nss-K^+, nss-SO_4^{2-}, NO_3^-, EC, and OC (*top to bottom*) concentrations in $PM_{2.5}$. *Vertical gray shaded bar* indicates the monsoon season

Inorganic composition

Water-soluble inorganic ions comprise a large part of aerosol mass, especially in urban environments and play an important role in the aerosol chemistry (Satsangi et al. 2013). The average concentrations of chemical species in fine aerosols were classified into three sets based on the season. The mean concentration of measured water soluble inorganic ions was 13.16 $\mu g/m^3$, accounting for 35% of $PM_{2.5}$ mass concentration. SO_4^{2-} was the most abundant species in all measured inorganic ions, with an average value of 4.80 ± 3.17 $\mu g/m^3$, followed by Cl^-, Na^+, NO_3^-, and NH_4^+ and accounting for 13, 9, 5, 3, and 2% of total measured inorganic composition of $PM_{2.5}$, respectively. The rest of measured inorganic ions had a minor contribution to the total mass. There is a clear indication of seasonal variation of all the measured inorganic ions in $PM_{2.5}$ as listed in Table 1 and shown in Fig. 3. In winter season, concentration of SO_4^{2-} (16%) was maximum followed by Cl^- (7%), Na^+ (4%), NO_3^- (3%), K^+, NH_4^+, and Ca^{2+} (1% each), with meager contribution from Mg^{2+} towards total mass of $PM_{2.5}$. During summer, SO_4^{2-} was the most abundant chemical component followed by Cl^-, Na^+, NO_3^-, NH_4^+,

Table 3 Matrix of correlation coefficients for components in $PM_{2.5}$

	EC	OC	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Cl^-	Ca^{2+}	K^+	Mg^{2+}
EC	1	*+0.81*	*+0.56*	*+0.49*	+0.22	−0.04	−0.18	−0.18	+0.21	−0.13
OC	*+0.81*	*1*	*+0.55*	*+0.57*	*+0.42*	+0.20	+0.03	+0.13	+0.24	+0.14
SO_4^{2-}	*+0.56*	*+0.55*	*1*	*+0.48*	+0.27	+0.07	−0.12	−0.09	*+0.69*	+0.25
NO_3^-	*+0.49*	*+0.57*	*+0.48*	*1*	*+0.45*	+0.36	+0.17	+0.10	+0.16	+0.30
NH_4^+	+0.22	*+0.42*	+0.27	*+0.45*	1	+0.03	+0.11	+0.36	+0.03	*+0.80*
Na^+	−0.04	+0.20	+0.07	+0.36	+0.03	1	*+0.64*	+0.34	−0.03	*+0.80*
Cl^-	−0.18	+0.03	−0.12	+0.17	+0.11	*+0.64*	1	*+0.53*	−0.07	*+0.65*
Ca^{2+}	−0.18	+0.13	−0.09	+0.10	+0.36	+0.34	*+0.53*	1	−0.11	*+0.57*
K^+	+0.21	+0.24	*+0.69*	+0.16	+0.03	−0.03	−0.07	−0.11	1	+0.25
Mg^{2+}	−0.13	+0.14	+0.25	+0.30	*+0.80*	*+0.80*	*+0.65*	*+0.57*	+0.25	1

Correlations higher than 0.4 are highlighted in italics

Ca^{2+}, K^+, and Mg^{2+}. In monsoon, concentration of Cl^- was maximum followed by those of SO_4^{2-}, Na^+, Ca^{2+}, NO_3^-, Mg^{2+}, K^+, and NH_4^+. Concentration of Mg^{2+} was comparatively less during all the seasons. This seasonal variation may be due to the influence of prevailing meteorological factors and different sources of emissions. SO_4^{2-} and NO_3^- are mainly formed in the urban atmosphere from the transformation of their respective gaseous precursors SO_2 and NO_x which are oxidized to H_2SO_4 and HNO_3 in the atmosphere, which in turn form the SO_4^{2-} and NO_3^- (Matsumoto and Tanaka 1996). The mass ratio of NO_3^-/SO_4^{2-} could be used as an indicator of the relative importance of mobile and stationary sources of sulfur and nitrogen in the atmosphere (He et al. 2017). In the present study, the average ratios of NO_3^-/SO_4^{2-} were 0.24 ± 0.18, indicating that the greater contribution of SO_4^{2-} which shows the dominance of stationary sources (industrial activities) over vehicular activity. During summer, the average ratio of NO_3^-/SO_4^{2-} was recorded 0.30 ± 0.12 followed by monsoon (0.26 ± 0.20) and winter (0.16 ± 0.12).

To see the effect of marine influence on the fine aerosol composition, sea salt ratios were calculated using Na^+ as reference element and using sea water composition by Goldberg et al. (1971). The concentrations of sea salt were found to be higher (39%) in the monsoon, followed by summer (20%) and winter (18%). This may be due to influence of marine air being transported from over the ocean region, i.e., from the Arabian Sea. Na^+ correlated well with Cl^- and Mg^{2+}, indicating marine sources for them. The nss-K^+ can be used as a tracer for identifying the regional impact of biomass burning emissions (Andreae 1983; Paris et al. 2010; Srinivas and Sarina 2014). Nss-K^+/EC ratio is also used to identify the relative dominance contribution from fossil fuel combustion in relation to biomass burning emissions (Andreae and Merlet 2001; Mkoma et al. 2013). In the present study, the nss-K^+/EC ratio for entire period varied from 0.01 to 1.04 (Avg: 0.12 ± 0.09) at Pune which indicates fossil fuel dominance at Pune. Occasional high values of this ratio indicate that the respective samples were impacted by biomass burning during that period. Andreae (1983) reported that fossil fuel combustion generates a small amount of potassium, while Winchester and Nifong (1971) reported K^+/EC ratios for fuel oil combustion being as low as 10^{-5}. The contribution to EC from biomass/biofuel burning can be estimated using measured nss-K^+ and EC values and a typical nss-K^+/EC ratio value of 0.52 for biomass/biofuel burning (Cachier et al. 1991; Ferek et al. 1998; Alfaro et al. 2002). Contribution to EC form biomass/biofuel can be computed as $EC_{biomass/biofuel} = 100^*((nss\text{-}K^+/0.52)\ /EC))$. Results from this calculation yield biomass/biofuel burning contributions to EC of 29 ± 18% in winter, 20 ± 10% for summer, and 9 ± 5% for monsoon. Budhavant et al. (2015a) reported ^{14}C–EC based source apportionment which shows that both fossil and biomass combustion processes are almost equally responsible for the emission of EC in South Asia.

The source categorization of $PM_{2.5}$ was carried out using the method applied by Safai et al. (2010) and Budhavant et al. (2011). For terrestrial or crustal sources, Al^{3+}, Fe^{2+}, and Si^{4+} are the good tracers of soil, but we could not select them as the reference element because they were not measured. Therefore, Ca^{2+} was chosen as a reference element or tracer of crustal and

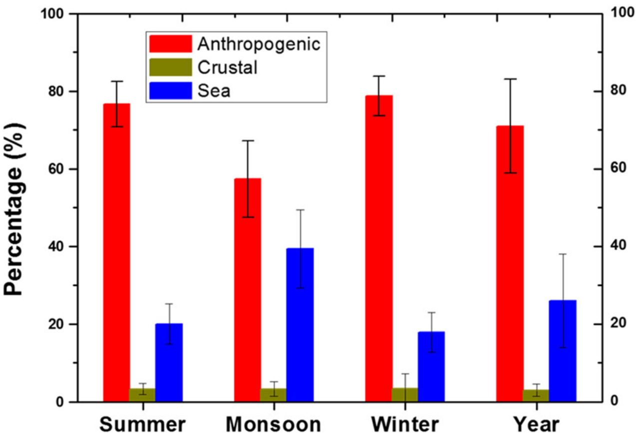

Fig. 4 Season wise percentage contributions of different sources in $PM_{2.5}$ mass at Pune during April 2015 to April 2016

terrestrial sources, considering all Ca^{2+} to be of crustal origin and using crustal composition by Horn and Adams (1966). The anthropogenic source comprised EC, OC, and sum total of the non-sea salt and non-crustal fractions of all the abovementioned water-soluble ions (except NO_3^- and NH_4^+). It was observed that at sampling location, the major contribution was from anthropogenic sources (71%) followed by sea (26%) and crustal (3%) sources (Fig. 4).

Conclusions

Here, we present the first comprehensive dataset on the $PM_{2.5}$ aerosol mass concentration, aerosol major ion, and carbon species chemical composition, from the Pune, India, for the period of April 2015 to April 2016. The results suggest that chemical constituents and sources of $PM_{2.5}$ largely affected and vary with the seasons. High concentrations of most of the ions were observed during the winter season, which is a combined effect of fossil fuel/biomass burning from local as well as distant sources and prevailing meteorological conditions. The concentrations of TC (OC + EC) during the winter season were on an average two times higher than during other seasons in Pune. Organic matter (OM) estimated from measured OC and EC together formed the dominant component (56%) of $PM_{2.5}$ at Pune and OC alone accounted for nearly 77% of the total carbon. Good correlation observes between EC, OC, SO_4^{2-}, and NO_3^- shows common combustion sources for them. Ca^{2+} was correlated with Mg^{2+} and Cl^- which shows the possible presence of calcium and magnesium chloride. One-year averaged ratio of NO_3^-/SO_4^{2-} was 0.24 ± 0.18 indicating the dominance of stationary sources at the sampling site. The mean nss-K^+/EC ratio was 0.12 ± 0.09 which indicates fossil fuel dominance at Pune.

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