

Size-segregation and distribution of organic aerosol in different Industrial areas of Raipur region

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Abstract: Organic aerosol contributes a significant fraction of particulate matters PM which is responsible for the various cardiovascular and respiratory diseases in urban environments globally. In the present study, we have discussed the comparative studies of composition, sources, and distribution of organics ambient aerosols of various sugars primary saccharides (glucose, sucrose, trehalose, and fructose,) and sugar alcohols (mannitol and arabitol), together with laevoglucose, have been studied in ambient aerosols compounds are associated to PM10 in the various Industrial area (IA) of the most polluted city of central India, Raipur are discussed. The mean concentration levels of the organic aerosols (OA) in 07 locations of Raipur city such as Siltara, Urla, Hirapur, Bhanpuri, Mandir Hasod, Bhilai Steel Plant and Gudhiyari and the concentration varies of Sugar, Lignin, Fatty acid, Sterols, Fatty Alcohol, PAHs, Phthalate esters and n- alkane ranged from 37-890, 6-121, 356-1467, 40-1437, 51-436, 1-18, 1490-2847 and 13-475 ng m⁻³ with mean value (p = 0.05) of 188±287, 27±42, 279±427, 328±502, 85±131, 4±6, 314±480 and 109±167 ng m⁻³ respectively during Dec 2019. The concentration of organic aerosols in the industrial area was > 2-fold higher than in the city samples. The toxicity, composition and sources of organic aerosols are illustrated.

Keywords: PM10, Industrial pollution, Sources apportionment, Organic, Ambient aerosols.

Introduction

Aerosols can be introduced into the atmosphere either directly (primary aerosols) or formed from gas-phase precursors in the atmosphere (secondary aerosols). They scatter solar radiation either directly or by acting as CCN thus tending to balance the warming effect of greenhouse gases (IPCC, 2001). They also uptake numerous gaseous compounds in the atmosphere and provide the appropriate surfaces for heterogeneous chemical reactions thus altering the chemical composition of the particulate phase (Ravishankara, 1997). The sources of aerosols as well as the processes they undergo affect their size distribution. Natural occurring particles (e.g., dust, sea salt) or aerosol products from physical mechanisms (e.g. rock grinding, seawater droplet formation) mostly produce relatively large particles. On the other hand, anthropogenic particles especially near their sources are normally fine (e.g. combustion processes biomass burning and fossil fuel combustion). The Mediterranean, neighboring extended deserts in the south (e.g., Sahara) and industrialized areas of Europe in the north, is one of the areas heavily affected by aerosols. Indeed, PM10 measurements performed at various places both in the west and the eastern basin of the Mediterranean report a significant number of exceedances of the limits from the proposed legislation (Rodriguez et al., 2001; Querol et al., 2004; Andreae et al., 2002; Gerasopoulos et al., 2006). Natural mechanisms such as dust transport can significantly influence (up to 80%) the levels of measured PM10 (Viana et al., 2002). Under such circumstances, the utilization of PM10 for decreased systems is exceptionally sketchy. Increased air pollution has recently become a major health concern in the developing countries of Asia (Singh et al., 2004; Ramchandran et al., 2007). Several studies demonstrated that atmospheric particulate matter (PM) has an impact on climate, biogeochemical cycling in ecosystems, visibility, and human health (Broecker et al., 2000; Rinandli et al., 2007; Tsai et al., 2004; Vega et al., 2010; Kendall et al., 2011; Fuentes, 2009). More specifically, air pollution appears to have an adverse effect on respiratory and cardiovascular systems, which might result in an acute reduction of lung function, aggravation of asthma, increased rate of pneumonia in the elderly and high death rates in new-born (Nastos et al., 2010; Wilson et al., 2004). Because of PM's ability to enter the body via the respiratory tract, its size has important toxicological and regulatory relevance. Several studies in India have focused on particle size distributions including mass size distributions, number size distributions, or both. However, there is a lack of detailed analysis of size distributions of elements in particulate matter samples from India (Khemani et al., 1982; Balchandran et al., 2000; Venkatraman et al., 2002; Reddy et al., 2007; Chelani et al., 2010; Monkkonen et al., 2004; Sharma et al., 1992; Monkkonen et al., 2005; Baxla et al., 2009).

Experimental Methods

The samples were collected from Raipur (21°23' N, 81.63E) a city in Chhattisgarh state India for this study. It is the capital of the state of Chhattisgarh with a population of ≈ 2 million. Raipur is located near the center of a large plain and its vicinity is becoming an important regional commercial and industrial locale for various industries such as coal, power, steel, and aluminum industries, etc. At least 1000 steel rolling mills, sponge iron plants, steel foundries, metal-alloy plants, agro-industries, and plastic industries are running around the city. At 12% of the forest of the country is reserved in this state (SIA, 2016; NAAQS, 2009). The Anderson air sampler was installed in the Gudhiyari zone (21.2619° N, 81.6226° E) and other industrial areas Siltara, Urla, Hirasapur, Bhanpuri, Mandir Hasod, Bhilai Steel Plant for the collection of the PM10 segregated aerosols due to occurrence in the center of the city with dense habitats and large anthropogenic activities i.e., cooking and transportation (Fig. 1).

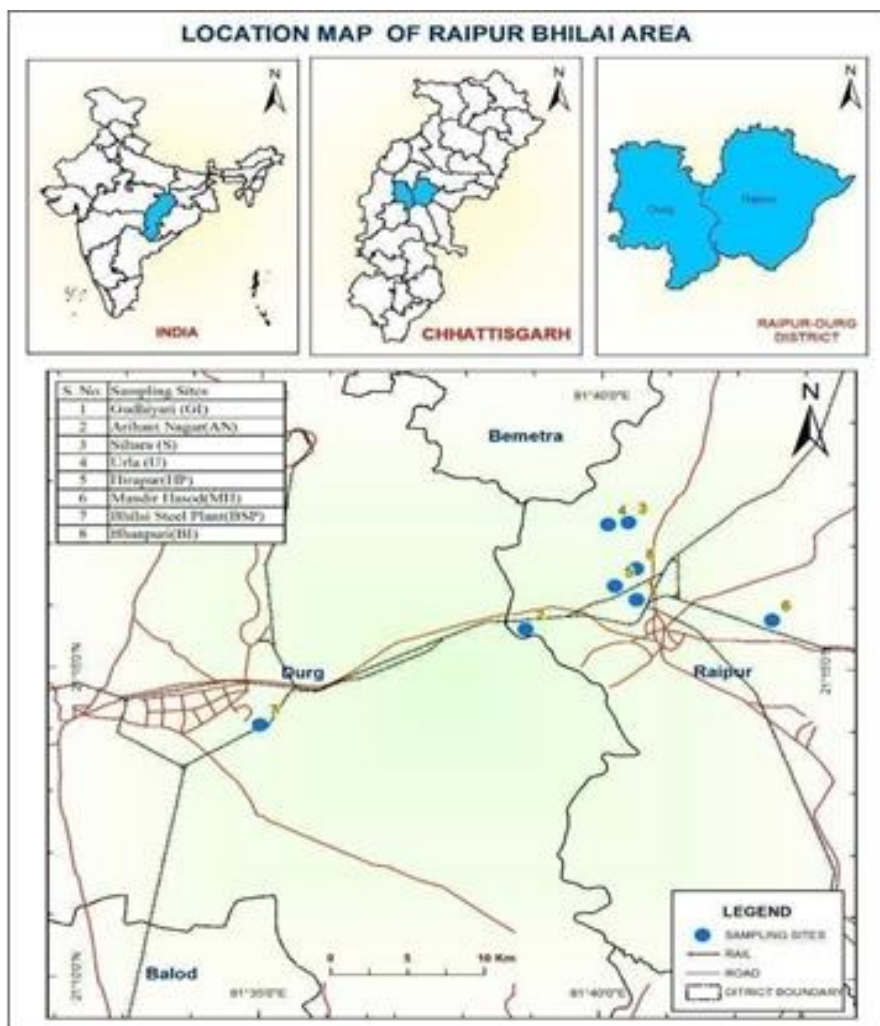


Fig. 1. Representation of sampling location in Industrial area, Raipur, CG.

Meteorology

The meteorological data such as temperature (T), humidity (H), rainfall (RF), vapour pressure (VP), evaporation pressure (EP), sunshine (SS), and wind speed (WS) for the study period were collected from the meteorological station at the Indira Gandhi Agricultural University, Raipur which is 50 Km far from the sampling location.

Collection of size segregated particulate matter

The collection of size-segregated PM was performed at the terrace of the double-storied building Industrial Area such as (Siltara, Urla, Hirasapur, Bhanpuri, Mandir Hasod, Bhilai Steel Plant and Gudhiyari) Raipur at an altitude of approximately 15 m from the ground level to make radiometer free

from nearby topographic targets like tall buildings and trees. Ambient PM samples were collected for the month of October on the Anderson sampler (1531-107B-G289X) with nine stages: PM_{10.0-9.0}, PM_{9.0-5.8}, PM_{5.8-4.7}, PM_{4.7-3.3}, PM_{3.3-2.1}, PM_{2.1-1.1}, PM_{1.1-0.7}, PM_{0.7-0.4}, and PM_{0.1} was used for the collection of size-segregated PM. The flow rate of the nine-stage cascade impactor was 28.3 per minute to make sure that fluctuation in flow rate, the flow rate of the nine-stage cascade impactor was checked five times during the sampling period. Aerosol particles were retained on 80 mm Whatmann 41 glass filters. The sampler was run for 48 hrs at the different industrial areas of the different zone. The loaded and blank filters were dried in oven for 6 hrs at 50 °C and weighed out their masses before sampling. The Power failure during the sampling hours was added for an additional sampling time period. The sampling was performed at a rate of 1.7 m³/h and in total 40.8 m³/day of air passed through each filter, nine-stage cascade impactor separated particles into nine size fractions between 0.1 and 10.0 µm, according to the following equivalent aerodynamic cutoff diameter, 10.0–9.0 (stage 1), 9.0–5.8 (stage 2), 5.8–4.4 (stage 3), 4.4–2.5 (stage 4), 2.5–2.1 (stage 5), 2.1–1.0 (stage 6), 1.0–0.7 (stage 7), 0.7–0.4 µm (stage 8) and ≥ 0.1 µm (stage 9). The PM₁₀, PM_{2.5-10}, PM_{2.5}, and PM₁ particles are presented in the sum up of particles of stage 0 to stage 8, stage 0 to stage 3, stage 4 to stage 7, and stage 6 to stage 7, respectively. After the collection of PM samples, the nine-stage cascade impactor (protected in polyethylene disposal plates) loaded with sampled filters was transported from the sampling site to the laboratory (SIA et al., 2004; Fu et al., 2008; Schauer et al., 1996; Pope et al., 2006). The filters were unloaded in a dust-free room and subsequently stored in petri dishes and transported to the weighing room for gravimetric analysis and all the filters were preserved in the freezer at -4 °C. They were sent to the Chinese Academy of Science, Beijing for the analysis of organic aerosols.

Gravimetric Analysis

The mass concentration of the collected size-segregated PM was determined by the gravimetric analysis. The filters were placed in vacuum desiccators for ~24 h before and after the sampling to remove the absorbed water and weighted in a controlled environment chamber after taking the filters out of the desiccators, using an electronic balance. All weight measurements were repeated three times to ensure reliability. The gravimetric mass (µg) was calculated as the subtraction of the weight of the filter after sampling from that of the prior sampling and the concentration (µg/m³) was determined by dividing the aerosol mass by the total volume of air sampled (m³). To ensure the quality of weighing, field blanks i.e., filters brought to the field and installed in the sampler but through which no air was pumped, were also collected. The filter mass obtained were corrected for field blank values (Deshmukh et al., 2010a; Deshmukh et al., 2011a; Deshmukh et al., 2010b).

Extraction

An aliquot of the filter (~10 cm²) was cut into pieces and extracted thrice with dichloromethane and methanol (2:1, v/v) under ultrasonication for 10 min (Zhu et al., 2005, Giri et al., 2013). The dissolvable concentrates were sifted through quartz wool pressed in a Pasteur pipette, concentrated by the utilization of a rotating evaporator, and afterward blown down to dryness with unadulterated nitrogen gas. The extracts were allowed to react with 50 ml of N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride and 10 ml of pyridine at 70°C for 3 hrs to derivatize the organics. The subsidiaries were diluted with 140 ml of n-hexane containing the inside standard (C13 n-alkane, 1.43ng ml⁻¹). Field and laboratory blank filters were treated as real samples for quality assurance.

Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) examinations of the derivatized complete concentrates were performed on a Hewlett-Packard model 6890 GC coupled to a Hewlett-Packard model 5973 mass-selective detector (MSD). The GC separation was achieved on a DB-5MS fused silica capillary column with a GC oven temperature program as described in the literature (Giri et al., 2013). The sample was injected on a split less mode at the injector temperature 280 °C. The mass spectrometer was worked on the electron impact (EI) mode at 70 eV by scanning from 50 to 650 Da. Mass spectral data was acquired and taken care of with the Chemstation software. Individual mixtures were recognized by contrasting mass spectra and those of writing and library information and authentic norms and by an understanding of mass fracture designs. GC-MS reaction variables of the individual compound were resolved utilizing authentic standards. Recovery experiments were performed by

spiking 10 cm² of blank filter with values of 100–200 ng of each standard and were treated as a real sample. This recovery experiment was repeated thrice. The results showed that average recoveries of the 66 standards, including n-alkanes, fatty alcohols, fatty acids, sugars, lignin and sterols in products, phthalate esters, aromatic acids, and sterols, were $\geq 80\%$. The field and the laboratory blank filters were also analyzed by the procedure described earlier in this section. The results showed no significant contamination except for bis (2-ethylhexyl) phthalate, whose field blank levels sometimes were higher compared to real samples and thus were not used in this study. The data reported here were corrected for the field blanks but not corrected for the recoveries. Filters were solvent-extracted with dichloromethane (DCM) followed by methanol using an accelerated solvent extraction (ASE) 300 apparatus (Dionex, California). The ASE parameters were 100 °C, static time 5 min, flush 50%, static cycles 2, and purge time 240 sec. For analysis of the particle phase polycyclic aromatic hydrocarbons (PAHs), a portion of the DCM extract was concentrated using a Turbovap® II (Caliper Life Sciences, Massachusetts) at 30 °C to ~600 μL , and then further concentrated to ~300 μL using a micro N₂ stream concentrator. The concentrated sample was spiked with isotopically labelled internal standards. The list of surrogate and internal standard compounds is given elsewhere (Giri et al., 2013). Two procedural blank filters were also extracted for the analysis. For total extract analyses, aliquots of the DCM and methanol extracts were combined (200 to 1000 μL total) and filtered. Aliquots (25 %) of these total extracts were converted to trimethylsilyl derivatives by reaction with N, O- bis- (trimethylsilyl) trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane and pyridine for 3 hrs at 70 °C prior to GC-MS.

Gas chromatography-mass spectrometry (GC-MS) in the selective ion monitoring (SIM) mode with both electron impact (EI) ionization and electron capture negative ionization (ECNI) was used for the identification and quantification of the particle phase PAHs and pesticides (Giri et al., 2013). Chromatographic separations were achieved on a DB-5MS column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The total extract of each sample was also analysed by GC-MS both as native and derivatized aliquots (20 μL). The GC-MS analyses were conducted using a Hewlett-Packard Model 6890 GC coupled to a Hewlett-Packard Model 5937 quadrupole MS operated in the full scan and electron impact mode at 70 eV ionization potential. The GC was equipped with a fused silica capillary column coated with DB-5MS (Agilent Scientific, 30 m x 0.25 mm i.d., film thickness 0.25 μm). The GC was temperature programmed as follows: hold at 65 °C for 2 min, ramp to 300 °C at 6 °C min⁻¹, and then hold isothermal at 300 °C for 20 min. The injector and MS ion source temperatures were maintained at 280 °C and 230 °C, respectively. The carrier gas was helium at a flow rate of 1.3 mL min⁻¹. Samples were injected in the splitless mode (splitless time: 30 s). The scan range was set from 50 to 650 Da at 1.27 scan s⁻¹. Compound identification was performed by comparison with the chromatographic retention characteristics and mass spectra of authentic standards reported mass spectra, and the mass spectral library of the GC-MS system. The mass spectra of unknown compounds were interpreted based on their fragmentation patterns. Compounds were quantified using total ion current (TIC) peak area and converted to compound mass using calibration curves of external standards: tetracosane for n- alkanes and n-alkenones, hexadecanoic acid for n- alkanic acids, alkyl alkanates and n- alkanols; sitosterol for sterols, triterpenoids and isoprenoids; sedoheptulose for monosaccharides; and sucrose for disaccharides. Two procedural blanks were analysed and presented no significant background interferences (Fig. 2).

Identification and quantification

Compound identification was performed by comparison with the chromatographic retention characteristics and mass spectra of authentic standards reported mass spectra and the mass spectral library of the GC-MS system. The mass spectra of unknown compounds were interpreted based on their fragmentation patterns. Compounds were quantified using total ion current (TIC) peak area and converted to compound mass using calibration curves of external standards: tetracosane for n-alkanes and n-alkenones, hexadecanoic acid for n- alkanic acids, alkyl alkanates and n-alkanol; sitosterol for sterols, triterpenoids and isoprenoids; sedoheptulose for monosaccharides; and sucrose for disaccharides with their MS key ion pattern (i.e., fragment grams m/z 85, 117, 75, 103, 217, 204, 193, 297, 312, 327, 239, 129, 163, 149, 357, 372, 306, 178, 202, 219, 234, 216, 228, 252, 276, 278, 300 respectively) and gas chromatographic retention times. Two procedural blanks were analyzed and presented no significant background interferences (Fig. 3).

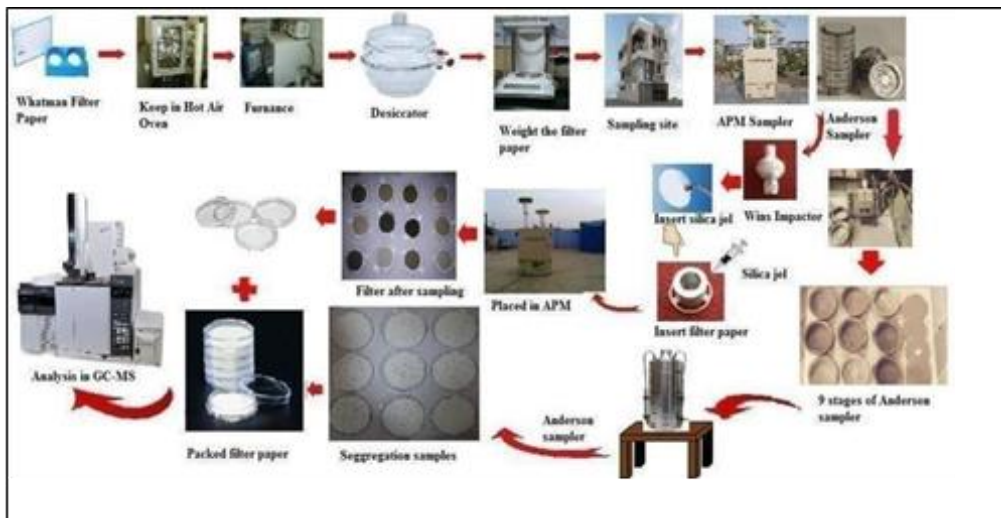
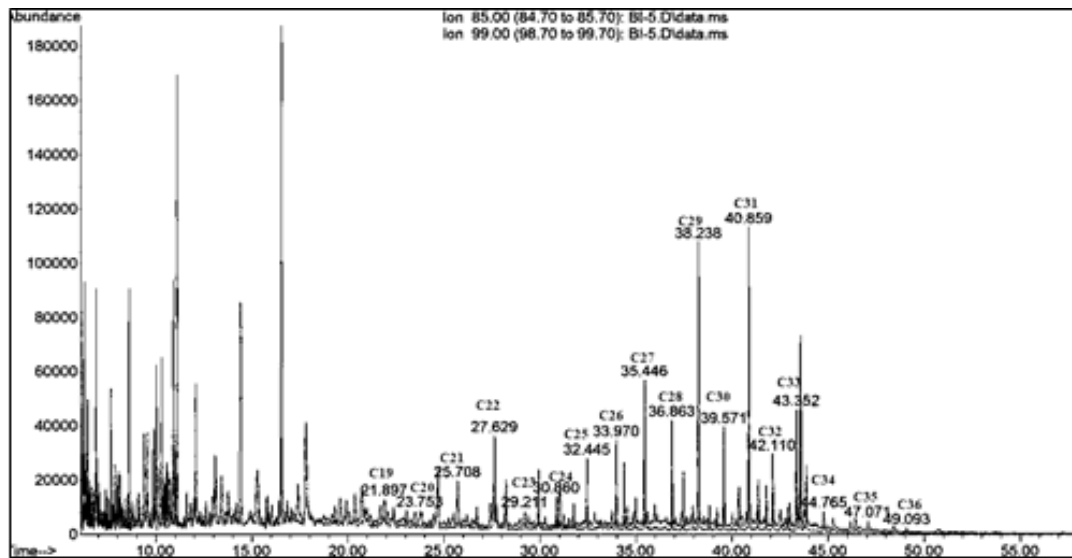
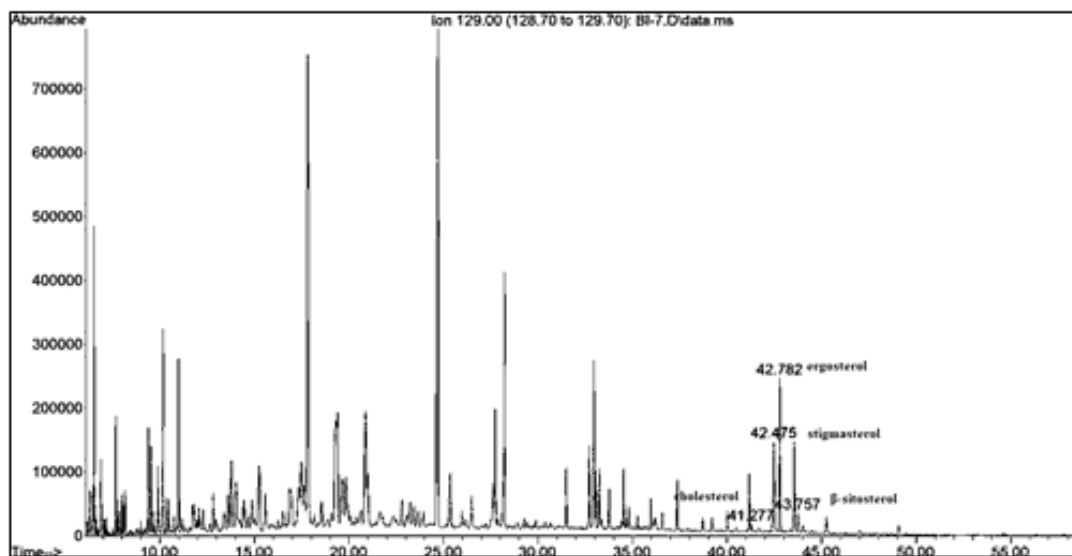


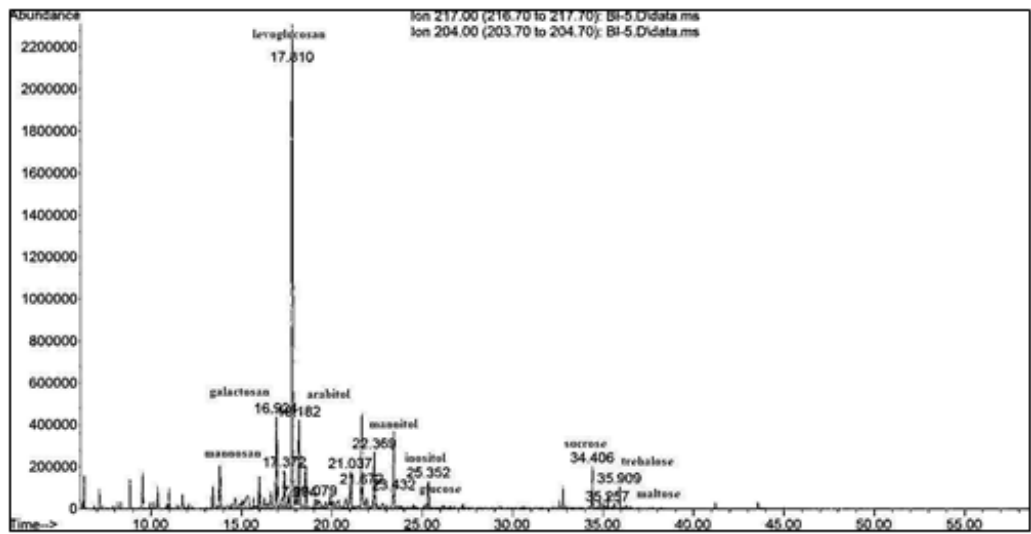
Fig. 2. Representation of sampling methodology in Industrial area, Raipur, CG.



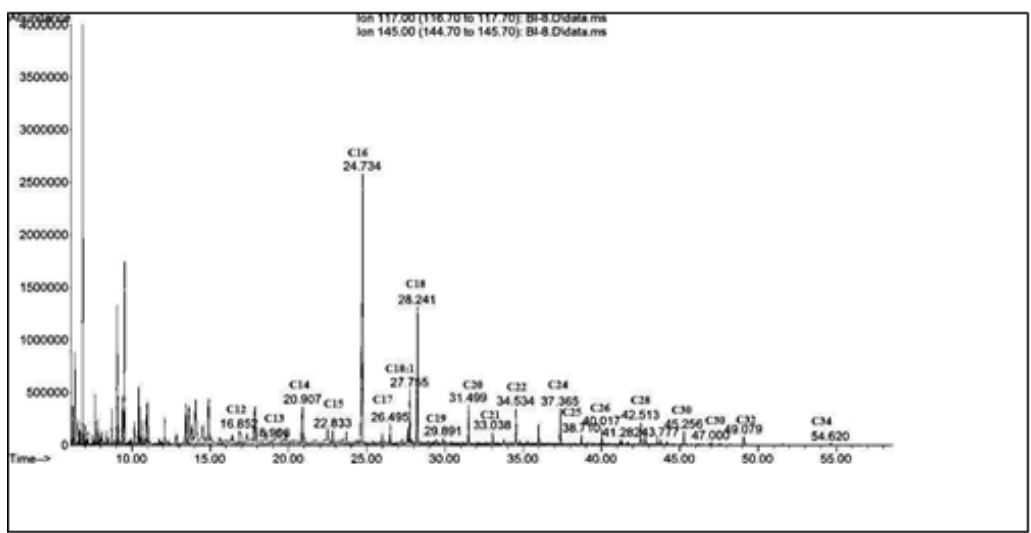
(a)



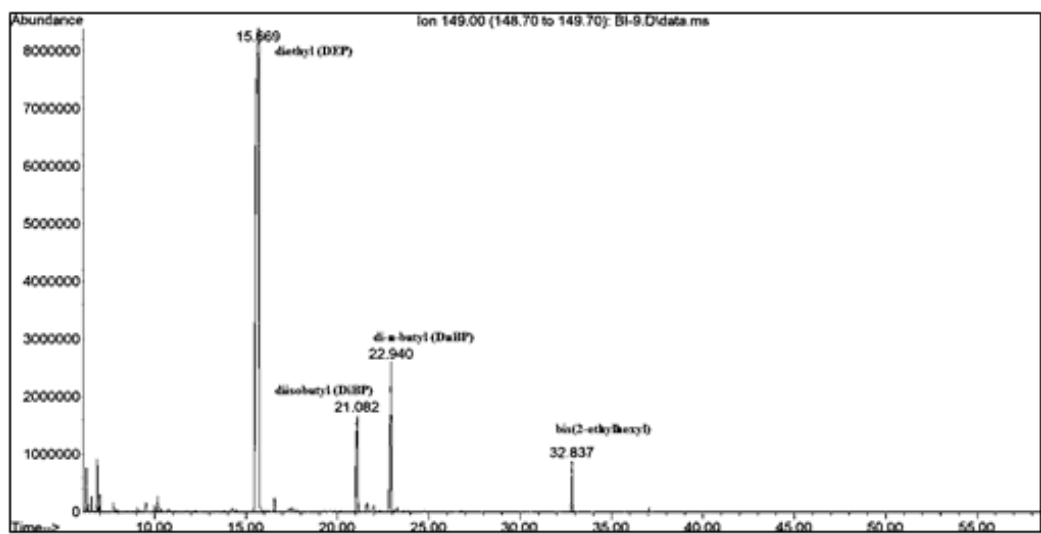
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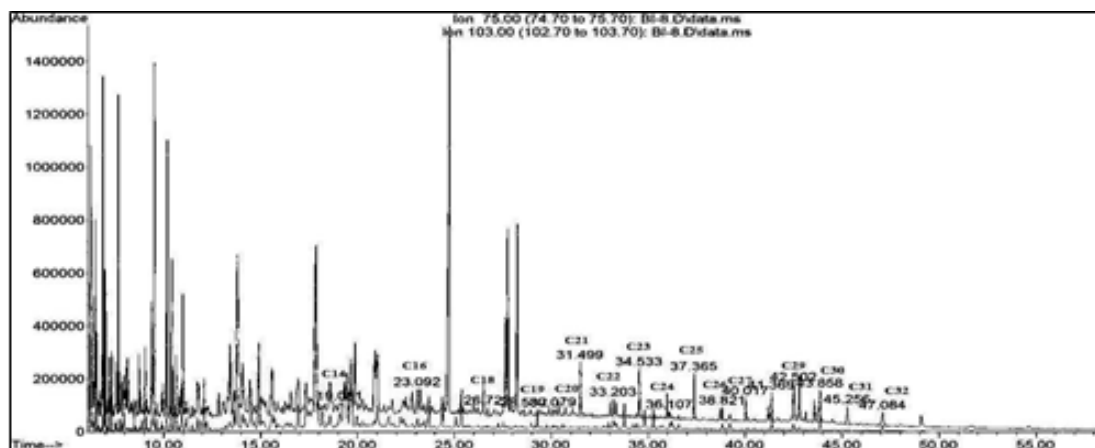
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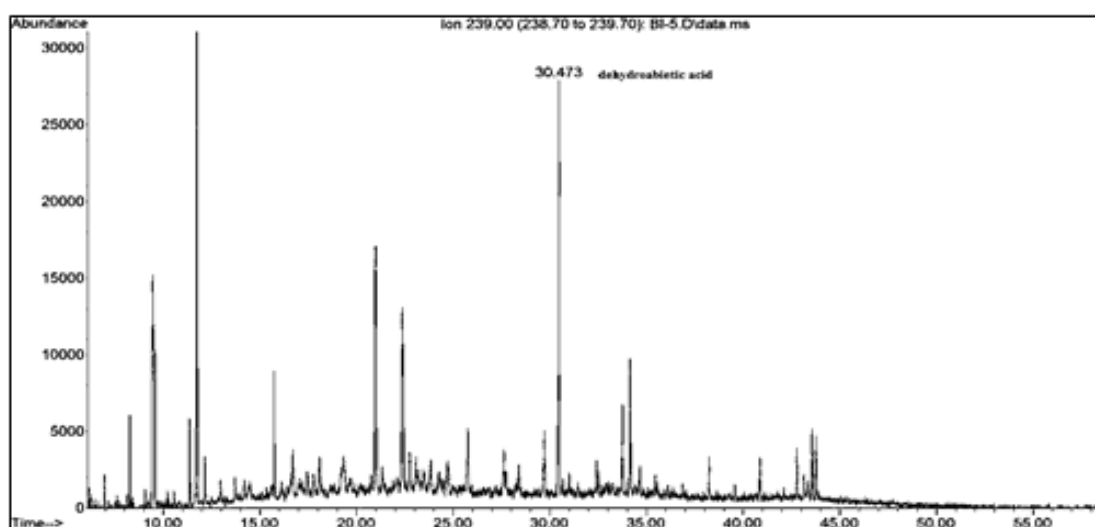
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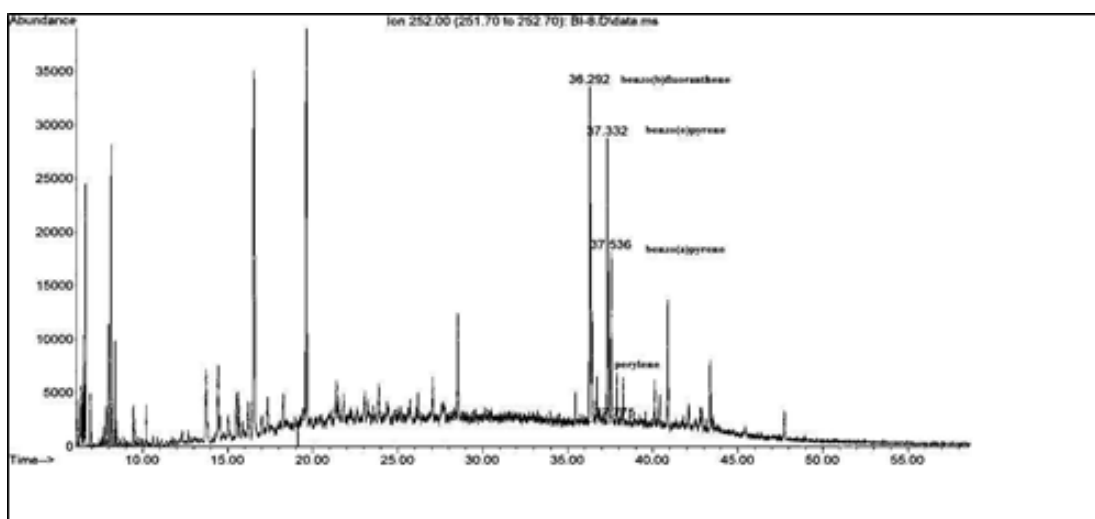
(e)



(f)



(g)



(h)

Fig. 3. Representation of GC-MS total ion current (TIC) traces of the major organic components detected in extracts from PM samples: (a) n-alkanes, (b) fatty acids, (c) fatty alcohols, (d) PAHs, (e) sterols, (f) sugar, (g) phthalate esters and (h) lignin and resin products.

Results and Discussion

Segregation

Selected trace organic compounds have been of interest for many years for adverse health effects (Didyk et al., 2000). Epidemiological studies have indicated that particles smaller than 10 μm have a significantly adverse effect on human health. Fine particles contain numerous trace organic species that are known to be carcinogenic and mutagenic and are small enough to penetrate deep into the lungs (Chen et al., 2015; Chen et al., 2016). The organic compounds i.e. Sugars, Lignin and Resin, Fatty acid, Sterols, Fatty alcohols, Polycyclic aromatic hydrocarbons, Phthalate esters and n-alkane associated to PM_{10} were segregated into nine modes i.e. $\text{PM}_{10.0-9.0}$, $\text{PM}_{9.0-5.8}$, $\text{PM}_{5.8-4.7}$, $\text{PM}_{4.7-3.3}$, $\text{PM}_{3.3-2.1}$, $\text{PM}_{2.1-1.1}$, $\text{PM}_{1.1-0.7}$, $\text{PM}_{0.7-0.4}$ and $\text{PM}_{0.1}$ was ranged from 37–890, 6–121, 356–1467, 40–1437, 51–436, 1–18, 1490–2847, 13–475 with the mean value ranged from 285 ± 188 , 30 ± 27 , 613 ± 279 , 334 ± 328 , 143 ± 85 , 5 ± 4 , 1859 ± 314 , 125 ± 109 ng m^{-3} respectively. All classes (except phthalates and PAHs) of compounds exhibited higher accumulation tendency in the fine and ultrafine modes (Fig. 4) (Fu et al., 2008; Zhu et al., 2005; Giri et al., 2013). The PAHs showed higher accumulating tendency only in the ultrafine mode. However, phthalates largely accumulated in the coarse modes. Similar size segregated accumulation patterns of organic compounds have been reported by Sevimglu et al. (2015) (Table 1).

Organic Composition

Sugars: Thirteen sugar compounds i.e. (Galactosan, Mannosan, Levoglucosan, Arabitol, Fructose, Glucose, Mannitol, Inositol, Sucrose, Trehalose, Xylose and Maltose) was detected and concentration in nine modes was ranged from 1–112, 1–79, 27–462, 0–10, 0–17, 1–25, 1–105, 0–22, 1–152, 0–83, 0–9, 2–33, 0–15 ng m^{-3} with the mean value of 24 ± 25 , 18 ± 17 , 140 ± 107 , 4 ± 2 , 6 ± 4 , 9 ± 5 , 16 ± 22 , 7 ± 5 , 30 ± 33 , 13 ± 17 , 2 ± 2 , 12 ± 7 , 3 ± 3 ng m^{-3} respectively. The higher concentrations of PM in the sugar compounds are found in the fine to ultrafine modes i.e. ($\text{PM}_{1.1-0.7}$ and $\text{PM}_{0.7-0.4}$) in all the study locations area and among them, the highest concentration is found in the levoglucosan which is used as a specific indicator of emissions from burning of biomass (Fraser et al., 2000) (Fig. 5).

Lignin and Resin: Five lignin and resin products such as (3-hydroxybenzoic acid, 4-hydroxybenzoic acid, vanillic acid, syringic acid, dehydroabietic acid) were determined. The concentration was ranged from 1–66, 2–27, 1–16, 0–10 and 0–2 ng m^{-3} with the mean value ranged from 15 ± 16 , 8 ± 6 , 2 ± 4 , 1 ± 2 ng m^{-3} respectively. The higher concentration of lignin and resin is found in fine to ultrafine mode i.e. ($\text{PM}_{1.1-0.7}$ and $\text{PM}_{0.7-0.4}$) and the highest concentration is found in the 3-hydroxybenzoic acid may be due to the chemical industries which produce numerous amounts of synthetic organic compounds and they are used for different purpose and cause adverse health impacts (Simoncit et al., 2005) (Fig. 5).

Fatty Acids: Twenty-four compounds of fatty acids C12:0 – C34:0 and C18:1 – C18:2 is analyzed. The concentration of PM is found higher in the fine to ultrafine mode i.e. ($\text{PM}_{1.1-0.7}$ and $\text{PM}_{0.7-0.4}$) and in each nine modes concentration varies from 19–41, 1–4, 34–98, 4–18, 110–414, 1–21, 0–47, 0–13, 1–53, 1–62, 0–17, 0–42, 0–13, 0–77, 0–18, 0–63, 0–10, 0–54, 0–22, 1–85, 70–326 ng m^{-3} respectively, with the mean value ranged from 28 ± 4 , 2 ± 1 , 67 ± 15 , 9 ± 3 , 206 ± 78 , 6 ± 5 , 13 ± 10 , 3 ± 3 , 14 ± 12 , 16 ± 14 , 5 ± 4 , 10 ± 9 , 3 ± 3 , 18 ± 17 , 4 ± 4 , 13 ± 14 , 3 ± 3 , 8 ± 12 , 4 ± 5 , 18 ± 18 , 155 ± 63 ng m^{-3} . The highest concentration of PM is found in the C16:0 (n- Hexadecanoic acid) in the fine modes i.e. ($\text{PM}_{0.7-0.4}$) stage as it indicates the multiple sources from microbial land lesser vascular plant detritus (Volkman et al., 1981) (Fig. 5).

Sterols: Five sterols compounds are detected such as (Cholesterol, b-cholesterol, ergosterol, stigmasterol, b-sitosterol) and the concentration of each compound was ranged from 0–19, 5–50, 0–570, 0–607, 0–191 ng m^{-3} respectively, with the mean value ranged from 1 ± 4 , 5 ± 9 , 11 ± 133 , 4 ± 145 , 20 ± 46 ng m^{-3} . The higher concentration was found in the fine or ultrafine modes i.e. ($\text{PM}_{1.1-0.7}$ and $\text{PM}_{0.7-0.4}$) and the remarkable high concentration was found in the ergosterol and stigma sterol may be due to biogenic sources which occur in all ecosystems and they can be utilized to identify the origin and fate of organic mass present in the environment (Volkman et al., 1981) (Fig. 5).

Fatty Alcohol: Nineteen compounds of fatty alcohols i.e. (Σ C14 - C32) are analyzed. The total concentration of PM is found to be high in the ultrafine mode i.e. ($PM_{1.1-0.7}$ and $PM_{0.7-0.4}$) and the concentration was ranged from 0–3, 6–15, 0–3, 1–9, 1–7, 1–17, 0–17, 0–54, 0–18, 0–41, 1–9, 0–57, 1–16, 0–4, 2–40, 1–89, 2–50, 0–18, 1–64 $ng\ m^{-3}$ respectively, with the mean value ranged from 2 ± 1 , 9 ± 2 , 1 ± 1 , 6 ± 2 , 2 ± 1 , 4 ± 3 , 13 ± 12 , 5 ± 4 , 6 ± 9 , 4 ± 2 , 11 ± 13 , 7 ± 3 , 2 ± 1 , 16 ± 7 , 19 ± 22 , 21 ± 10 , 4 ± 4 , 13 ± 13 $ng\ m^{-3}$ respectively, and the highest concentration of PM is found in C29 (1-Nonacosanol) may be due to multiple sources from microbial and lesser vascular plant detritus (Rushdi et al., 2006) (Fig. 5).

Polycyclic Aromatic Hydrocarbons

In this study twenty compounds of PAHs were detected i.e. (anthracene (Ant), anthanthrene (AA), benzo(b)fluorene, benzo(a)anthracene (Baa), chrysene (Chry), benzo(b) fluoranthene (Bbf), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), indeno (1,2,3-cd)pyrene (Ind), dibenz(a,h)anthracene (Dba), benzo(ghi)perylene (BghiP), coronene (Cor) and benzo(k)fluoranthrene (Bkf), fluoranthene (Fla), phenanthrene (Phe), pyrene (Pyr), perylene (Per), retene, 1,3,4-triphenylbenzene, 1,2,4-triphenylbenzene) were detected and out of these eight compounds such as (1,3,5-phenylbenzene, 1,2,4-phenylbenzene, anthracene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(e)pyrene, benzo(a) pyrene, benzo(ghi)perylene) concentration was ranged from 0–4, 0–3, 1–5, 0–4, 0–1, 0–2, 0–1, 0–3 $ng\ m^{-3}$ with the mean value of 0 ± 1 , 1 ± 1 , 3 ± 1 , 0 ± 1 , 0 ± 1 $ng\ m^{-3}$ respectively. The remarkable high concentration was found in the fine to ultrafine mode ($PM_{1.1-0.7}$ and $PM_{0.7-0.4}$) and Anthracene has highest concentration as compare to other compounds due to the pyrolysis products from the incomplete combustion of organic matter which are mainly associated with fine particles (Wogan et al., 2004) (Fig. 5).

Phthalate Ester

Six compounds of phthalate esters such as (Dimethyl (DMP), Diethyl (DEP), Di- iso-butyl (DiBP), Di-n-butyl (DnBP), Di-(2-ethylhexyl) (DEHP), BPA) were detected. The concentration was ranged from 0–2, 1011–2468, 97–258, 23–146, 32–69, 0–7 $ng\ m^{-3}$ with the mean value ranged from 1 ± 0 , 1591 ± 277 , 152 ± 37 , 71 ± 31 , 43 ± 9 , 2 ± 2 $ng\ m^{-3}$ respectively. The higher concentration is found in all the nine modes i.e. ($PM_{10.0-9.0}$, $PM_{9.0-5.8}$, $PM_{5.8-4.7}$, $PM_{4.7-3.3}$, $PM_{3.3-2.1}$, $PM_{2.1-1.1}$, $PM_{1.1-0.7}$, $PM_{0.7-0.4}$ and $PM_{0.1}$) and the remarkable high concentration was found in the Diethyl (DEP) ester as compare to other compounds as they are used as plasticizers to increase its stability and flexibility to prevent brittleness as a solvent for fragrances ingredients (Jakkola et al., 2008) (Fig. 5).

n-Alkane: Eighteen compounds of n-alkane i.e. (C19–C36) were identified. The concentration of each compound was ranged from 1–2, 0–1, 1–2, 0–4, 0–1, 0–1, 0–6, 0–2, 1–38, 0–12, 1–56, 0–20, 1–168, 0–40, 0–111, 0–6, 0–5 $ng\ m^{-3}$ with the mean value ranged from 1 ± 0 , 2 ± 0 , 1 ± 1 , 1 ± 0 , 2 ± 1 , 1 ± 1 , 10 ± 9 , 3 ± 3 , 17 ± 12 , 5 ± 5 , 41 ± 40 , 9 ± 9 , 27 ± 27 , 2 ± 2 , 1 ± 1 , 1 ± 1 $ng\ m^{-3}$ respectively. The higher concentration was found to be accumulated in the fine modes to ultrafine modes ($PM_{1.1-0.7}$ and $PM_{0.7-0.4}$) and the highest concentration was found in the C31 (n- hentriacontane) as lipid components contributes by many sources such as terrestrial plant waxes, emissions from the fossil fuels, etc. (Lin et al., 2004, Katiyar et al., 2002; Karar et al., 2006; Rushdi et al., 2006) (Fig. 5).

PMF Analysis: Positive matrix factorization (EPA PMF 5.0) model was used to identify PM_{10} sources and to estimate their sources contribution. According to PMF model results, Factor 1 represents higher loading of different Sugar congeners including glucose, arabitol and fructose which contributes 0.8% of total sources. It includes high loading of Triacontanoic acid and fructose sugars. This factor was highly constituent with the characteristic emissions sources from the burning of wood combustion, moreover, burning of crop straws, plant wax and other sources. Therefore, factor 1 was designated to biomass burning which is shown in Figure 6. Another is factor 2 which represents higher loading of levoglucosan and mannitol. It contributes 18.4% of the total sources and it clearly showed various mixed combustion sources i.e., wood, petroleum and coal combustion and factor 2 represents deposition from mobile pyrogenic and biomass combustion emission i.e., mixed combustion sources in the study area, (Fig. 6). Factors 3 was greatly loaded with fructose, Sucrose and galactosan which contributed 80.8% of total sources which indicated the highest among all the factor contributions. Higher loading was

found Sucrose and galactosan which are also been called as organic molecular marker of coal combustion which when used in power plant, steel and iron industries and coke oven, etc. Thus, factor 3 was designated to coal combustion and industrial sources (Fig. 6).

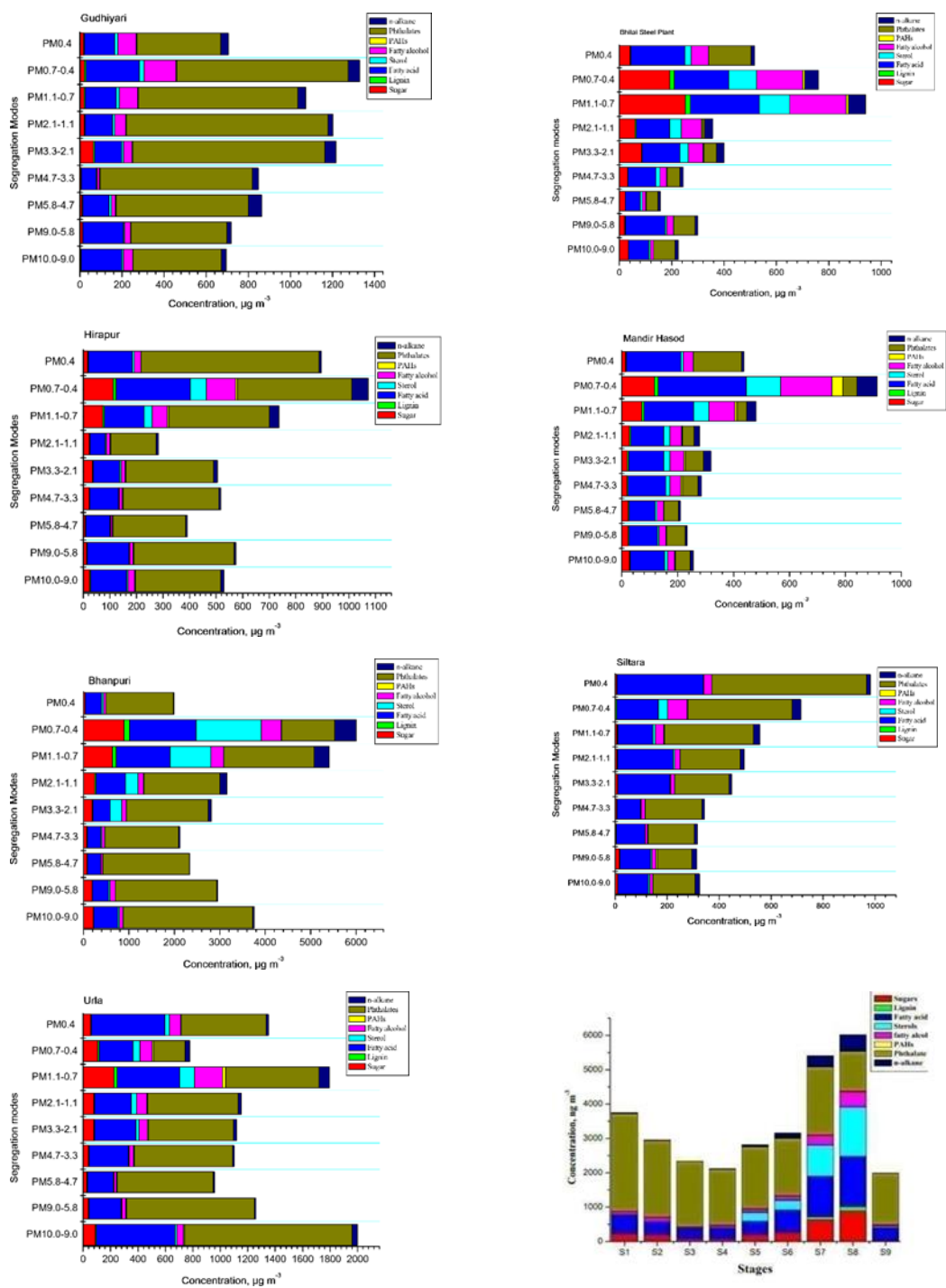


Fig. 4. Segregation of PM₁₀ associated organics (Fatty acids, Phthalate, Fatty alcohols, Sugars, PAHs, Sterols, n-alkane, Lignin) in ambient air from (A-H).

Table1. Concentration of organic compounds in PM₁₀ of segregation.

n-alkanes			S1	S2	S3	S4	S5	S6	S7	S8	S9
Compounds	Formula	MW									
n-nonadecane	C ₁₉ H ₄₀	268	1	1	1	1	2	2	2	1	1
n-icosane	C ₂₀ H ₄₂	282	0	0	0	1	0	0	0	0	0

n-heneicosane	C21H44	296	2	1	1	1	1	1	2	2	2
n-docosane	C22H46	310	0	0	0	0	4	0	1	1	0
n-tricosane	C23H48	324	1	0	0	0	0	1	0	1	0
n-tetracosane	C24H50	338	1	1	0	0	1	0	1	1	0
n-pentacosane	C25H52	352	1	1	0	1	2	2	4	6	0
n-hexacosane	C26H54	366	1	1	0	1	2	2	2	2	0
n-heptacosane	C27H56	380	4	2	1	2	5	11	27	38	1
n-octacosane	C28H58	394	1	1	0	1	4	5	6	12	0
n-nonacosane	C29H60	408	11	6	1	6	11	20	35	56	2
n-triacontane	C30H62	422	1	1	0	1	3	8	13	20	0
n-hentriacontane	C31H64	436	9	6	1	5	14	48	119	168	3
n-dotriacontane	C32H66	450	1	1	0	1	3	13	26	40	1
n-tritriacontane	C33H68	464	2	2	0	2	7	33	82	111	2
n-tetatriacontane	C34H70	478	0	0	0	0	2	4	4	6	0
n-pentatriacontane	C35H72	492	0	0	0	0	1	1	2	6	0
n-hexatriacontane	C36H74	506	0	0	0	0	0	1	1	5	0
Total			37	23	7	23	63	155	329	475	13

PAHs

Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
1,3,4-triphenylbenzene	C35H72	306	0	0	0	0	0	0	0	4	0
1,2,4-triphenylbenzene	C36H74	306	0	0	0	0	1	3	3	0	0
Phenanthrene	C24H18	178	0	0	0	0	0	0	0	0	0
Anthracene	C24H18	178	2	1	1	2	5	5	4	4	1
Fluoranthene	C14H10	202	0	0	0	0	0	0	0	0	0
Pyrene	C14H10	202	0	0	0	0	0	0	0	0	0
Benzo(b)fluorene	C16H10	216	0	0	0	0	0	0	0	0	0
Benzo(a)anthracene	C16H10	228	0	0	0	0	0	0	0	0	0
Chrysene	C20H12	228	0	0	0	0	0	0	0	0	0
Benzo(b) fluoranthene	C18H12	252	0	0	0	0	0	0	0	4	0
Benzo(e) pyrene	C18H12	252	0	0	0	0	0	0	1	0	0
Benzo(a)pyrene	C20H12	252	0	0	0	0	0	0	0	2	0
Perylene	C20H12	252	0	0	0	0	0	0	1	1	0
Benzo(k)fluoranthren	C20H12	252	0	0	0	0	0	0	0	0	0
Indeno(1,2,3-cd)pyrene	C20H12	276	0	0	0	0	0	0	0	0	0
Dibenz(a,h)anthracene	C22H12	278	0	0	0	0	0	0	0	0	0
Benzo(ghi)perylene	C22H14	276	0	0	0	0	0	0	0	3	0
Anthanthrene	C22H12	276	0	0	0	0	0	0	0	0	0
Coronene	C22H12	300	0	0	0	0	0	0	0	0	0
Retene	C24H12	219	0	0	0	0	0	0	0	0	0
Total			2	1	1	2	6	9	8	18	1

Lignin and Resin

Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
3-hydroxybenzoic acid	C7H6O3	138	2	2	1	1	2	11	47	66	1
4-hydroxybenzoic acid	C7H6O3	138	4	3	4	3	4	7	17	27	2

Vanillic acid	C8H8O3	168	2	2	2	1	2	3	11	16	1
Syringic acid	C9H10O5	198	0	0	0	0	1	2	5	10	0
Dehydroabietic acid	C20H28O2	300	1	1	1	1	1	2	2	2	0
Total			9	9	7	6	9	25	82	121	6

Sugars

Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
Galactosan	C6H10O5	180	4	4	1	3	11	17	64	112	2
Mannosan	C6H10O5	162	2	2	1	3	10	23	42	79	1
Levoglucozan	C6H10O5	162	46	38	27	36	99	164	366	462	27
Arabitol	C5H10O5	152	5	2	2	6	10	2	2	4	0
Fructose	C6H12O6	180	12	3	1	1	2	5	11	17	0
Glucose	C6H12O6	180	25	5	2	3	7	6	17	17	1
Glucose	C6H12O6	180	17	6	2	2	5	3	105	4	1
Mannitol	C6H14O6	182	3	19	6	7	22	1	7	1	0
Inositol	C6H12O6	182	3	73	18	1	6	15	3	152	1
Sucrose	C12H22O11	342	83	0	0	7	9	4	6	8	1
Tehalose	C12H22O11	342	6	0	0	3	9	2	0	0	0
Xylose	C5H10O5	150	11	33	17	2	4	5	12	19	2
Maltose	C12H22O11	342	0	3	1	0	1	2	0	15	0
Total			217	188	78	75	194	249	635	890	37

Sterols

Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
Cholesterol	C27H46O	386	1	1	0	2	3	9	10	19	1
b-cholestetrol	C27H46O	386	13	14	8	13	17	12	17	50	5
Ergosterol	C28H44O	396	10	8	0	10	37	120	367	570	11
Stigmasterol	C29H44O	412	0	0	0	0	54	99	407	607	4
β -sitosterol	C29H50O	536	7	6	0	6	141	39	99	191	20
Total			31	28	9	30	252	278	899	1437	40

Fatty Acids

Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
Dodecanoic acid	C12H24O2	200	41	27	26	21	29	25	33	28	19
Tridecanoic acid	C13H26O2	214	2	1	1	1	2	2	4	3	1
Tetradecanoic acid	C14H28O2	228	94	54	58	48	34	71	91	59	98
Pentadecanoic acid	C15H30O2	242	11	8	6	4	5	10	18	15	6
Hexadecanoic acid	C16H32O2	256	230	151	121	110	123	188	396	414	117
Heptadecanoic acid	C17H34O2	270	2	2	2	2	3	3	19	21	1
Octadecanoic acid	C18H36O2	284	0	0	0	0	0	0	0	0	0
Nonadecanoic acid	C19H38O2	298	5	4	2	3	6	16	31	47	0
Eicosanoic acid	C20H40O2	312	1	0	0	0	1	4	8	13	2
Heneicosanoic acid	C21H42O2	326	3	2	1	3	7	19	36	53	1
Docosanoic acid	C22H44O2	340	0	0	0	1	2	11	21	33	3
Tricosanoic acid	C23H46O2	354	4	3	1	4	8	22	35	62	1
Tetracosanoic acid	C24H48O2	368	1	0	0	1	3	7	12	17	2
Pentacosanoic acid	C25H50O2	382	2	2	0	2	7	13	20	42	0
Hexacosanoic acid	C26H52O2	396	0	0	0	0	2	5	6	13	3
Heptacosanoic acid	C17H34O2	270	3	3	0	3	11	24	43	77	0
Octacosanoic acid	C28H56O2	424	0	0	0	1	4	6	10	18	0

Nonacosanoic acid	C29H58O2	438	3	2	0	0	0	18	30	63	3
Triacontanoic acid	C14H28O2	228	0	0	0	2	10	3	0	10	0
Henatriacontanoic acid	C31H62O2	466	0	0	0	0	0	9	7	54	0
Dotriacontanoic acid	C32H64O2	480	0	0	0	0	3	1	22	15	0
Tetracontanoic acid	C34H68O2	508	0	0	0	0	0	0	0	0	0
Octadecenoic acids	C18H34O2	282	4	3	3	2	11	9	43	85	1
Octadecadienoic acid	C18H32O2	280	127	92	70	84	116	179	304	326	98
Total			532	357	290	292	387	645	1187	1467	356
Fatty Alcohols											
Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
Myristyl alcohol	C14H30O	214	2	2	2	3	1	2	0	0	3
Cetyl alcohol	C16H34O	242	8	8	7	7	6	11	15	14	9
Heptadecyl alcohol	C17H36O	256	1	0	1	0	1	2	0	3	0
Stearyl alcohol	C18H38O	270	9	5	7	5	8	6	3	-1	8
Nonadecan-1-ol	C19H40O	284	1	1	1	2	1	2	3	7	1
Arachidyl alcohol	C20H42O	298	1	1	2	1	1	3	5	17	2
Heneicosyl alcohol	C21H44O	312	7	5	0	5	8	1	34	54	3
Docosanol	C22H46O	326	2	2	0	2	2	5	12	18	1
Tricosan-1-ol	C23H48O	340	0	41	2	1	1	1	2	2	0
Lignoceryl alcohol	C24H50O	354	4	2	2	2	3	4	6	9	1
Pentacosan-1-ol	C25H52O	368	3	3	2	0	1	1	31	57	3
Ceryl alcohol	C26H54O	382	6	5	1	6	7	8	9	16	2
1-Heptacosanol	C27H56O	396	0	2	2	1	1	1	3	4	3
Montanyl alcohol,	C28H58O	410	15	12	2	14	20	16	18	40	4
1-Nonacosanol	C29H60O	424	1	5	3	5	1	1	66	89	3
Myricyl alcohol,	C30H62O	438	16	12	2	14	22	28	50	42	6
1-hentriacontanol	C31H64O	452	0	5	2	0	12	18	0	0	0
1-Dotriacontanol	C32H66O	466	3	2	1	1	5	14	23	64	1
Total			79	115	38	67	100	123	281	436	51
Phthalate Esters											
Compounds	Formula	MW	S1	S2	S3	S4	S5	S6	S7	S8	S9
Dimethyl (DMP)	C10H10O4	194	2	1	1	1	1	1	0	0	0
Diethyl (DEP)	C12H14O4	222	2468	1922	1657	1439	1480	1439	1695	1011	1204
Diisobutyl (DiBP)	C16H22O4	278	258	234	162	122	116	125	140	97	115
Di-n-butyl (DnBP)	C16H22O4	278	68	44	56	28	146	30	109	23	136
Bis 2-ethylhexyl	C24H38O4	390	52	33	33	34	59	69	38	32	35
BPA	C15H16O2	228	0	0	0	0	2	7	5	3	0
Total			2847	2235	1909	1624	1803	1671	1987	1166	1490

Table 2. Total Concentration of organic compounds in PM10 of size segregation.

Locations	Size	T°C	RH %	WS	Suga	Ligni	FA	Stero	F	PAH	Pht	n-
Bhilai Steel	PM10.0-9.0	94°F	22.50	12.7	34	0	78	7	12	0	81	13
	PM9.0-5.8				21	2	151	6	27	1	81	11
	PM5.8-4.7				22	0	57	8	14	1	46	8
	PM4.7-3.3				32	1	107	15	26	1	50	12
	PM3.3-2.1				86	1	145	32	56	2	50	27
	PM2.1-1.1				60	5	127	45	76	4	8	32
	PM1.1-0.7				251	20	264	116	21	9	0	66
	PM0.7-0.4				193	17	207	107	17	7	0	53
	PM0.4				41	3	206	24	67	1	161	14

Bhanpuri	PM10.0-9.0	98°F	17%	18	217	9	532	31	79	2	284	37
	PM9.0-5.8				188	9	357	28	11	1	223	23
	PM5.8-4.7				78	7	290	9	38	1	190	7
	PM4.7-3.3				75	6	292	30	67	2	162	23
	PM3.3-2.1				194	9	387	252	10	6	180	63
	PM2.1-1.1				249	25	645	278	12	9	167	155
	PM1.1-0.7				635	82	1187	899	28	8	198	329
	PM0.7-0.4				890	121	1467	1437	43	14	116	475
Urla	PM0.4	33°C	15%	15	37	6	356	40	51	1	149	13
	PM10.0-9.0				90	7	572	14	50	7	122	37
	PM9.0-5.8				37	5	234	6	29	5	932	10
	PM5.8-4.7				29	3	187	6	18	4	703	7
	PM4.7-3.3				40	4	287	5	32	5	716	11
	PM3.3-2.1				78	7	301	23	59	7	621	24
	PM2.1-1.1				77	8	267	37	75	6	659	24
	PM1.1-0.7				224	23	455	109	20	24	681	74
Mandir	PM0.7-0.4	23°C	43%	22	107	11	246	51	91	8	229	33
	PM0.4				54	5	538	31	84	2	619	17
	PM10.0-9.0				27	3	123	12	24	2	54	11
	PM9.0-5.8				23	3	101	7	24	2	67	7
	PM5.8-4.7				23	3	94	6	23	2	52	7
	PM4.7-3.3				19	4	134	15	39	5	57	12
	PM3.3-2.1				20	5	125	23	50	5	64	27
	PM2.1-1.1				28	4	117	23	42	3	41	20
Hirapur	PM1.1-0.7	88°F	42%	42.5	71	8	17A	55	93	7	35	33
	PM0.7-0.4				116	14	316	122	18	39	52	71
	PM0.4				14	2	196	7	36	1	173	7
	PM10.0-9.0				24	3	136	5	26	3	321	11
	PM9.0-5.8				12	3	157	2	14	3	376	7
	PM5.8-4.7				7	2	92	2	6	2	274	5
	PM4.7-3.3				22	2	108	3	12	3	360	7
	PM3.3-2.1				34	3	99	7	15	3	329	14
Siltara	PM2.1-1.1	39°C	42.60	15	23	2	57	5	14	2	171	8
	PM1.1-0.7				73	7	148	31	58	5	379	36
	PM0.7-0.4				113	10	279	61	11	8	430	61
	PM0.4				16	3	166	7	25	1	670	8
	PM10.0-9.0				11	0	117	5	11	1	163	16
	PM9.0-5.8				16	2	119	4	17	4	132	20
	PM5.8-4.7				4	1	109	1	10	1	179	11
	PM4.7-3.3				6	2	90	2	14	2	217	11
Gudhiyari	PM3.3-2.1	35.5°	84%	13	9	2	199	3	16	1	208	10
	PM2.1-1.1				7	2	214	5	22	1	230	16
	PM1.1-0.7				7	4	134	10	32	2	343	25
	PM0.7-0.4				1	5	161	34	75	3	402	33
	PM0.4				6	2	331	2	31	0	595	14
	PM10.0-9.0				3	2	193	9	44	1	420	24
	PM9.0-5.8				11	3	192	6	28	2	457	20
	PM5.8-4.7				10	4	125	12	18	2	628	64
	PM4.7-3.3				5	2	70	4	12	2	723	30
	PM3.3-2.1				64	5	128	11	39	3	915	52
	PM2.1-1.1				20	3	132	11	51	3	958	25
	PM1.1-0.7				19	6	146	17	86	3	758	37
	PM0.7-0.4				22	6	254	23	15	4	816	54
	PM0.4				16	5	144	15	88	4	398	35

Correlation

The correlation coefficient matrix for PM10 and organic constituents is summarized in Table 3. The organics i.e., FA, Alk, PAH, PhT and sugar has a partial correlation with the PM₁₀. The organics i.e., n- alkane, fatty alcohols, fatty acids, polycyclic aromatic hydrocarbons and sterols among themselves had a partial correlation. The phthalates had a negative correlation with the fatty acids, sugars, and resin,

and lignin products. However, the resin and lignin products exhibited partial correlation with all elements except phthalate.

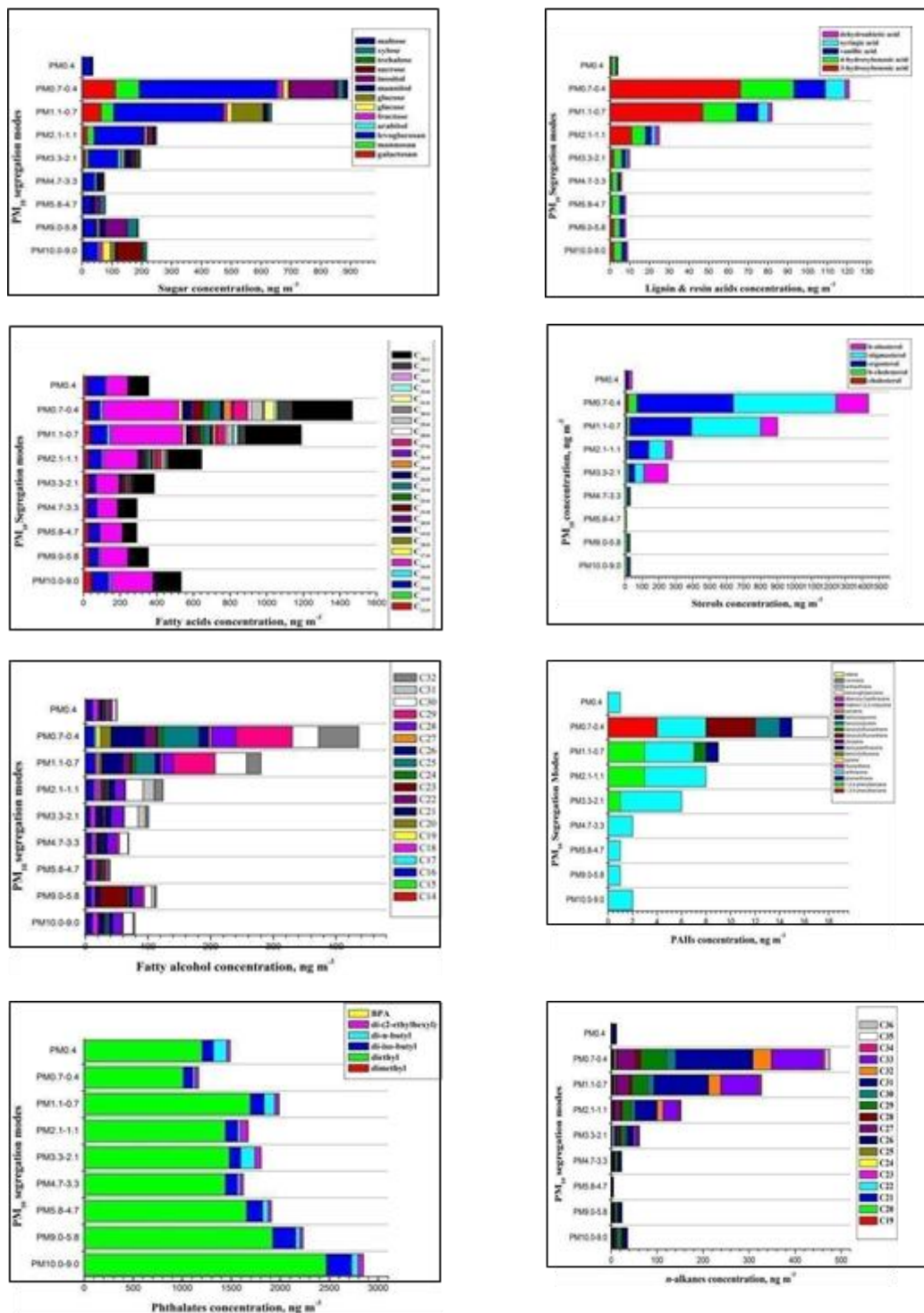


Fig. 5. Segregation modes of PM10 in different organic compounds.

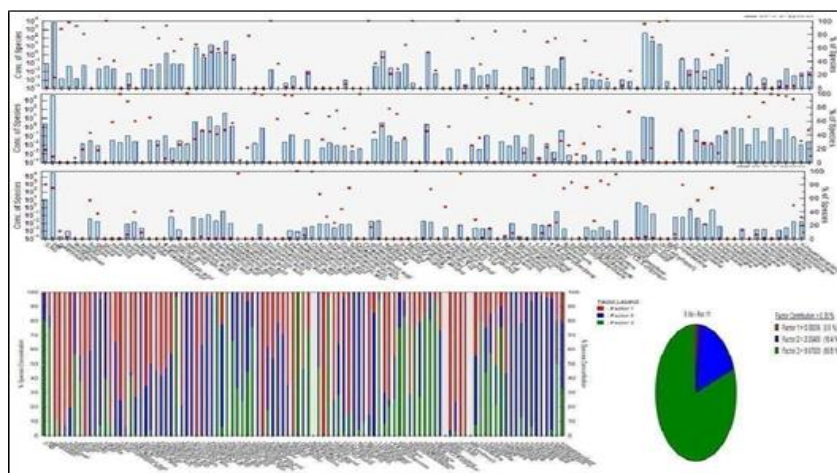


Fig. 6. Source profile for the PMF analysis.

Table 3. Correlation matrix of PM and organic constituents.

	PM10	OA	SU	LIG	FA	Sterols	F Alc	PAHs	Phth	Alk
PM10	1									
OA	0.34	1								
SU	0.37	0.97	1							
LIG	0.30	0.93	0.98	1						
FA	0.25	0.97	0.98	0.98	1					
Sterols	0.30	0.92	0.98	0.99	0.97	1				
F Alc	0.38	0.94	0.99	0.99	0.97	0.98	1			
PAHs	0.36	0.81	0.89	0.89	0.89	0.93	0.91	1		
Phth	0.01	-	-	-	-	-0.48	-0.41	-0.54	1	
Alk	0.30	0.93	0.98	0.99	0.99	0.99	0.98	0.93	-	1
									0.44	

Conclusions

The data reported in this study constitute the results of size-segregated PM measurement in the urban area of Industrial area in Raipur, Chhattisgarh, India. The results showed that the annual mean concentrations of PM₁₀ and PM_{2.5} were considerably higher than the NAAQS of India. Therefore, the magnitude of PM pollution in Raipur likely has a significant impact on the surrounding region. Therefore, it is recommended that some effective control measures should be implemented in order to reduce at least the local anthropogenic pollution in Raipur and to protect human health. PM₁₀ is proved to be mainly constituted of PM_{2.5}, thereby increasing the concerns for PM health hazards. As indicated in this study, coarse mode PM (PM_{10-2.5}) was largely attributed to crustal sources like dust, while fine mode was particularly from anthropogenic sources. All organics except phthalates are accumulated in the fine and ultrafine modes in all the industrial area.

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