Spatial Variation, Distribution and Source Impacts in Urban Organic Aerosols

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In this work, comparative studies of the distribution, composition and sources of organics (*n*-alkanes, lignin and resin products, sterols, phthalate esters and polycyclic aromatic hydrocarbons) associated to PM_{10} in the residential, highway and industrial areas of the most polluted city of central India, Raipur city is described. The mean concentration levels of organic aerosols in 13 locations of Raipur city ranged from 10006-36601 ng m^{-3} with a mean value (p = 0.05) of 18703 ± 5942 ng m^{-3} during December-January, 2013-14. The concentration of organic aerosols in highway and industrial sites were > 2 fold higher than in the city samples. The composition, toxicity and sources of organic aerosols are discussed.

Keywords: Organic aerosols, Air quality, Urban pollution.

INTRODUCTION

Organic aerosols in ambient air are composed of complex mixtures of several organics [1,2]. They are generated from chemical reactions in the atmosphere (multi-functional oxygenates) or from incomplete combustion processes (*e.g.*, polycyclic aromatic hydrocarbons, *etc*.) The gas-phase oxidation of atmospheric organics produce a wide variety of multifunctional organic products, some having sufficiently low vapours pressures to exist primarily in the condensed (particulate) form [3]. In addition, semi-volatile organic compounds in the atmosphere distribute between the gas and particle phases. The partition between the two phases is important for understanding both atmospheric chemistry and human toxicology. Both major and minor chemical constituents of atmospheric aerosols have been used as atmospheric tracers and indicators of aerosol sources [4]. Organic compounds constitute a major fraction of particulate matter in the atmosphere in urban areas, often over 40 % of fine particulate mass (PM). Fine particulate mass has an important impact on air quality [5-7].

The organic composition of atmospheric aerosols is needed to understand human health impact, cloud nucleation properties, radiative forcing and visibility degradation [8-12]. The comprehensive studies on the organic composition of urban aerosols during the last decade have been performed for urban locations in Belgium, China, Hong Kong, India and USA [13-19]. The concentrations, seasonal patterns and source-receptor relationships that govern the individual compounds present in carbonaceous aerosol is known poorly [20].

The distribution and sources of organic traces in the ambient air of Raipur region during winter season at some locations were reported [19]. In this work, the comparative investigation of organic tracers such as *n*-alkanes, polycyclic aromatic hydrocarbons, sterols, lignin and resins and phthalates esters distribution in the PM_{10} of Raipur region at residential, highway and industrial locations during period: December-January of year, 2013-14 was carried out to know their spatial variations, composition, sources and toxicities.

EXPERIMENTAL

Study area: The industrial and vehicular, emissions generate significant amounts of particulates in ambient air of Raipur city of India, causing climate, environmental and health impacts

[21,22]. Raipur (21º23′ N, 81.63E) is a capital of Chhattisgarh state with population of approximately two millions. It is located near the centre of a large plain, and its vicinity is becoming an important regional commercial and industrial locale for coal, power, steel and aluminium industries. At least 1000 steel rolling mills, sponge iron plants, steel foundries, metal-alloy plants, agro-industries, and plastic industries are running in and around the city [21].

Meteorology: All meteorological data such as temperature, humidity, rain fall, vapour pressure, evaporation, sun shine and wind speed for the study period was collected from the meteorological station operated at the Indira Gandhi Agricultural University, Raipur, India.

Collection of particulate matter: Thirteen PM_{10} samples were collected from different 13 locations, *i.e.* Professor colony (PC), Santoshinagar (SN), Telibandha (TB), Avanti vihar (AV), Devendra nagar (DN), Kalibadi (KB), Tatiya para (TP), Arihant nagar (AN), Ramnagar (RN), Kota (KT), Gogaon (GG), Sarora (SA) and Siltara (SI) of Raipur city as shown in Fig. 1.

An APM 250 combined PM_{10} and $PM_{2.5}$ air sampler (Lata Envirotech, New Delhi) with 16 L/min flow rate was used for the collection of particulate matter (PM) using quartz fibre filters in moulded filter cassettes. A sample blank was also taken from each location. The sampler was installed on the roof of a building, ≈ 10 m above ground level. Filters were heated to 600 ºC prior to use to lower their background levels and placed in cleaned polyethylene dishes. Weighed filters were put in the sampler and run continuously for 12 h from 6.00 a.m.-6.00 p.m. The loaded filters were dismounted, wrapped with aluminium foil, placed in a polyethylene dish and brought to the laboratory. The filters were transferred into desiccators and weighed to record the total particulate matter (PM) content. Total 13 PM_{10} samples were collected during the month of December-January, 2013-14. The filter was preserved in at - 4 ºC and analyzed the organic aerosols contents at the Chinese Academy of Science, Beijing, China.

Extraction: An aliquot of the filter (≈ 10 cm^2) was cut into pieces and extracted thrice with dichloromethane and methanol (2:1, v/v) under ultrasonication for 10 min [23]. The solvent extracts were filtered through quartz wool packed in a Pasteur pipette, concentrated by the use of a rotary evaporator and then blown down to dryness with pure 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 ºC for 3 h to derivative the organics. The derivatives were diluted with 140 mL of *n*-hexane containing the internal standard (C13 *n*-alkane, 1.43 ng mL^{-1}). Field and laboratory blank filters were treated as the real samples for quality assurance.

Gas chromatography-mass spectrometry: Gas chromatography-mass spectrometry (GC-MS) analyses of the derivatized total extracts were performed on a Hewlett-Packard model 6890 GC coupled to 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 [23]. The sample was injected on a splitless mode at the injector temperature at 280 ºC. The mass spectrometer was operated on the electron impact (EI) mode

at 70 eV by scanning from 50 to 650 Da. Mass spectral data were acquired and processed with the Chemstation software. Individual compounds were identified by comparing mass spectra with those of literature and library data and authentic standards and by interpretation of mass fragmentation patterns. GC-MS response factors of individual compound were determined using authentic standards.

Recovery experiments were performed by spiking10 cm^2 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 Andres in products, phthalate esters, aromatic acids, and sterols were ≥ 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 ºC, static time 5 min, flush 50 %, static cycles 2 and purge time 240 s. For analysis of the particle phase polycyclic aromatic hydrocarbons (PAHs), a portion of DCM extract was concentrated using a Turbovap® II (Caliper Life Sciences, Massachusetts) at 30 ºC to ~600 μL and then further concentrated to ~300 μL using a micro N_2 stream concentrator. The concentrated sample was spiked with isotopically labelled internal standards. The list of surrogate and internal standard compounds is given elsewhere [24]. Two procedural blank filters were also extracted for the analysis.

For total extract analyses, aliquots of dichloromethane 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 BSTFA containing 1 % trimethylchlorosilane and pyridine for 3 h at 70 ºC 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 [23]. Chromatographic separations were achieved on a DB-5MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The total extract of each sample was also analyzed 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 × 0.25 mm i.d., film thickness 0.25 μm). The GC was temperature programmed as follows: hold at 65 ºC for 2 min, ramp to 300 ºC at 6 ºC min^{-1} and then hold isothermal at 300 ºC for 20 min. The injector and MS ion source temperatures were maintained at 280 and 230 ºC, respectively. The carrier gas was helium at a flow rate of 1.3 mL min^{-1}. Samples
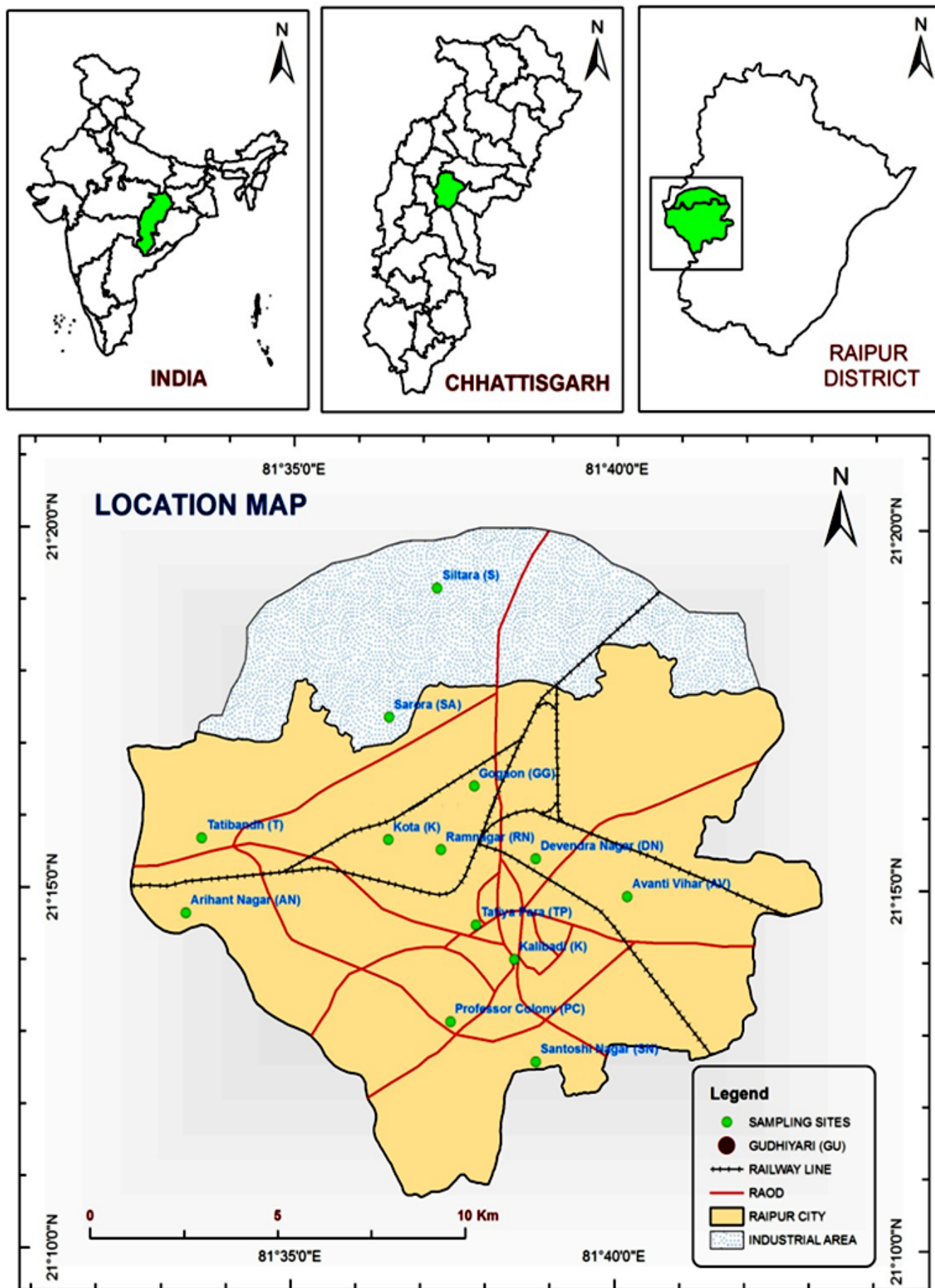
Fig. 1. Representation of sampling location of Raipur city

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 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*-alkanones, hexadecanoic acid for *n*-alkanoic acids, alkyl alkanoates and *n*-alkanols; sitosterol for sterols, triterpenoids and isoprenoids; sedoheptulose for monosaccharides; and sucrose for disaccharides. Two procedural blanks were analyzed and presented no significant background interferences.

Identification and quantification: The identification of *n*-alkanes, sterols, lignin and resin, polycyclic aromatic hydrocarbon and phthalates ester is based primarily on their MS key ion pattern (*i.e.*, fragment grams *m/z* 85, 193, 297, 312, 327, 239, 129, 163, 149, 357, 372, 306, 178, 202, 219, 234, 216, 228, 252, 276, 278 and 300, respectively) and gas chromatographic retention times. Retention times were compared with those of external standards. Quantification was performed from the total ion current (TIC) GC profiles using the external standard method with authentic compounds of each homologous series. Average response factors were calculated for each compound. All quantifications were based on the peak areas of the compounds derived from the TIC trace.

RESULTS AND DISCUSSION

Meteorology and aerosol concentration: Generally, the wind blew from South-West (SW) to North-East (NE) during the sample collection months in Raipur city. The meteorological parameters for the study period are summarized in (Table-1). The temperature, relative humidity, vapour pressure, evaporation, wind speed and sun shine for the study period ranged from 18-22 ºC, 58-67 %, 7.4-11.4 mm, 2.3-3.4 mm day^{-1}, 0.3-5.4 km h^{-1} and 4.19.5 h day^{-1} with mean value of 20 ºC, 61 %, 9.5 mm, 2.8 mm day^{-1}, 1.7 km h^{-1} and 7.9 h day^{-1}, respectively. Among them, VP and SS had fare positive and negative correlation with PM_{10} and organic aerosol concentration, respectively (r = 0.50 - 0.56 and -0.59 - 0.73) (Table-2). The concentration of PM_{10} ranged from 291-783 µg m^{-3} with mean valve of 468 ± 82 µg m^{-3}. The concentration of PM_{10} was remarkably higher (> 1.4-2.2 folds) in the highway and industrial area of the city (Table-1). The concentration of PM_{10} was found several folds higher than recommended value of 20 g m^{-3} at different locations [25].

Organic compounds: Homolog's of 8 compound classes of organic aerosols (OA) such as *n*-alkanes, lignin and resin products, sterols, phthalate esters and polycyclic aromatic hydrocarbons (PAHs) were determined in the aerosol samples (Table-3). The total concentration of organic aerosols was ranged from 2232-36601 ng m^{-3} with mean value (p = 0.05) of 16816 ± 4713 ng m^{-3}. The organic aerosols concentration in the residential, highway and industrial area of the city ranged from 2232-10866, 11276-25231 and 26734-36601 ng m^{-3} with

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TABLE-1
PM₁₀ SAMPLING DETAILS AND METEOROLOGY

S. No.	Sampling location	Date	PM_{10} (µg m^{-3})	Temp. (°C)	RH (%)	VP (mm)	WS (km h^{-1})	EP (mm day^{-1})	SS (h day^{-1})
1	Professor Colony (PC)	05.12.2013	325	19.1	59	9.9	1.4	3.4	8.7
2	Santoshi Nagar (SN)	07.12.2013	383	18.6	67	9.6	1.8	3.3	9.1
3	Telibandha (T)	10.12.2013	372	18.0	59	8.7	1.0	3.0	8.7
4	Avanti Vihar (AV)	11.12.2013	291	19.2	58	8.5	1.7	3.0	9.1
5	Devendra Nagar (DN)	13.12.2013	458	19.4	59	7.4	0.7	2.4	8.3
6	Kalibadi (K)	15.12.2013	354	18.7	59	8.1	2.7	3.3	9.5
7	Tatiya Para (TP)	17.12.2013	454	20.1	58	8.5	0.3	2.3	7.6
8	Arihant Nagar (AN)	19.12.2013	309	21.3	64	9.6	5.4	2.6	7.4
9	Ramnagar (RN)	20.12.2013	736	20.5	64	10.1	1.3	3.0	8.5
10	Kota (K)	22.12.2013	472	20.3	66	11.4	0.9	2.4	8.4
11	Go Gaon (GG)	23.12.2013	372	22.0	61	9.6	0.7	2.4	6.7
12	Sarora (SA)	31.12.2013	783	19.1	64	10.8	1.5	2.7	6.6
13	Siltara (SI)	21.01.2014	750	18.6	60	11.3	2.2	3.1	4.1

TABLE-2
CORRELATION MATRIX OF PM AND ORGANIC CONSTITUENTS

	T	RH	V	W	PM_{10}	Phth	PAH	Sterols	Alk	LRP
T	1									
RH	0.02	1								
V	0.16	0.68	1							
W	-0.06	0.17	-0.15	1						
PM_{10}	0.49	0.27	0.04	-0.09	1					
Phth	0.51	-0.18	-0.60	0.33	0.42	1				
PAH	0.10	0.08	0.12	-0.18	0.75	-0.07	1			
Sterols	-0.30	0.16	0.08	-0.15	0.05	-0.31	0.25	1		
Alk	-0.06	0.19	0.10	-0.08	0.43	-0.22	0.42	0.48	1	
LRP	0.23	0.01	0.19	-0.28	-0.08	-0.16	-0.07	-0.25	-0.30	1

TABLE-3
CONCENTRATION OF ORGANIC COMPOUNDS IN PM OF SPATIAL VARIATION

Compound	m.f.	m.w.	SA 1	SA 2	SA 3	SA 4	SA 5	SA 6	SA 7	SA 8	SA 9	SA 10	SA 11	SA 12	SA 13
_n_-alkanes															
_n_-Nonadecane	$C_{19}H_{40}$	268	6	10	8	7	35	7	14	11	7	8	7	19	31
_n_-Eicosane	$C_{20}H_{42}$	282	12	3	10	5	42	5	11	4	11	14	8	12	45
_n_-Heneicosane	$C_{21}H_{44}$	296	13	11	17	15	52	26	34	33	66	54	17	60	59
_n_-Docosane	$C_{22}H_{46}$	310	19	7	9	9	79	3	10	8	163	18	8	36	67
_n_-Tricosane	$C_{23}H_{48}$	324	12	11	13	9	51	7	23	12	311	42	12	40	69
_n_-Tetracosane	$C_{24}H_{50}$	338	9	13	18	11	73	12	21	20	328	45	14	42	71
_n_-Pentacosane	$C_{25}H_{52}$	352	38	26	34	7	111	26	154	33	381	85	27	67	82
_n_-Hexacosane	$C_{26}H_{54}$	366	54	34	36	23	127	46	43	37	224	72	22	48	68
_n_-Heptacosane	$C_{27}H_{56}$	380	79	74	65	44	143	104	287	71	243	121	30	77	66
_n_-Octacosane	$C_{28}H_{58}$	394	71	69	63	35	138	170	62	58	171	111	20	54	41
_n_-Nonacosane	$C_{29}H_{60}$	408	123	136	134	84	201	257	124	173	220	209	47	114	84
_n_-Triacontane	$C_{30}H_{62}$	422	69	75	85	39	143	230	73	90	128	120	24	63	39
_n_-Hentriacontane	$C_{31}H_{64}$	436	107	142	150	194	208	242	155	220	187	232	51	135	76
_n_-Dotriacontane	$C_{32}H_{66}$	450	39	52	63	32	102	147	75	66	101	95	17	53	23
_n_-Tritriacontane	$C_{33}H_{68}$	464	59	80	93	51	135	130	122	156	122	175	32	107	35
_n_-Tetratriacontane	$C_{34}H_{70}$	478	18	23	28	10	37	64	31	27	47	51	10	32	15
_n_-Pentatriacontane	$C_{35}H_{72}$	492	24	36	35	17	93	25	54	82	38	53	11	44	9
Hexatriacontane	$C_{36}H_{74}$	506	13	18	24	7	45	13	40	38	21	32	0	27	8
Total			**764**	**819**	**887**	**600**	**1817**	**1514**	**1332**	**1139**	**2770**	**1539**	**357**	**1031**	**556**
CPI			**1.59**	**1.90**	**1.78**	**2.62**	**1.28**	**1.29**	**3.06**	**2.46**	**1.36**	**1.93**	**1.94**	**1.95**	**1.33**
PAHs															
1,3,4-Triphenyl-benzene	$C_{24}H_{18}$	306	0	0	1	0	1	0	1	1	2	0	1	1	1
1,2,4-Triphenyl-benzene	$C_{24}H_{18}$	306	4	3	5	6	10	6	13	5	15	0	8	8	2
Phenanthrene	$C_{14}H_{10}$	178	0	0	0	0	0	0	0	0	1	0	0	0	0
Anthracene	$C_{14}H_{10}$	178	34	36	26	22	100	72	94	36	78	0	48	130	86
Fluoranthene	$C_{16}H_{10}$	202	19	1	10	7	34	9	27	30	18	0	10	151	99
Pyrene	$C_{16}H_{10}$	202	0	0	0	0	19	0	15	0	22	0	0	19	8
Benzo(b)fluorene	$C_{17}H_{12}$	216	0	0	0	0	0	0	0	0	7	0	0	3	1
Benzo(a)anthracene	$C_{18}H_{12}$	228	0	4	8	4	5	3	12	7	50	0	3	9	0
Chrysene	$C_{18}H_{12}$	228	9	0	0	0	3	0	30	2	44	0	2	124	21
Benzo(b)fluoranthene	$C_{20}H_{12}$	252	32	6	25	17	132	28	189	85	198	0	63	394	54
Benzo(e) pyrene	$C_{20}H_{12}$	252	1	0	1	0	13	0	22	0	24	0	3	30	14
Benzo(a)pyrene	$C_{20}H_{12}$	252	0	0	0	0	43	1	60	0	76	0	7	76	0
Perylene	$C_{20}H_{12}$	252	0	0	0	0	0	0	1	0	10	0	0	0	0
Benzo(k)fluoranthren	$C_{20}H_{12}$	252	0	0	0	0	0	0	1	0	0	0	1	0	0
Indeno(1,2,3-cd)-pyrene	$C_{22}H_{12}$	276	0	0	0	0	34	0	63	9	55	0	2	45	2
dibenz(a,h)anthracene	$C_{22}H_{14}$	278	0	0	0	0	5	0	9	0	10	0	0	8	0
Benzo(ghi)perylene	$C_{22}H_{12}$	276	0	0	0	0	24	0	51	0	62	0	0	30	0
Anthanthrene	$C_{22}H_{12}$	276	0	0	0	0	0	0	0	0	0	0	0	2	0
Coronene	$C_{24}H_{12}$	300	0	0	0	0	14	0	19	0	10	0	2	17	0
Retene	$C_{18}H_{18}$	219	1	0	0	0	5	0	0	0	6	0	0	2	1
Total			**103**	**52**	**78**	**58**	**444**	**122**	**608**	**177**	**689**	**0**	**152**	**1050**	**292**
Lignin and Resin															
3-Hydroxybenzoic acid	$C_7H_6O_3$	138	1	0	2	2	13	2	30	4	43	46	4506	20	14
4-Hydroxybenzoic acid	$C_7H_6O_3$	138	24	11	19	19	81	32	139	44	239	241	539	83	46
Vanillic acid	$C_8H_8O_3$	168	12	17	9	6	29	7	72	21	74	65	27	144	38
Syringic acid	$C_9H_{10}O_5$	198	4	2	1	2	10	4	69	2	57	70	6	22	4
Dehydroabietic acid	$C_{20}H_{28}O_2$	300	13	4	4	8	62	9	55	10	134	203	20	52	6
Total			**53**	**33**	**35**	**36**	**195**	**55**	**366**	**82**	**547**	**624**	**5099**	**321**	**108**

Sterols																
Cholesterol	$C_{27}H_{46}O$	386	88	85	96	71	263	65	134	145	54	235	49	178	34
β-Cholestetrol	$C_{27}H_{46}O$	386	163	192	110	134	2243	137	372	322	439	326	99	240	164
Ergosterol	$C_{28}H_{44}O$	396	475	462	420	309	873	412	660	839	445	1444	173	881	147
Stigmasterol	$C_{29}H_{44}O$	412	0	10	9	5	32	9	31	0	19	13	4	15	3
β-Sitosterol	$C_{29}H_{50}O$	536	135	245	130	154	401	183	394	500	218	412	26	305	60
Total			**861**	**994**	**765**	**672**	**3811**	**806**	**1591**	**1806**	**1176**	**2430**	**352**	**1618**	**408**
Phthalate esters																
Dimethyl (DMP)	$C_{10}H_{10}O_4$	194	4	1	3	0	1	1	0	3	0	0	1	0	0
Diethyl (DEP)	$C_{12}H_{14}O_4$	222	0	0	0	559	0	330	0	0	0	0	0	0	28596
Diisobutyl (DiBP)	$C_{16}H_{22}O_4$	278	1957	1808	4040	3449	1523	2333	1328	2523	0	1539	1165	2069	972
di-*n*-butyl (DnBP)	$C_{16}H_{22}O_4$	278	149	57	60	96	44	69	153	155	0	162	51	334	322
Bis 2-ethylhexyl	$C_{24}H_{38}O_4$	390	1117	1073	852	1020	888	806	1411	895	748	1953	694	977	428
BPA	$C_{15}H_{16}O_2$	228	0	0	0	0	0	0	8	0	17	8	0	0	72
Total			**3227**	**2938**	**4955**	**5124**	**2456**	**3539**	**2900**	**3577**	**765**	**3662**	**1911**	**3380**	**30390**

CPI, carbon preference index: $(C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33})/(C_{20} + C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32})$ for *n*-alkanes.

mean value of 8063 ± 3170, 18573 ± 4256 and 31668 ± 9669 ng m^{-3}, respectively. At least > 2-folds higher concentration of organic aerosol was observed in the highway and industrial locations of the city. The organic aerosol content with PM$_{10}$ had fair correlation (r = 0.81), indicated emission by the multiple sources. Among them *n*-alkanes and phthalate esters are the major classes of compounds, while the others were relatively minors.

Alkanes: The lipid components (*i.e. n*-alkanes) in ambient aerosols are contributed by sources such as terrestrial plant waxes, marine/microbial detritus and emissions from fossil fuel use [26]. The alkanes, ranging from C$_{19}$ to C$_{36}$ were identified, and their concentrations varied from 377 to 2770 ng m^{-3} with a mean value of 1189 ± 340 ng m^{-3}. Similar concentration range, 874 ± 438 ng m^{-3} of *n*-alkanes in the ambient PM of capital city of India, Delhi was reported [27]. Four alkanes such as C$_{27}$, C$_{29}$ and C$_{31}$ and C$_{33}$ were detected at moderate levels, 100- 161 ng m^{-3}. While, remaining others were identified at low levels, ranging from 13-91 ng m$_{-3}$. The concentration of alkanes was significantly higher (≈ 2 folds) in the highway areas (Fig. 2). The sum of total concentration of odd (C$_{19}$ + C$_{21}$ + C$_{23}$ + C$_{25}$ + C$_{27}$ + C$_{29}$ + C$_{31}$ + C$_{33}$) and sum (C$_{20}$ + C$_{22}$ + C$_{24}$ + C$_{26}$ + C$_{28}$ + C$_{30}$ + C$_{32}$ + C$_{34}$) *n*-alkanes was found to be 9690 and 5010 ng m^{-3} in a mass ratio of 1.9. The carbon preference index (CPI) was calculated by using the odd-carbon and even-carbon number of *n*-alkane concentrations in the respective samples as follows [28]:

$$\text{Carbon preference index} = \frac{C_{23} + C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32} + C_{34}}$$

The CPI values ranged from 1.1-2.8 with a mean value of 1.8 ± 0.3. The results indicated the domination of biogenic emission sources (CPT > 1) of *n*-alkanes. The alkane proxy (P$_{aq}$) index was calculated by using the following equation [29]:

$$\text{Alkane proxy (P}_{aq}\text{) index} = \frac{C_{23} + C_{25}}{C_{23} + C_{25} + C_{29} + C_{31}}$$

The alkane proxy (P$_{aq}$) ranged from 0.05-0.63 with a mean value of 0.25 ± 0.09, indicating emission from terrestrial (< 0.1) and emergent (0.1 - 0.4) plants [30].

Phthalates: Phthalates, pesticides and bisphenol-A (BPA) are three groups of chemicals, implicated in endocrine disruption and commonly found in the local environment that have been implicated in the pathogenesis of asthma and allergies [23]. Phthalates are used as plasticizers to increase stability and flexibility to prevent brittleness, as a solvent for fragrances and as inert ingredients. Phthalates with the highest production volume are diisononyl phthalate (DiNP), diisodecyl phthalate (DiDP), and di-2-ethyl-hexyl phthalate (DEHP) [31]. Recent results showed that phthalate (*e.g*. DBP, DEHP and DINP) exposure affects human reproductive development and can result in estrogenic consequences [32]. Therefore, long term exposure to these plasticizers may have a significant impact on the health of the local population. Phthalate esters such as dimethyl (DMP), diethyl phthalate (DEP), di-isobutyl phthalate (DiBP), di-*n*-butyl phthalate (DnBP), *bis*(2-ethylhexyl)phthalate (DEHP) and bisphenol-A (BPA) were identified in present samples. The total concentration of phthalates ranged from 765-30390 ng m^{-3} with the mean value of 5294 ± 4145 ng m^{-3}. Two phthalates *viz*., DiBP and DEP were detected at significant concentration, 1900-2268 ng m^{-3}. The DnBP and DEHP were present at moderate levels, 127-989 ng m^{-3}. Others plasticizers, DMP and BPA were detected at low levels, 1-8 ng m^{-3}. Several folds higher concentrations of the phthalates were marked in the industrial area of Raipur city (Fig. 2). The concentration of phthalates in the ambient aerosols of the present location was found higher than in Delhi and Chinese cities [15,18].

Lignin and resin products: Chemical industries produce numerous and varied amounts of synthetic organic compounds. These chemicals are used for different purposes and may have health impacts if they are unwisely disposed into the environment. Plasticizers, silicones and other synthetic organic compounds from fugitive sources can be part of the components of atmospheric PM in urban areas. Direct out-gassing of vinyl chloride and other volatile compounds, and burning of plastics are the major sources of plasticizers in the atmosphere [33]. Five lignin and resin products such as3-hydroxybenzoic acid, 4-hydroxybenzoic acid, vanillic acid, syringic acid and one resin ingredient (dehydroabietic acid) were detected in present study. The total concentration (n = 13) of lignin and resin products ranged from 33 to 5099 ng m^{-3} with a mean value (p = 0.05) of 581 ± 746 ng m^{-3}. 3-Hydroxybenzoic acid and 4-hydroxybenzoic acid were present at higher levels, 360-581 ng m^{-3}, whereas vanillic acid, syringic acid and dehydroabietic acid were present at low levels, 20- 117 ng m^{-3}. However, a tremendous high concentra-
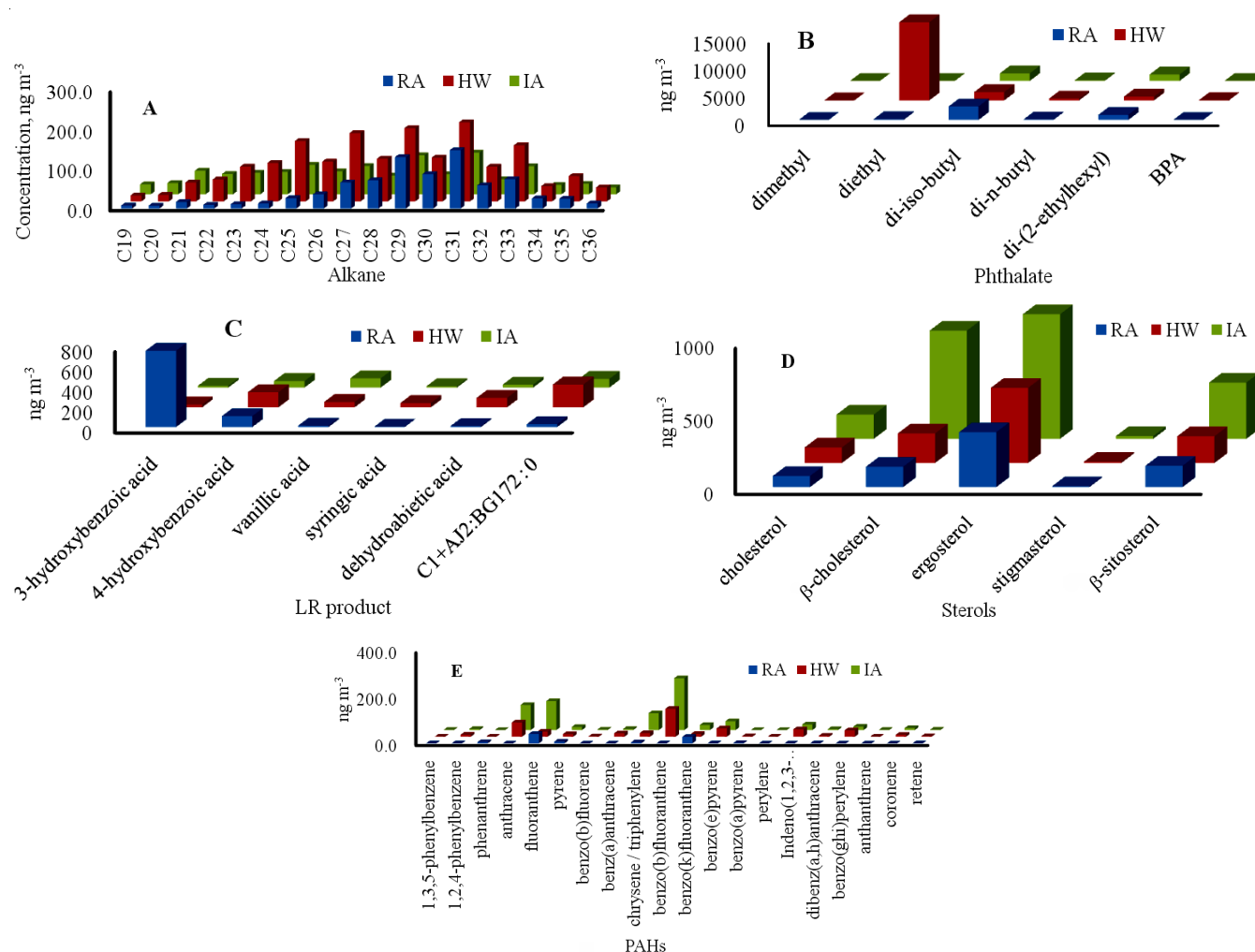
Fig. 2. Spatial variations of *n*-alkane, phthalate esters, lignin and resin, sterols and PAHs

tion of two acids, *i.e.* 3-hydroxybenzoic acid and 4-hydroxybenzoic acid, 4506-51099 ng m^{-3} at location *i.e.* Gogoan was detected. The highest concentration of lignin and resin products was observed in residential areas than the highway and industrial areas (Fig. 2). The highest concentration of lignin and resin related compounds in the aerosols of Raipur city was observed than in Chinese cities [18,27].

Sterols: Steroids are derived from biogenic sources, occur in all ecosystems and can be utilized to identify the origin and fate of organic mass in the environment [34]. They comprise a variety of compounds and generally range from C$_{26}$-C$_{30}$ [35]. Cholesterol (C$_{27}$) is a major compound in faunal lipids, plankton and some terrestrial plants. Steroids in higher plants are known as phytosterols and they range from C$_{28}$-C$_{30}$ with one or two carbon-carbon bonds, typically one in the sterol nucleus and a second in alkyl side chain [36]. Five sterols *viz.*, cholesterol, β-cholesterol, ergosterol, stigmasterol and β-sitosterol were detected in the samples. The concentration (n = 13) ranged from 352-3811 ng m^{-3} with the mean value (p = 0.05) of 1330 ± 519 ng m^{-3}. Cholesterol, β-cholesterol, ergosterol and β-sitosterol were present at high levels, 115-580 ng m^{-3}. A remarkable high concentration of sterols (> 2-folds) in the highway locations of Raipur city was identified (Fig. 2). Significantly, high concentration of sterols in ambient aerosol of Raipur city was observed as compared to Chinese cities [17,18].

Polycyclic aromatic hydrocarbons: Polycyclic aromatic hydrocarbons (PAHs) have been investigated extensively because of their mutagenic and carcinogenic potential [37]. These compounds are the pyrolysis products from the incomplete combustion of organic matter and are mainly associated with fine particles [38]. In this study, 20 PAHs compounds such as phenanthrene (Phe), anthracene (Ant), anthanthrene (AA), benzo(b)fluorene, benzo(a)anthracene (Baa), chrysene (Chry), benzo(b)fluoranthene (Bdf), benzo(e)pyrene (BeP), benzo(a)pyrene (BaP), indenzo-(1,2,3-cd)pyrene (Ind), dibenz(a,h)anthracene (Dba), benzo-(ghi)perylene (BghiP), coronene (Cor) and benzo(k)fluoranthren (Bkf), fluoranthene (Fla), pyrene (Pyr), perylene (Per), retene, 1,3,4-triphenylbenzene and 1,2,4-triphenylbenzene were detected (Table-4). The concentration of PAHs ranged from 0-1049 ng m^{-3} with a mean value of 292 ± 172 ng m^{-3}. Among them, anthracene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(ghi)perylene, chrysene, indenzo(1,2,3-cd)pyrene and fluoranthene were detected at moderate levels, 13-94 ng m^{-3}. Eleven other PHAs were detected at low concentration levels, 0.2-8.0 ng m^{-3}. Several folds higher concentration of the PAHs in the highway and industrial locations of the city was marked, (Fig. 2). The higher concentration of the PAHs was found than reported in mega cities *i.e.* Kolkota (63.5 ng m^{-3}) and Beijing (142.8 ng m^{-3}) [29]. Among them, the tolerance limit of the most toxic PAHs, BaP, in the air was reported to be 1 ng m^{-3}

TABLE-4
BAPE VALUES AND RATIOS OF POLYCYCLIC AROMATIC HYDROCARBON

Locations	Baa	Bbf	Bkf	BaP	Ind	Dba	Flu/Flu + Pyr	Flu + Pyr	LMW/HMW
Professor colony (PC)	0	2.27	0	0	0	0	1.00	19	0.50
Santoshi nagar (SN)	0	0.44	0	0	0	0	1.00	1	1.37
Telibandha (TB)	0	1.75	0	0	0.013	0	1.00	10	0.52
Avanti vihar (AV)	0	1.21	0	0	0	0	1.00	7	0.62
Devendra nagar (DN)	0	9.25	1	0	2.74	3	0.00	54	0.29
Kali badi (KB)	0	1.99	0	0	0	0	1.00	9	1.44
Tatiya para (TP)	1	13.22	2	1	5.06	5	0.64	42	0.18
Arihant nagar (AN)	0	5.93	0	0	0.74	0	0.98	31	0.26
Ram nagar (RN)	3	13.86	2	10	4.39	6	0.45	41	0.13
Kota (KT)	0	0.00	0	0	0	0	0.00	0	0.00
Gogaon (GG)	0	4.44	0	0	0.19	0	1.00	10	0.46
Sarora (SA)	1	27.58	2	0	3.63	5	0.89	170	0.14
Siltara (SI)	0	3.77	1	0	0.19	0	1.00	19	0.50

[39]. In the highway and industrial locations, BaP concentration was found to be several folds higher than limit value of 1 ng m^{-3}.

Two diagnosis ratios:[LMW]/[HMW] and [Fla]/[Fla + Pyr] were used to find out the source of PAHs in the air [24,40]. The abundance ratio of lower (3-ring) hydrocarbons to higher (4 to 6 rings) [LMW]/[HMW] was used to distinguish petrogenic and pyrogenic sources. The [LMW]/[HMW] ratio, < 1.0 and >1.0 indicated the pyrogenic and petrogenic sources, respectively [40]. The [Fla]/[Fla + Pyr] ratio was used to discriminate the petroleum and combustion sources of PAHs. The ratios with values > 0.5, 0.5> - > 0.4 and < 0.4 indicated the PAHs emission from combustion of grass/wood and coal and petroleum combustion/contamination, respectively [24]. The [LMW]/[HMW] and [Fla]/[Fla + Pyr] ratio in the aerosols ranged 0-1.4 and 0-1.0 with mean value of 0.5 ± 0.3 and 0.8 ± 0.2, respectively, [41-47]. Generally, pyrogenic sources were observed which mainly originating from biomass burnings (Table-4).

Among 20 polycyclic aromatic hydrocarbons detected, five compounds -Baa, Bbf, Bkf, Dba and Ind were reported toxic and their carcinogenic potentiality were standardized with respect to benzo[a]pyrene (Table-4). The benzo[a]pyrene equivalent (BapE) value was calculated by using the following equation [48,49].

$$BapE = 0.06 \, (Baa) + 0.07 \, (Bbf) + 0.07 \, (Bkf) + 1.00 \, (Bap) + 0.6 \, (Dba) + 0.08 \, (Ind)$$

The BapE value (n = 13) ranged from 0-39 ng m^{-3} with mean value of 11 ± 8 ng m^{-3}. The significantly higher carcinogenic toxicity values (21-22 ng m^{-3}) at highway and industrial locations were observed, probably due to industrial and vehicular emissions.

Variations: The city is settled over 500 km^2 in which 20 million populations are residing. The PM$_{10}$ sampling was carried out in three types of locations which situated in a residential area (RA), highway (HW) and industrial area (IA) according to the nature and frequency of emission sources. Three categories of organic traces were evaluated. In residential area, the remarkably high concentration of the resin and lignin products was observed (Fig. 3). In industrial area, the significant concentration of PAHs and phthalate ester were marked (Fig. 3).

Composition of organic aerosols: The organic fraction of aerosols in PM$_{10}$ of the studied area ranged from 2.8-5.5 %
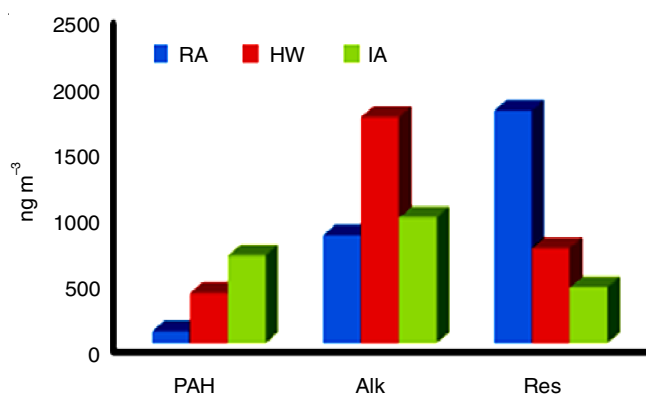

Fig. 3. Spatial variation of organic tracers in air

with mean value of 4.0 ± 0.6 %. The organic aerosol fractions in PM$_{10}$ of the residential, highway and industrial area were found to be 3.2 ± 0.2, 4.9 ± 0.9 and 4.2 ± 1.4 %, respectively. The mean fraction of PAHs, lignin and resin products, alkanes, sterols and phthalates was found to be 0.06 ± 0, 0.11 ± 0.02, 0.23 ± 0.01, 0.25 ± 0.04, and 1.00 ± 0.17 %, respectively. The species *i.e.* phthalates were present at significant levels (> 0.68 %).

Conclusion

The main tracers identified in ambient aerosols were alkanes (C$_{21}$-C$_{31}$), β-cholesterol, ergosterol, benzo(b)fluoranthene, 3-hydroxybenzoic acid, dehydroabietic acid, di-isobutyl phthalate (DiBP) and diethyl phthalate (DEP). Their enriched concentrations were observed in the highway locations. The PAH concentration was observed several folds higher than the permissible limit. The biomass burning, fuel combustion, cooking, evaporation, resin and plasticizers were apportioned major sources for the organic tracers.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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