Distribution of VOCs in urban and rural atmospheres of subtropical India: Temporal variation, source attribution, ratios, OFP and risk assessment

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HIGHLIGHTS

- First study to quantify the VOCs in urban and rural sites located in subtropical region of India.
- m/p-xylene and toluene may be the main contributors in ozone formation at urban and rural sites, respectively.
- Urban sites have mainly vehicular emissions while rural site is influenced by nearby urban areas sources.
- Risk assessment in terms of non-cancer and cancer indicated the people of the both urban and rural sites are at risk.

GRAPHICAL ABSTRACT
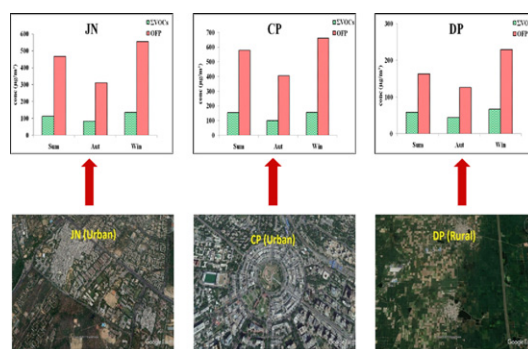
Sum of VOCs ($\sum$VOC) and total OFP in μg/m^3 at urban and rural sites located in subtropical India.

ARTICLE INFO

ABSTRACT

This paper reports the first study which comprises the seasonal, diurnal variability, source characterization, ozone forming potential and risk assessment of volatile organic compounds (VOCs) at three sites (two urban and one rural) in the National Capital Territory of Delhi, India. The study was performed during three seasons of the year 2013–14 and two different categories of VOCs (aromatics and halogenated) have been selected. The study used the sampling and analytical procedures of NIOSH methods. Results showed that the mean concentration of sum of VOCs ($\sum$VOC) is significantly higher at urban sites (110.0 and 137.4 μg/m^3 for JN and CP, respectively) as compared to the rural site, DP (56.5 μg/m^3). The contribution of individual to total VOC concentrations is noticed to be very similar at all the three sites. Most of the VOCs are observed to be significantly higher in winter followed by summer and autumn. Diurnal cycles of aromatic VOCs are highly influenced by the vehicular traffic and photochemical oxidations which showed higher and lower levels during morning/evening and daytime, respectively. Diagnostic ratios of the toluene/benzene (ranged from 0.65 to 13.9) infers the vehicular traffic might be the main contributing source in the urban sites while xylene/benzene ratio (ranged from 0.7 to 2.8) confirms the VOCs are transported to rural site from the nearby urban areas. Correlation and factor analysis suggested the sources are group of different species (traffic emissions, solvent usage and industrial) rather than single gas. The analysis of reactivity in terms of Prop-Equiv concentrations and ozone forming potential indicated that m/p-xylene and

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toluene are the main VOC contributing to the total ozone formation in urban and rural sites, respectively. Hazard ratios and lifetime cancer risk values exceeded the permissible standards established by USEPA and WHO suggests that the people are at significant risk.

1. Introduction

VOCs comprise diversity of organic species with high vapour pressure and low boiling points which can be stored and react in air (Bo et al., 2008; Kountouriotis et al., 2014). It plays an important role in the formation of photochemical smog, ozone (O_3) and secondary organic aerosol (SOA) in the troposphere, stratospheric O_3 depletion and phenomenon of climate forcing (Ghude et al., 2008; Murphy et al., 2010; Huang et al., 2017). O_3 is considered as greenhouse gas and formed through chemical reactions involving VOCs, CO and NOx in the presence of solar radiation (Kumar et al., 2014a). Furthermore, SOA is also a product of chemical reactions of VOCs with OH and NO_3 radicals by nucleation/condensation processes (Atkinson, 2000).

Globally, VOCs are emitted from both biogenic and anthropogenic sources range from about 1200 to 1600 TgC/yr where biogenic emissions are highly dominant over anthropogenic emissions (Bon et al., 2011; Zhao et al., 2017). It can be also formed as the products of photochemical oxidation among the other VOC species (Wang et al., 2014). Biogenic emissions mainly include isoprene and monoterpene released from terrestrial plants. In contrast, gasoline/diesel vehicles, fuel storage, biomass burning and industrial emissions are the major contributors for anthropogenic VOCs (Tiwari et al., 2010; Tan et al., 2012; Kumar et al., 2017). The variation of VOC emissions over the region are largely influenced by emission source strength, meteorological conditions and vegetation cover. Regardless of global emissions, any of the above emissions can be dominant at local or regional scales. In general, the regions of high population density have significant contribution in the increasing levels of VOCs.

Apart from the role of VOCs in the atmospheric chemistry, they are also known for adverse impact on human health and vegetation, even at trace levels (Parra et al., 2006; Zhang et al., 2009; Stojić et al., 2015). A number of epidemiological studies have reported the incidences of detrimental impacts on public health due to their toxicity, mutagenicity and carcinogenicity (Ramírez et al., 2012; Kumar et al., 2014b; Gong et al., 2016; Tyagi et al., 2016; Tuet et al., 2017). Exposure to VOCs can have acute and chronic effects on public health due to their chemical diversity which includes non-carcinogenic (sensory irritation, respiratory disorders, liver-kidney impairment) and carcinogenic (lung, blood, kidney and biliary tract cancer) effects (Ras et al., 2009; Zhou et al., 2011; Ramírez et al., 2012; Kumar et al., 2013; Singh et al., 2016).

In context of VOCs roles in the atmospheric photochemistry and their detrimental effects on public health, ambient VOCs measurements in the urban and rural atmosphere have been widely investigated across the world (Hoque et al., 2008; Tang et al., 2008, 2009; Yuan et al., 2009; Zhang et al., 2013; Alghamdi et al., 2014; Strandberg et al., 2014; Koss et al., 2015; Toro et al., 2015; Yang et al., 2016). The sources and contribution of VOCs and their contribution in O_3 formation are currently the subjects of grave concern among scientific research (So and Wang, 2004; Tan et al., 2012; Seco et al., 2013). In context of India, the present study is first attempt which gives comparative account of ambient VOCs levels for urban and rural sites of any region of India to our knowledge. The present study investigates the seasonal and diurnal variability of ambient VOCs (eight aromatics and four halogenated) levels in the urban (JN and CP) and rural (DP) atmospheres of National Capital Territory of Delhi (NCT), India during three seasons (summer, autumn and winter) of year 2013–14. The study also aimed for estimation of emission sources using various approaches such as diagnostic ratios, interspecies correlation and factor analysis. Finally, ozone forming potential (OFP) and exposure assessment (non-cancer and cancer risk) were also estimated for the urban and rural sites.

2. Methodology

2.1. Study area

The study was conducted in the NCT, India which is highly developing region with a population of 16.8 million (Census of India, 2011). It lies in sub-tropical climatic zone at 28.70° N and 77.10° E with an altitude of 216 m above mean sea level and has four distinct seasons. The ranges of ambient average daily temperature during summer, autumn and winter are as 25–44 °C, 20–30 °C and 5–20 °C, respectively. Atmosphere is unstable for most part of the day in summer and relatively calm and stable for major part of the day in winter. It has experienced huge transportation growth (10.1 million vehicles) during the last decade (Transport Department, NCT, 2016) with increase in commercial activities and small to large scale industries (power generation plants, textiles, leather, paper, plastic manufacturing etc.) inside and outside of the NCT periphery.

Three locations, two urban and one rural sites were selected for study campaign which have been presented in Fig. 1. The two urban sites namely JN and CP have presented as urban-background and urban-commercial sites, respectively. JN, a university campus is located in the south of the NCT covering an area of 1000 acres largely dominated by natural vegetation. Although the volume of traffic inside JN campus is comparatively very low, it is surrounded by major roads plying high volume of traffic on three sides of the campus. CP is located in the mid of NCT and is highly urbanized area having largest commercial, financial and business center of NCT. It is surrounded by huge road circles having heavy traffic density. The rural site, DP is situated in the west of NCT which is located at 25 and 35 kms far away from JN and CP, respectively. It is characterized by small shops serving the daily needs of the village population, houses and one or two lane roads having very low to moderate traffic. From the economic activity point, around 60–70% of the area is under crop cultivation.

2.2. Sampling and analytical procedure

Ambient VOC sampling and analytical procedure was conducted using National Institute of Occupational Safety and Health (NIOSH) methods. It is a collection of methods for sampling and analytical procedures of pollutants in various environmental matrices (air, water and soil) including VOCs (Mukund et al., 1996; Wang and Austin 2006; Sakurai et al., 2013; NIOSH, 2016) (detailed description given in para S-1 in Supplementary material). The sampling was carried out during summer (May to June), autumn (mid-September to mid-November) and winter (December to January) for ten days at each site of year 2013–14. Ambient air samples were collected continuously at four time intervals as morning period (07:00 to 10:00 h), daytime (10:00 to 13:00 and 13:00 to 16:00 h), and evening (16:00 to 19:00 h) continuously in each season at each site. A total number of 40 samples were collected at each site in each season. The ambient air was drawn by indigenous mini portable sampler with flow rate of 100 ml/min through Orbo™-32 sampling glass tubes (7 cm in length × 6 mm o.d. purchased from Supelco) containing 100 and 50 mg of activated charcoal in front and back sections, respectively. After sample collection, the open sides of
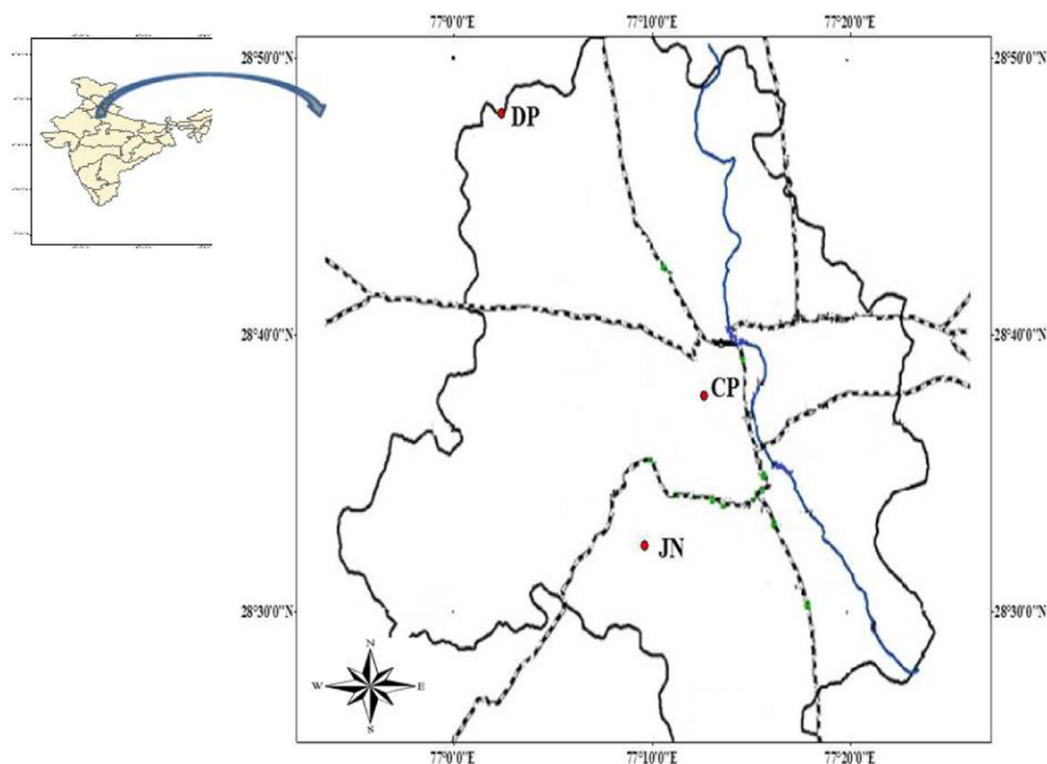
Fig. 1. Map of NCT of Delhi, India showing the sampling sites marked with red circles (dotted and blue lines infer the major roads and river, respectively).

the Orbo™-32 tubes were closed with teflon tape to prevent further contamination. Then, the tubes were labelled, wrapped with aluminium foil and kept in teflon bag, returned to the laboratory and stored in refrigerator (<4 °C) for analysis within seven days of collection.

The analytical procedure was initiated with activated charcoal of the Orbo™-32 tubes by transferring it into 2 ml amber colored glass vial followed by addition of 1 ml of low-benzene carbon disulfide (99% purity with <0.001% benzene) purchased from Supelco as an extraction solvent to desorb VOCs. The sample vials were again sealed with PTFE tape and put in ultrasonication bath for 30 min. Next to desorption period, 1 μl of sample extract was injected into the gas chromatograph (GC-450 Bruker) equipped with capillary column Equity 1 (60 m, 0.25 mm ID, 1.0 μm film thickness procured from Sigma-Aldrich) and flame ionization detector. The temperature program of oven was initially set at 40 °C (hold time 6 min), which was then raised to 200 °C (hold time 6 min) at the rate of 6 °C/min. Three different gases N_2 (carrier gas), H_2 (fuel gas) and synthetic air (oxidizing gas) have been used for the performance of gas chromatography. For QA/QC analysis, five different standard solutions (JMHW VOC mix, 1000 μg/ml each in methanol, procured from Sigma-Aldrich) were prepared to obtain a calibration curve. Aliquots of 1 μl of these standard solutions were injected into the GC and run at a specified chromatographic condition. In all cases, a good linear fit was observed with $R^2 > 0.99$. Individual VOC were identified and quantified based on the retention times and peak areas form the calibration of VOCs standards under specified chromatographic condition. A midrange of calibration standard was analyzed to confirm the GC performance. If the percentage difference in response factor for any compound was >20%, the initial calibration was assumed to be invalid and the GC was recalibrated. The extracting solvent carbon disulfide was analyzed to determine if any contamination was present. Blank samples were also analyzed to assess the possible contamination during sample collection and analytical procedure. Detection limit of all VOCs varied in the range of 0.2–0.3 μg/m³. Following twelve VOCs were identified and quantified: benzene (B), toluene (T), m/p-xylene (m/p-X), o-xylene (o-X), ethylbenzene (Eb), styrene (S), 1,2,4-trimethylbenzene (1,2,4-TMB), 1,3,5-trimethylbenzene (1,3,5-TMB), chloroform (CHL), carbon tetrachloride (CTC), trichloroethylene (TCE), and tetrachloroethene (PERC).

3. Results and discussions

3.1. Seasonal variability of VOCs

The statistical results of measured VOCs in the urban (JN and CP) and rural (DP) sites during the three seasons is documented in Table 1. The statistical significant difference in the levels of VOCs has been noticed for the selected sites where urban sites showed higher levels while lower levels detected in the rural site. The major reason could be the higher vehicular emissions, fuel evaporations, solvent usage and other human activities at the selected sites (Khoder, 2007). The mean seasonal concentration of twelve VOC ($\sum$VOC) ranged from 57.4 to 168.8 μg/m³, 69.3 to 204.3 μg/m³ and 43.5 to 65.9 μg/m³ at JN, CP and DP, respectively. Fig. 2 illustrates the comparison of individual VOC at the urban and rural sites during the whole observation period. ANOVA test has been carried out to see the differences in the levels of VOCs among the sites (Table S-2 in Supplementary material). Aromatic VOCs were recorded highest as compared to halogenated at all sites during the targeted seasons. The observed mean levels of benzene, toluene, m/p-xylene, o-xylene, ethylbenzene, styrene, 1,2,4-TMB and 1,3,5-TMB for three sites JN/(CP)/(DP) were 8.8/(11.8)/(6.1), 31.4/(39.1)/(25.4), 25.4/(31.3)/(6.3), 13.9/(16.1)/(2.9), 5.5/(6.6)/(3.6), 6.9/(8.5)/(3.3), 2.5/(3.4)/(1.3) and 2.4/(3.2)/(1.4) μg/m³, respectively. In case of halogenated VOCs, mean levels of CHL, CTC, TCE and PERC for JN/(CP)/(DP) were noticed to be 3.1/(4.2)/(1.6), 3.8/(5.1)/(1.9), 2.6/(3.5)/(1.3) and 3.3/(4.5)/(1.7) μg/m³, respectively. The results clearly imply the contribution and intensity of different emission sources for atmospheric VOCs at the three selected sites.

The concentration of VOCs showed distinct seasonal differences at the three sampling sites (Table 1). The levels of $\sum$VOC are decreased in the order of winter > summer > autumn at all sites having different amplitudes. In addition to this, same seasonal trend has been noticed for most of the individual VOC concentration. Seasonal variability of OH

Table 1
Seasonal variability of selected VOCs (mean ± SD in μg/m³) at urban (JN and CP) and rural (DP) sites.

	*DL	JN				CP				DP			
		Summer (n = 40)	Autumn (n = 40)	Winter (n = 40)	Mean	Summer (n = 40)	Autumn (n = 40)	Winter (n = 40)	Mean	Summer (n = 40)	Autumn (n = 40)	Winter (n = 40)	Mean
B	0.20	6.3 ± 2.3	8.2 ± 3.1	11.7 ± 3.4	8.8	8.0 ± 3.2	10.4 ± 4.2	17.1 ± 6.2	11.8	3.8 ± 1.6	6.0 ± 3.0	8.4 ± 3.6	6.1
T	0.24	23.1 ± 6.3	28.8 ± 11.1	42.2 ± 11.2	31.4	53.3 ± 17.7	30.3 ± 8.1	33.7 ± 11.6	39.1	34.1 ± 10.4	19.3 ± 7.6	22.8 ± 13.5	25.4
m/p-X	0.24	21.6 ± 7.9	16.9 ± 6.0	37.6 ± 11.5	25.4	25.6 ± 14.8	22.6 ± 7.6	45.7 ± 18.1	31.3	3.1 ± 2.3	5.6 ± 3.1	10.2 ± 67	6.3
o-X	0.24	21.0 ± 5.1	9.4 ± 3.9	11.5 ± 4.3	13.9	20.5 ± 12.7	13.7 ± 6.2	13.8 ± 3.1	16.1	2.7 ± 2.3	1.1 ± 0.5	4.2 ± 2.6	2.7
Eb	0.25	8.8 ± 3.0	4.5 ± 1.4	2.9 ± 0.8	5.5	10.5 ± 3.6	3.9 ± 0.8	5.4 ± 1.5	6.6	3.0 ± 1.9	1.9 ± 1.0	5.7 ± 3.9	3.6
S	0.26	10.1 ± 3.0	4.6 ± 1.6	6.2 ± 1.7	6.9	12.8 ± 3.3	3.8 ± 3.0	8.4 ± 2.1	8.3	3.7 ± 1.9	2.4 ± 1.3	3.9 ± 2.0	3.4
1,2,4-TMB	0.28	2.2 ± 0.6	1.2 ± 0.4	4.1 ± 1.2	2.5	2.8 ± 0.4	1.8 ± 0.5	5.6 ± 1.8	3.5	1.0 ± 0.4	0.8 ± 0.3	2.1 ± 0.7	1.3
1,3,5-TMB	0.28	3.9 ± 1.1	1.2 ± 0.3	2.1 ± 0.4	2.4	2.5 ± 0.3	2.1 ± 0.5	5.2 ± 1.1	3.3	0.8 ± 0.4	0.9 ± 0.5	2.4 ± 1.0	1.4
CHL	0.23	3.1 ± 0.4	2.3 ± 0.5	4.2 ± 1.1	3.1	5.6 ± 1.6	3.1 ± 0.7	3.9 ± 0.8	4.2	1.3 ± 0.6	1.7 ± 0.9	1.9 ± 0.9	1.6
CTC	0.23	5.2 ± 2.3	2.5 ± 1.2	3.8 ± 1.2	3.8	4.9 ± 1.6	3.5 ± 1.1	6.9 ± 2.6	5.1	1.8 ± 1.0	2.4 ± 1.3	1.6 ± 0.9	1.9
TCE	0.29	3.3 ± 1.2	1.8 ± 0.7	2.7 ± 0.6	2.6	4.6 ± 1.4	2.4 ± 1.1	3.4 ± 0.6	3.5	1.7 ± 0.6	1.1 ± 0.5	1.0 ± 0.5	1.3
PERC	0.29	3.1 ± 0.7	1.5 ± 0.5	5.5 ± 2.1	3.3	3.7 ± 1.0	2.2 ± 0.8	7.5 ± 3.1	4.5	1.5 ± 0.5	1.0 ± 0.4	2.7 ± 1.1	1.7

n = number of samples, *DL: Detection limit.

radicals, distribution and strength of emission sources and meteorological conditions are the key factors contributing to significant differences in observed levels of VOCs. The increased dispersive dilution and convection phenomenon due to high mixing depth of the pollutants could be responsible for lowering of VOCs in the summer (Monod et al., 2001). Apart from this, higher loss of VOCs via photochemical degradation due to increased temperature and solar radiation in summer season resulting into formation of simpler molecules such as CO, CO_2 and other intermediates (Lai et al., 2013). On the other hand, occurrence of higher atmospheric stability and calm conditions restrict the dilution of pollutants correspondingly increased the higher levels of VOCs during winter (Dumanoglu et al., 2014).

3.2. Diurnal variability of VOCs

A number of factors such as physico-chemical processes, traffic volume and flow throughout the day, meteorological condition and human activities influence the diurnal cycle of any pollutant (Lyu et al., 2016). It also explains the sources, transport and chemical formation/destruction of the air pollutants. Fig. 3 illustrates the average diurnal variation of targeted VOCs for the urban and rural sites during the three seasons. Distinct seasonal differences were noticed in the diurnal variations of the aromatic VOCs while overall diurnal trend were the same and is consistent with patterns reported in previous studies (Alghamdi et al., 2014; Menchaca-Torre et al., 2015). While, halogenated VOCs have not followed the diurnal cycles as that of aromatics and showed no particular trend

which could be due to variable emission sources, low reactivity with OH and NO_3 radicals and varying meteorological conditions.

In general, aromatic VOCs exhibited higher values in the morning (7:00–10:00) h and evening (16:00–19:00) h while lower values during daytime (10:00 to 16:00) h during all seasons. The higher levels during morning/evening hours could be due to more emissions from traffic during peak hours. Besides traffic emissions, diurnal course of meteorological variations also have significant role in the diurnal variation of aromatic VOCs. A combination of lower boundary layer height, poor mechanical mixing due to atmospheric stability and release of VOCs were the major reasons for the higher levels of aromatic VOCs during morning (Garzón et al., 2015). In contrast, increased dispersion and dilution of the pollutants due to elevation of planetary boundary layer during daytime lead to the lowering of aromatic VOCs levels (Zhang et al., 2012). In addition to this, oxidation of aromatic VOCs with OH radicals in the daytime could be also attributed to lower values of VOCs in daytime (Tang et al., 2007; Tan et al., 2012). Atmospheric reactions of VOCs in the presence of sunlight produced secondary air pollutants viz. carbonyls, O_3, SOA and VOCs of shorter chain lengths than the originals (Atkinson, 2000). Afterwards, weakening of photochemical reactions due to lower OH, sharp decrement in boundary layer height and vehicular emissions increased in the evening causing a rebound of aromatic VOCs (Lyu et al., 2016). In case of halogenated VOCs, most of compounds were observed to be higher during daytime which might be attributed to emissions from the use of industrial solvents, paints and adhesives, pesticidal fumigants, building materials, chlorine based household products and chlorinated tap water.

3.3. Source estimations

3.3.1. Diagnostic ratios (T/B and X/B)

The identification and assessment of VOCs emission sources can be evaluated using the diagnostic ratios (Tiwari et al., 2010; Singh et al., 2015). An examination of toluene to benzene (T/B) and xylene (sum of o-, m-, p- xylene isomers) to benzene (X/B) concentrations ratios is useful in identifying the distance of vehicular emission sources and photochemical age of air mass (Monod et al., 2001; Khoder, 2007). A value approaching in the range of 1.5–4.3 for T/B ratio suggests the traffic originated emission sources while the ratio reaching the value 10 or higher infers the strong industrial sources nearby (Niu et al., 2012; Kumar et al., 2017). Further, lower reactivity of benzene than xylene leading to higher atmospheric lifetime of benzene where the ratio of X/B infers the photochemical age of air parcel and evidence of transport. Higher and lower values of X/B ratios suggested fresh air (local sources) and old air (transported) mass, respectively. In addition to this, T/B ratio can also be used as an indicator for age of air mass having fresh air mass values between 3 and 5 and decreasing values the older air mass (de Blas et al., 2016; Navazo et al., 2008).

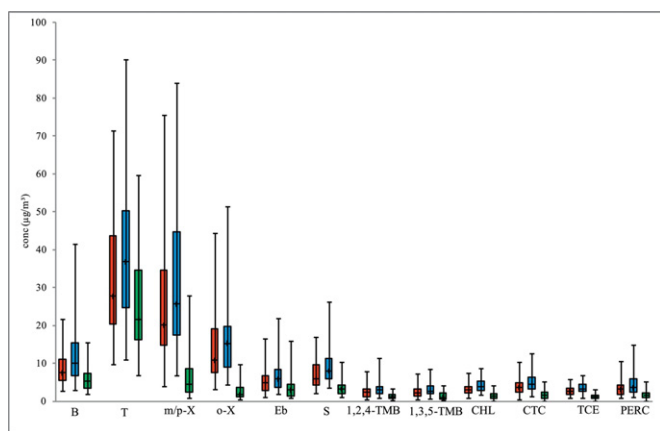**Fig. 2.** Comparison of ambient VOC levels (μg/m³) at three selected sites during whole observation period. The upper and lower bars show the maximum and minimum values. Lines inside boxes show the median values. Concentrations at JN, CP and DP are presented with red, blue and green, respectively.
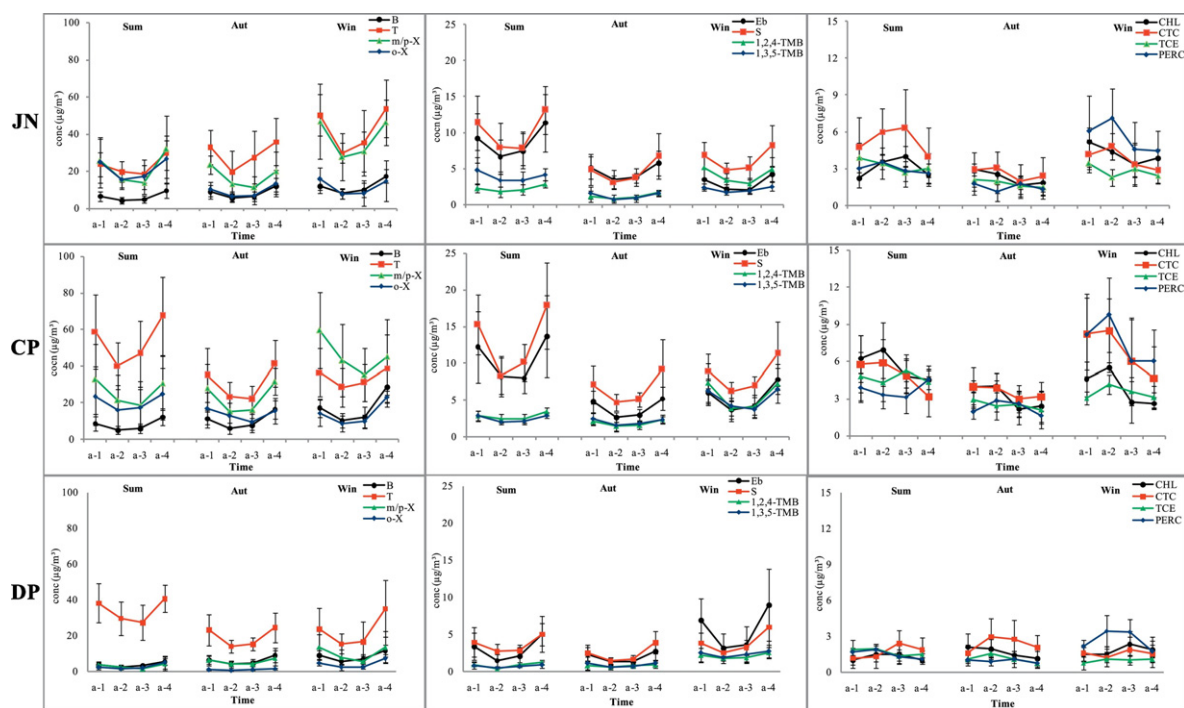
Fig. 3. Diurnal variation of aromatic and halogenated VOCs at urban (JN and CP) and rural (DP) sites during three seasons. x-axis represents time interval: a-1- 07:00–10:00 h, a-2- 10:00–13:00 h, a-3- 13:00–16:00 h, a-4- 16:00–19:00 h.

The diagnostic ratios of T/B and X/B at the three sampling sites during whole studied period are illustrated in Fig. 4. The statistical significant difference was noticed in the diagnostic ratios at three sites based on ANOVA test ($p < 0.05$) (Table S-3 in Supplementary material). The observed ratios of T/B exhibited the mean values of 3.8, 4.3 and 5.3 for JN, CP and DP, respectively. It suggested that the vehicular emissions are the major sources in the urban sites. The higher T/B values at rural site could be due to some additional sources apart from vehicular emissions. The difference in emission sources, photochemistry and meteorology influences the variability of the T/B ratios in the three selected sites. Moreover, X/B values exhibited as 4.9 and 4.5 for JN and CP, respectively suggested the fresh air mass/local sources. Further, the observed T/B ratios for JN and CP lied in the range of 3–5 inferred the fresh air mass. In contrast, rural site showed lower X/B ratio (1.4) indicated the old air mass which results from the diffusion/dispersion of the pollutants to rural area from nearby urban sources.
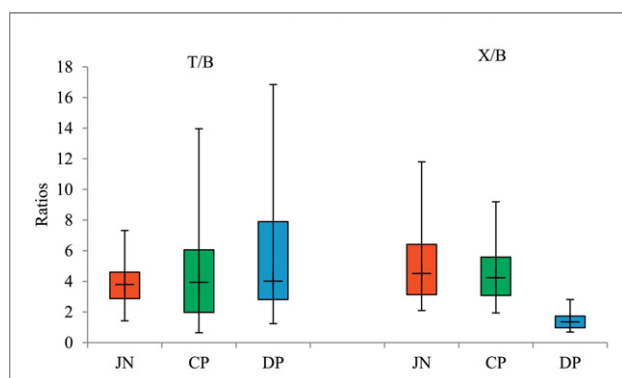
3.3.2. Correlation analysis

Pearson correlation analysis (r) has been carried out in order to examine the emission sources and the distribution pattern of VOCs (Singh et al., 2015; Ohura et al., 2005). Table 2 documents the correlation coefficients among the studied VOCs at three locations. Most of the aromatic VOCs were found to be significantly positive correlation with few exceptions which indicate that they have similar emission sources. Moderate to strong positive correlations have been observed at three sites where correlations were higher at rural site as compared to urban sites. It is noted that JN experienced strong positive correlations (r > 0.7) among BTX and moderate positive correlation (r > 0.5) for most of the compounds with some exceptions. The another urban site CP showed moderate positive correlations among BTX compounds while weak to strong association were observed for styrene, 1,2,4-TMB and 1,3,5-TMB with BTX compounds. On the other hand, rural site exhibited good correlation coefficient (r) for benzene with m/p-xylene (0.81), o-xylene (0.60), ethylbenzene (0.64), styrene (0.60), 1,2,4-TMB (0.71) and 1,3,5-TMB (0.71). The halogenated VOCs did not show any significant correlation with each other and aromatics also at all three sites. The observed differences in the correlation among VOCs could be due to the composition of emission sources and prevailing meteorological conditions. The variability in the correlations is also influenced by the differential decay rate of organic compounds to oxidants (OH and NO_3) in the atmosphere (Table S-4 in Supplementary material) (Kumar et al., 2017).

3.3.3. Factor analysis

Factor analysis with varimax rotation was also performed to examine the sources and possible relationships among the VOCs. It has been widely used as multivariate statistical method mainly based on the reduction of variables to a smaller set of orthogonal factors (Lü et al., 2009). PCA was done for data matrix of number of samples and 12 variables in rows and columns, respectively at the three sites. The factor with eigenvalues >1 and factor loadings >0.4 were selected for the interpretation. VOCs having more than two factors with significant loading indicate that there is more than one source. Loadings of the factors, communalities of VOCs, fractions of variances

Fig. 4. Diagnostic ratios (T/B and X/B) variability at urban (JN and CP) and rural (DP) sites. The upper and lower bars show the max and min values. The lower and upper horizontal lines of the box indicate first and third quartile values. Horizontal lines inside the boxes show median values.

Table 2
Pearson correlation analysis (r) of aromatic VOCs at urban (JN and CP) and rural (DP) sites.

JN (n = 120)	B	T	m/p-X	o-X	Eb	S	1,2,4-TMB	1,3,5-TMB	CHL	CTC	TCE
B	–										
T	0.74**	–									
m/p-X	0.75*	0.70*	–								
o-X	0.51	0.07	0.27	–							
Eb	0.64	0.21	0.47	0.64**	–						
S	0.15	−0.38	0.09	0.28	0.43	–					
1,2,4-TMB	0.53**	0.58*	0.64*	0.19	0.11	0.16	–				
1,3,5-TMB	0.25	0.39	0.14	0.50*	0.57*	0.67**	0.22	–			
CHL	0.14	0.17	0.24	0.05	0.11	0.08	0.21	0.17	–		
CTC	0.31	0.14	0.07	0.08	−0.04	0.17	0.11	0.14	0.42*	–	
TCE	0.18	0.37	0.18	−0.12	0.12	0.07	0.27	−0.27	0.18	0.37	–
PERC	0.21	0.09	0.41**	0.31*	0.17	0.14	0.27	0.47*	0.58*	0.21*	0.15
CP (n = 120)											
B	–										
T	0.65*	–									
m/p-X	0.69**	0.35	–								
o-X	0.44	0.55*	0.33	–							
Eb	0.15	0.87**	0.23	0.56*	–						
S	0.41	0.76**	0.34	0.67*	0.79*	–					
1,2,4-TMB	0.76*	0.22	0.72**	0.17	0.21	0.32	–				
1,3,5-TMB	0.74*	0.14	0.81*	0.19	0.13	0.22	0.88*	–			
CHL	0.24	0.11	0.27	0.09	0.17	0.08	0.11	−0.14	–		
CTC	0.18	0.08	0.14	0.07	0.04	0.07	0.27	0.24	0.06	–	
TCE	−0.21	0.37*	0.20	−0.08	−0.11	0.18	0.22	−0.19	0.11	0.34*	–
PERC	0.41*	0.08	0.45*	0.37*	0.27	0.11	0.17	0.45*	0.34*	0.21	0.17
DP (n = 120)											
B	–										
T	0.22	–									
m/p-X	0.81**	0.24	–								
o-X	0.60**	0.33	0.49**	–							
Eb	0.64**	0.48	0.61**	0.75**	–						
S	0.60**	0.69**	0.51**	0.70**	0.78**	–					
1,2,4-TMB	0.71*	0.23	0.73**	0.66**	0.71**	0.52*	–				
1,3,5-TMB	0.71**	0.20	0.72**	0.54**	0.59*	0.43	0.75**	–			
CHL	0.18	0.16	0.17	0.02	0.21	0.27	0.21	0.03	–		
CTC	0.23	0.05	0.17	0.02	0.01	0.05	0.11	0.01	0.33*	–	
TCE	−0.16	0.27*	−0.07	−0.09	−0.09	0.07	−0.24	−0.18	0.05	0.22	–
PERC	0.31*	0.04	0.34**	0.27*	0.25	0.20	0.51**	0.56*	0.27*	0.13	0.06

* $p < 0.05$.
** $p < 0.01$ (correlation coefficient and significance test).

explained by each factor and total variances at the three sites are explained in Table 3.

After varimax rotation, three factor accounts for 66.29% of total variance has been extracted for JN where F-1 is associated with T, Eb, m/p-X, o-X and 1,2,4-TMB as solvent usage, F-2 is associated with B, Eb, 1,2,4-TMB, 1,3,5-TMB and CHL as vehicle exhaust and F-3 has been associated with CTC, TCE, PERC and S as an industrial solvents. The poor correlation of toluene with vehicle exhaust could be due to differential decay rate of toluene with different radicals and varying meteorological conditions (Na et al., 2005). At CP, four factors are seen to explain with 76.14% of the total variance. F-1 accounts for 32.45% of the variance in the dataset with high loadings of B, T, 1,2,4-TMB, 1,3,5-TMB and PERC. Further, F-2 accounts for 20.18% of the total data variance with high loadings of T, Eb, m/p-X and o-X. However, F-3 shows variance 13.87% with high

Table 3
Factor analysis of measured VOCs at urban (JN and CP) and rural (DP) sites.

	JN (n = 120)			CP (n = 120)				DP (n = 120)		
	F-1	F-2	F-3	F-1	F-2	F-3	F-4	F-1	F-2	F-3
B		0.64		0.71				0.82		
T	0.78			0.54	0.47				0.87	
m/p-X	0.94				0.86			0.80		
o-X	0.40				0.81			0.64	0.51	
Eb	0.59	0.47			0.67			0.66	0.61	
S			0.76				0.92		0.81	
1,2,4-TMB	0.46	0.53		0.77				0.89		
1,3,5-TMB		0.64		0.65				0.87		
CHL		0.45					0.89			0.69
CTC			0.81			0.78				0.78
TCE			0.64			0.87				
PERC			0.52	0.48						
Eigenvalues	4.11	2.57	1.37	5.42	4.67	2.15	1.67	4.47	2.36	1.55
%age variance	34.54	20.38	11.37	32.45	20.18	13.87	9.64	37.28	19.74	12.99
Cumulative variance	34.54	54.92	66.29	32.45	52.63	66.5	76.14	37.28	57.03	70.02

loadings of CTC and TCE whereas variance of 9.64% in respect of F-4 with high loadings of S and CHL. Therefore, it may be inferred that vehicle exhaust, solvent usage, degreasing solvents and dry cleaners and industrial sources act as an indicator for F-1, F-2, F-3 and F-4, respectively. On the other hand, the rural area experienced three factors to explain 70.02% of the total variance where F-1, F-2 and F-3 explained 37.28, 19.74 and 12.99% variance, respectively. F-1 was correlated with B, m/p-X, o-X, Eb, 1,2,4-TMB, 1,3,5-TMB, and PERC as vehicle exhaust, F-2 was associated with T, o-X, Eb and S as solvent usage and degreasing solvents, while F-3 is only contained CHL and CTC as an industrial solvents. In general, vehicular emissions include all the studied aromatic VOCs while B is absent in the solvent usage (Na et al., 2005). The evaporative emissions are also contributed to VOCs emissions from the solvent usage, gasoline spills and gasoline evaporation (Na and Kim, 2001). In case of halogenated VOCs, the sources of CHL, CTC, TCE and PERC are mainly from emissions during manufacturing and use of industrial solvents, paints and adhesives, oils, fats, building related materials and chlorine based household products (Huang et al., 2014). In the context of CTC, India has started the "National CTC phase out plan" under the Ozone cell in Ministry of Environment and Forest in 2003. The production and consumption of CTC has been completely phased-out as of 1st January 2010 except the application in feedstock use.

3.4. Ozone formation potential

It is well known that VOCs have important atmospheric photo-chemically active materials and are considered as an important precursor of ozone formation in the atmosphere (Tan et al., 2012; Alghamdi et al., 2014). In this context, propylene equivalent concentration (Prop-Equiv) and maximum incremental reactivity (MIR) methods have been used to evaluate the photochemical reactivity of VOCs with OH radicals and estimation of contribution of individual organic compound in ozone formation (Cai et al., 2010; Zhang et al., 2012; Li et al., 2015). The Prop-Equiv concentration mainly expresses relative contribution of VOCs in terms of their rates of reaction with OH radicals. The Prop-Equiv concentration method was proposed by Chameides et al. (1992) and defined as follows:

$$\mathrm{Prop-Equiv}\,(i) = \mathrm{conc}\,(i) \times K_{\mathrm{OH}}\,(i)/K_{\mathrm{OH}}\,(\mathrm{C_3H_6}) \qquad (1)$$

where conc (i) is the concentration of VOC expressed in ppbC, $K_{\mathrm{OH}}\,(i)$ and $K_{\mathrm{OH}}\,(\mathrm{C_3H_6})$ are the rate constants for the reaction of compound i and $\mathrm{C_3H_6}$ (propylene) with OH, respectively. Prop-Equiv (i) is defined as the measure of concentration of VOC (i) on an OH-reactivity based scale normalized to the reactivity of $\mathrm{C_3H_6}$.

Ozone formation potential (OFP) for individual VOC (i) using MIR method proposed by Carter (1994) is defined by the following equation:

$$\mathrm{OFP}\,(i) = \mathrm{conc}\,(i) \times \mathrm{MIR_{coeff}}\,(i) \qquad (2)$$

Here, OFP (i) describes the ozone formation potential of individual VOC (i) and $\mathrm{MIR_{coeff}}\,(i)$ (dimensionless, gram of $\mathrm{O_3}$ per gram of VOC) stands for maximum incremental reactivity of compound i. Besides the reactivity of VOCs, the photochemical formation is also influenced by NOx concentrations, solar intensity and meteorological factors. MIR is considered as a good indicator for comparing the OFP of individual VOC.

Prop-Equiv concentrations and OFP of the measured aromatic VOCs at the three sites during the whole observation period are explained in Table 4 and Fig. 5, respectively. Since, halogenated VOCs have very low photochemical reactivity and unavailability of MIR values, Prop-Equiv concentrations and OFP calculations have not been carried out. Low reactivity and OFP of halogenated hydrocarbons is due to more replacement of hydrogen with chlorine atoms which forms stronger and stable bond between the carbon and halogen atoms. Results showed that the Prop-Equiv concentrations and OFP for most of the compounds were higher at CP followed by JN and DP. The observed values of Prop-Equiv for VOCs were consistent with the results of the OFP method. It is important to note that VOCs with large Prop-Equiv and OFP contributions does not necessarily have large ambient concentrations.

The total Prop-Equiv concentrations for all the targeted VOCs were found to be 85.0, 106.0 and 35.2 ppbC, respectively while total OFP showed 445.6, 549.9 and 171.1 μg/m³ for JN, CP and DP, respectively. It is noted that the Prop-Equiv for m/p-xylene was observed to be higher at urban sites as 34.2 and 42.2 ppbC for JN and CP, respectively while toluene was higher at the rural site, DP (107 ppbC). Further, m/p-xylene had highest contribution in OFP having values of 188.6 and 232.9 μg/m³ for JN and CP, respectively whereas toluene (68.6 μg/m³) was the major contributor in OFP at DP among studied VOCs. In general, the urban sites are often VOC-limited while NOx-limited in rural site.

The significant role of other VOCs such as o-xylene, 1,2,4-TMB, 1,3,5-TMB and styrene have also been observed in ozone formation. It infers that evaporative emissions, solvent usage and traffic emissions have important role in ozone production. Benzene had the least contributing factor in terms of Prop-Equiv and OFP at all three sites. Toluene and xylene-isomers were the most important contributors of ozone formation among aromatic hydrocarbons in the previously reported work (So and Wang, 2004; Zhang et al., 2007; Cai et al., 2010; Tan et al., 2012). The variability in the magnitudes of Prop-Equiv and OFP were mainly caused by the differential photochemical reactivity of the different VOCs (An et al., 2014).

3.5. Risk assessment

Based on the USEPA methodology, the potential outdoor health risks (non-cancer and cancer risks) have been estimated in the present section. Non-cancer risk is estimated by comparing the daily ambient concentration to their respective chronic non-cancer inhalation level at which no adverse effects are expected to single VOC. These levels are termed as Reference concentrations (RfCs) which is taken from USEPA Integrated Risk Information System (IRIS) (IRIS, 2011), Minimum Risk

Table 4
Prop-Equiv concentrations (ppbC) of the aromatic VOCs at urban (JN and CP) and rural (DP) sites.

|	JN			CP			DP		
	Absolute conc. (μg/m³)	ppbC	Prop-Equiv (ppbC)	Absolute conc. (μg/m³)	ppbC	Prop-Equiv (ppbC)	Absolute conc. (μg/m³)	ppbC	Prop-Equiv (ppbC)
B	8.8	16.5	0.8	11.8	22.3	1.1	6.1	11.4	0.5
T	31.4	58.2	13.2	39.1	72.5	16.4	25.4	47.0	10.7
m/p-X	25.5	47.4	34.2	31.5	58.6	42.2	6.3	11.7	8.4
o-X	13.9	25.9	13.5	16.1	30.0	15.6	2.7	4.9	2.6
Eb	5.4	10.1	2.7	6.6	12.4	3.3	3.6	6.6	1.8
S	6.9	12.9	4.9	9.3	17.2	6.6	3.3	6.2	2.4
1,2,4-TMB	2.6	4.7	5.8	3.4	6.3	7.8	1.3	2.5	3.1
1,3,5-TMB	2.5	4.6	9.9	3.2	5.9	13.0	1.4	2.6	5.7
Total	97.1	180.3	85	121.2	225.2	106	50.1	92.9	35.2
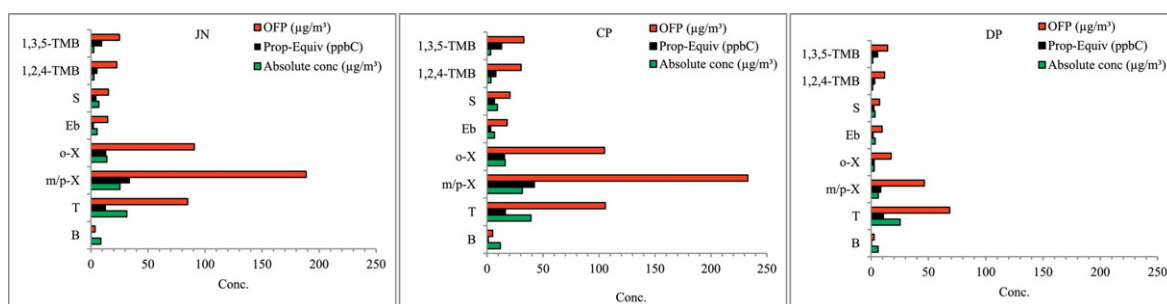
Fig. 5. Absolute and Prop-Equiv concentrations and their OFP contribution of VOCs at urban (JN and CP) and rural (DP) sites.

Levels (MRLs) used by Agency for Toxic Substances and Disease Registry (ATSDR) (ATSDR, 2011) and Reference Exposure Levels (RELs) used by the California Office of Environmental Health Hazard Assessment (OEHHA) (OEHHA, 2003). Therefore, hazard ratio (HR) of each compound (i) represented as the ratio of daily ambient concentration, (C_i in $\mu g/m^3$) to corresponding reference concentrations (RfC_i in $\mu g/m^3$).

$$HR_i = C_i / RfC_i \qquad (3)$$

On the other hand, lifetime cancer risk (LCR_i) via inhalation exposure is estimated by the multiplying the average daily concentration (C_i) with Unit Risk (UR) of each compound (i). UR values are taken from official agencies such as WHO (WHO, 2000), IRIS (IRIS, 2011) and OEHHA (OEHHA, 2003) (Table S-1 of Supplementary material). The UR of each compound infers the excess lifetime cancer risk as a result of the continuous exposure to a compound at concentration of 1.0 $\mu g/m^3$ over a lifetime of 70 years (IRIS, 2011).

$$LCR_i = C_i \times UR_i \qquad (4)$$

The non-cancer hazard ratio (HR) of individual and sum of VOCs for the three studied sites are documented in Table 5. None of the HR values except for benzene at CP were higher than the threshold value of 1.0E+00 at the three sites (USEPA, 1997; Hoddinott and Lee, 2000). However, sum of individual HR (HR_{total}) exceeded the threshold value as CP (2.6E+00), JN (2.0E+00) and DP (1.4E+00). The contribution of benzene was the highest to HR_{total} among selected organic contaminants. Next to benzene, the isomers of trimethylbenzene and toluene also had significant contribution to HR_{total}. McCarthy et al. (2009) stated that HR value >1.0E-01 is also of potential concern. Therefore, we can conclude that the HR values >1.0E-01 suggests that benzene, isomers of trimethylbenzene and xylene might have non-cancer threats to the population of the three studied sites.

Lifetime cancer risk (LCR) was calculated individually for only six VOCs due to lack of the Unit Risks of the other compounds. The observed LCR were compared with the prescribed value of 1.0E-06 (USEPA) and presented in Fig. 6 for the three sites. The other categorization of attributable cancer risk based on Sexton et al. (2007) classification was also used to interpret LCR. According to this, LCR > 1.0E-04 considered as "definite risks", 1.0E-04 > LCR > 1.0E-05 as "probable risk" and 1.0E-05 > LCR > 1.0E-06 as "possible risk". The observed LCR for urban sites (JN, CP) were calculated for benzene (5.2E-05, 7.1E-05), ethylbenzene (1.4E-05, 1.7E-05), CHL (7.3E-05, 9.8E-05), CTC (2.4E-05, 3.1E-05) and PERC (2.1E-05, 2.6E-05) belong to the "probable risk" category. However, TCE was observed to be in the range of "possible risk" as 1.2E-06 and1.5E-06 for JN and CP, respectively.

The estimated values of LCR for the DP are found to be lower in contrast to JN and CP as most of the compounds lies in the range of "probable risk". The sum of individual LCR (LCR_{total}) was found to be 1.9E-04, 2.4E-04 and 1.9E-04 for JN, CP and DP, respectively. The estimated LCR_{total} for all the sites were found to be higher than the standard guideline prescribed by USEPA (1.0E-06). The analysis suggested that the attributed non-cancer and cancer risks due to VOCs exposure are significant and should be taken into strong consideration regarding future health perspectives.

4. Conclusions

In the present work, different aspects of ambient VOCs (aromatics and halogenated) were studied for urban and rural sites located in National Capital Territory of Delhi, India. Results showed that mean concentrations of sum of studied VOCs ($\sum VOC$) were noticed to be higher at urban sites (110.1 and 137.3 $\mu g/m^3$ for JN and CP, respectively) as compared to rural site, DP (56.5 $\mu g/m^3$). In context of seasonal variability,

Table 5
Hazard ratios (HRs) for measured VOCs using RfC at urban (JN and CP) and rural (DP) sites.

	RfC	JN	CP	DP
B	9.6[a]	9.2E-01	1.2E+00	6.3E-01
T	5000[b]	6.3E-03	7.8E-03	5.1E-03
m/p-X	217[a]	1.0E-01	1.3E-01	1.1E-02
o-X	217[a]	6.4E-02	7.4E-02	1.6E-02
Eb	1300[a]	4.2E-03	5.1E-03	4.8E-03
S	852[a]	8.2E-03	9.8E-03	1.6E-03
1,2,4-TMB	7[d]	3.6E-01	4.9E-01	4.8E-01
1,3,5-TMB	6[d]	4.1E-01	5.4E-01	2.2E-01
CHL	98[a]	3.3E-02	4.3E-02	1.6E-02
CTC	100[b]	3.8E-02	5.1E-02	1.9E-02
TCE	600[c]	4.4E-03	5.8E-03	2.1E-03
PERC	271[a]	1.2E-02	1.7E-02	6.3E-03
HR_{total}		2.0E+00	2.6E+00	1.4E+00

[a] ATSDR (Agency for Toxic Substances and Disease Registry) (ATSDR, 2011).
[b] IRIS (Integrated Risk Information System) (IRIS, 2011).
[c] OEHHA (Office of Environmental Health Hazard Assessment) (OEHHA, 2003).
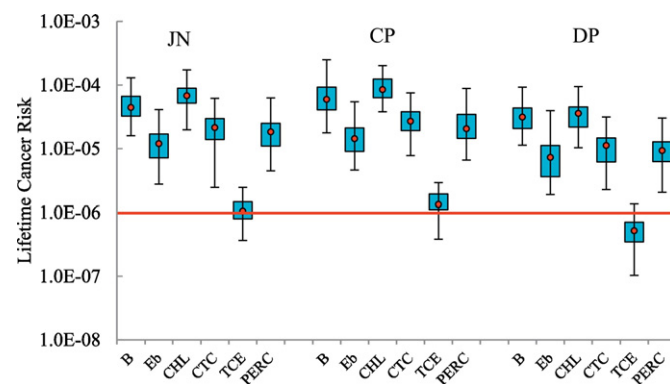[d] PPRTV (Provisional Peer Reviewed Toxicity Values of IRIS) (RAIS, 2009).

Fig. 6. Percentile distribution (25th–75th) of individual LCR from measured VOCs at three sites. The upper and lower bars show the max and min values. The lower and upper horizontal lines of the box indicate first and third quartile values. Horizontal red line shows the USEPA standard. (Red circle mark in the box represents the median LCR values).

∑VOC levels at both urban and rural sites were observed to be highest in winter followed by autumn and summer which could be due to emission source strength and their distribution, seasonal change in levels of OH radicals and prevailing meteorological conditions. Further, diurnal variability showed majority of the aromatic VOCs have higher values in morning/evening hours while lower in daytime indicates the role of photochemical processes. Diagnostic ratios of T/B suggested the vehicular emissions were the dominant source of VOCs at the urban sites. Moreover, lower X/B ratio at the rural site was an indicator of older air mass which might have come from the diffusion/dispersion of the pollutants to rural site from nearby urban areas. PCA results suggested that the vehicular emissions, solvent usage, degreasing and industrial solvents were the main sources of VOCs at the studied sites. The analysis of Prop-Equiv concentration and OFP revealed that m/p-xylene and toluene were the major contributors for the ozone formation in urban and rural sites, respectively while benzene contributed the least among studied VOCs. The health risk assessment based on the observed dataset indicated that the HR_{total} and LCR_{total} exceeded the prescribed threshold values established by USEPA and WHO.

This kind of study not only provides the scientific understanding of seasonal and diurnal variability, source characteristics, OFP and associated health risks of VOCs. The study can also be used in understanding of atmospheric chemical reactions, photochemical smog pollution, assessment and forecast of possible change in atmospheric environment on the regional/global scale. More comprehensive study related to different aspects of VOCs along with O_3 and NOx, use of different statistical and modeling approaches are required for better understanding and effective control measures of air pollutants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2017.09.096.

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