

Dynamic interaction of trace gases (VOCs, ozone, and NO_x) in the rural atmosphere of sub-tropical India

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Abstract The atmospheric chemistry and health implications of pollutants are important scientific concerns in the rural atmosphere. The current study investigates the estimation of seasonal and diurnal variability of VOCs, ozone, and NO_x in the rural area located in a tropical region of India during the year 2013–2014. Results showed that most of the targeted VOCs were higher in winter followed by summer and autumn. The diurnal variability of aromatic hydrocarbons showed similar pattern with different amplitudes as maxima and minima during morning (07:00–10:00 h) or evening (16:00–19:00 h) and daytime (10:00–16:00 h), respectively. The sum of aromatic VOCs are found to be in the range from 27.3 to 87.9 μg/m³. In addition to this, O₃ and NO_x were observed as 45.04 ± 15.19 μg/m³ and 12.41 ± 3.49 μg/m³, respectively, during the observation period. The estimated VOC/NO_x ratios (ranged from 3.4 to 3.7) indicated that the selected rural area was VOC limited in terms of ozone sensitivity. The sources of the VOCs have been explained by characteristic ratios, correlation, and principal component analysis. Further, ozone-forming potential (OFP) of the targeted aromatic VOCs has been evaluated using maximum incremental reactivity which suggested toluene (benzene) contributed the largest (lowest) in the ozone formation. Exposure assessment in terms of lifetime cancer and non-cancer risks lies within the acceptable range of USEPA guidelines.

Keywords VOCs · Ozone sensitivity · Source identification · Exposure assessment

Introduction

Volatile organic compounds (VOCs) are a diverse group of species comprising of non-methane, oxygenated, and halogenated hydrocarbons which are released from natural as well as anthropogenic sources (Kuo et al. 2014). They play a critical role in chemical and/or photochemical reactions, formation/destruction of ozone (O₃), secondary organic aerosols (SOAs), and air-borne toxic chemical formation (Baudice et al. 2016; Kim et al. 2008; Singh et al. 2016). O₃ is considered as secondary pollutant which is formed through a series of chemical reactions between VOCs and oxides of nitrogen (NO_x) in the presence of solar radiation (Kumar et al. 2014a, 2014b; Ras et al. 2009). The product of VOC concentrations and the OH reaction coefficient is often called the reactivity of VOC to determine the O₃ formation (Ran et al. 2009). The residence time of natural CH₄ is increased by 15% due to reactivity of VOCs with OH radicals. SOA is formed by the reactions between VOCs with hydroxyl (OH) and/or nitrate (NO₃) radicals by nucleation and condensation processes; although, the formation of SOA from VOCs are not clearly understood (Hallquist et al. 2009; Ramanathan et al. 2007; Sarkar et al. 2014).

The release of VOCs in the environment from biogenic (e.g., terrestrial plants) and anthropogenic sources (industrial, transport, evaporative emissions, waste water treatment plants, and solvent usage) are largely dependent on source strength and meteorological variable (Kansal 2009; Nguyen et al. 2009; Pagans et al. 2006; Yang et al. 2016). Global emissions of VOCs are estimated approximately in the range of 1200 to 1600 TgC/year into the atmosphere (Bon et al.

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2011). However, the relative emission varies from region to region depending upon the level of anthropogenic activities, climate, and vegetation cover. Anthropogenic VOCs emissions have significant role in the air pollution scenario of high population density.

Exposure to VOCs has also a significant concern to human beings besides the role in atmospheric chemistry and radiative balance. VOCs can have detrimental impacts on public health and welfare in terms of short-term and long-term exposure (Oiamo et al. 2015; Ramírez et al. 2012; Sánchez et al. 2014). Adverse impact ranges from sensory irritation, respiratory illness, and impairment in liver-kidney to carcinogenic effects such as lung, blood (leukemia and non-Hodgkin lymphoma), liver, kidney, and biliary tract cancer (Chang and Chen 2008; Huang et al. 2011; Saral et al. 2009). Inhalation is the major exposure route because of their relatively low boiling points and high vapor pressures (Du et al. 2014). As a matter of toxicity, the US Clean Air Act (1990) separates 97 compounds as VOCs among 188 hazardous air pollutants where some of the VOCs are reported to be carcinogenic (benzene, CHCl_3 , CCl_4) and mutagenic (α -pinene) (Demir et al. 2012; IARC 2006).

The understanding of VOCs in the ambient atmosphere is still complex because of its ubiquitous nature, formation, transformation processes, and emission pattern. In the last few decades, the qualitative and quantitative assessment of VOCs have been focused in the urban areas across the globe (Alghamdi et al. 2014; Filella and Peñuelas 2006; Kos et al. 2014; Strandberg et al. 2014; Tang et al. 2009; Toro et al. 2015; Yang et al. 2016). In Indian context, no studies pertain to the estimation of VOCs along with O_3 and NO_x in the rural atmosphere till date. The present study mainly focused with the following objectives: (1) seasonal and diurnal variability of VOCs, O_3 , and NO_x in the rural atmosphere of tropical India; (2) identification of emission sources using various statistical tools; and (3) estimation of ozone-forming potential and theoretical health risk assessment.

Study site and sampling

Ambient measurements of VOCs, O_3 , and NO_x were performed in the rural area (28.81°N, 77.00°E) located in the west of the capital city Delhi, India (shown in Fig. 1). The location is characterized by subtropical climate with hot and humid summer and short and intense winter. Sampling was conducted for three seasons, i.e., summer, autumn, and winter, during the year 2013–2014. There are small shops serving the daily needs of village population, houses, and one or two lane roads having very low to moderate traffic of vehicles. The village is located approximately 35 km from the main commercial area of the Delhi city. From the economic activity point, around 60–70% of the area is under crop cultivation. The village is connected to the nearby small towns and Delhi city connected

by bituminous roads. The sampling area was free from the influence of any emission source in its immediate vicinity and any other kinds of obstacles (e.g., high building and trees) in the surrounding areas.

Volatile organic compounds

Air samples of VOCs were collected and analyzed using National Institute of Occupational Safety and Health (NIOSH) methods 1003 and 1501. Twelve VOCs, namely, benzene (B), toluene (T), ethylbenzene (EtB), m/p-xylene (m/p-X), o-xylene (o-X), 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) have been examined. Their role in atmospheric chemistry and toxicity were the main selection criteria of these VOCs (Ramírez et al. 2012; Zhou et al. 2011). The VOCs were sampled from the atmosphere by drawing air (indigenous portable sampler) with flow rate of 100 ml/min through Orbo™-32 charcoal sampling tubes. The dimension of Orbo™-32 charcoal tube comprises 7 cm in length \times 6 mm o.d. which was acquired from Supelco. Three-hour averaged samples were measured at four time periods between 07:00 to 19:00 h. The samples were collected in the four time intervals, i.e., morning period (07:00 to 10:00 h), daytime (10:00 to 13:00 h and 13:00 to 16:00 h), and evening (16:00 to 19:00 h). Then, the Orbo™-32 charcoal tubes were rapidly sealed with Teflon tape to prevent any further contamination. Afterwards, the tubes were labeled, wrapped with aluminum foil, and kept at $<4^\circ\text{C}$ until analysis.

Analytical procedure is initiated by transferring the activated charcoal to 2-ml amber-colored glass vial, mixed with 1 ml of low-benzene CS_2 as an extraction solvent (99% purity with less than 0.001% benzene, purchased from Supelco), and ultrasonicated bath for 30 min. The extracted samples were analyzed with gas chromatograph (GC-450, Bruker) coupled with capillary column Equity-1 (60 m, 0.25 mm ID, and 1.0 μm film thickness) and FID detector. The oven temperature was set for 40°C (hold time 6 min), which was then raised to 200°C at a rate of $6^\circ\text{C}/\text{min}$ (hold time 6 min). The identification and quantification of targeted compounds were achieved by their retention time and peak area in relation to calibration VOC standards (JMHW VOC mix, 1000 mg/ml each in methanol, procured from Supelco) under the specified chromatographic conditions.

Ozone and oxides of nitrogen (NO_x)

Surface ozone was monitored with automatic ozone analyzer (Model EC 9810 series O_3) which employs photometric detection of the specific absorption of UV light by ozone. It is a microprocessor-controlled analyzer that

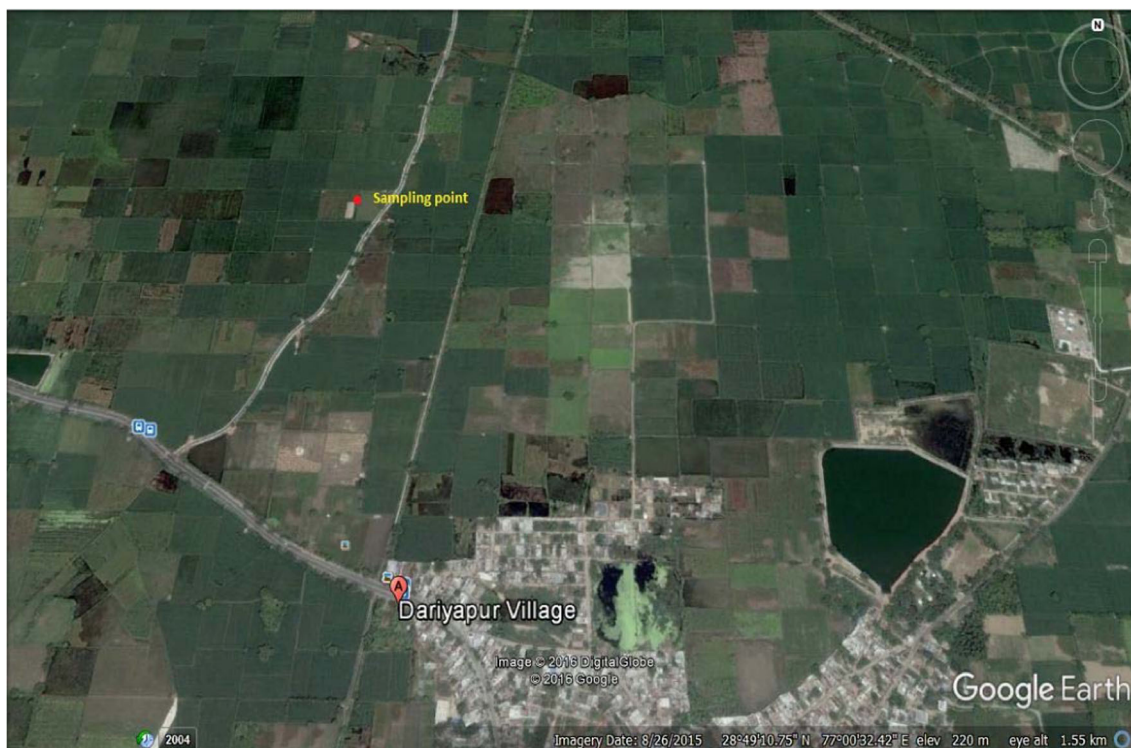
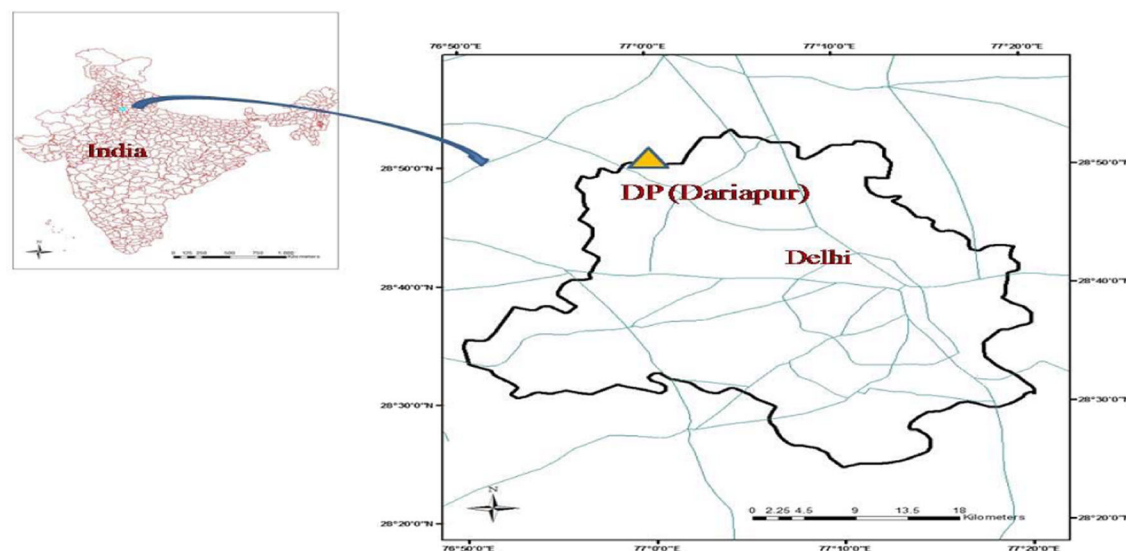


Fig. 1 Geographical location of the rural sampling site

uses the Beer-Lambert law for measuring the concentrations of O_3 in ambient air. However, NO_x ($NO + NO_2$) was monitored continuously using an ambient analyzer (Model EcotechSernious 40). The analyzer works on the principle that nitric oxide (NO) and ozone (O_3) react to produce a characteristic luminescence with intensity linearly proportional to the NO concentration. The O_3 and NO_x levels were monitored continuously for 24 h during the sampling campaign. Hourly averaged data were derived from the original 1-min average interval data.

Instrument maintenance (monthly and annually) was carried out as per manufacturer guidelines, and calibration was performed just before the sampling campaign. Particulate filter was used to prevent particles entering into the instruments from the ambient air and replaced once at the interval of 2 weeks. Further, an inverted Teflon funnel was fitted at the tube entrance to avoid dust and rainwater from entering the tube and measuring instruments. The instrument meets the technical specifications given by USEPA.

Exposure assessment

Using the Integrated Risk Information Systems of USEPA 1997, the exposure assessment parameters such as lifetime cancer risk (LCR) and hazard quotient (HQ) have been calculated using the following equations:

$$\text{LCR} = \text{CDI} \times \text{SF} \quad (1)$$

$$\text{HQ} = \text{CDI}/\text{RfD} \quad (2)$$

where CDI, SF, and RfD represent the chronic daily intake (mg/kg/day), slope factor (mg/kg/day)⁻¹, and reference dose (mg/kg/day) of the chemical. HQ denotes the non-cancer health hazard by individual chemical while hazard index (HI) represents the total non-cancer health hazard by all targeted chemicals. Equation (3) has been used to evaluate the CDI of each compound:

$$\text{CDI} = \frac{\text{CA} \times \text{IR} \times \text{ET} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT} \times 1000} \quad (3)$$

where CA is the VOC concentration (μg/m³), IR is an inhalation rate (m³/h), ET is the exposure time (h/day), EF is exposure frequency (day/year), ED is the exposure duration (year), BW is a body weight (kg), AT is averaging time (year), and 1000 is the conversion factor (μg/mg). For CDI calculation, Inhalation rates of 0.83 and 0.87 m³/h while body weights of 70 and 36 kg for adults and children were used, respectively. Other parameters such as ET, EF, ED, and AT were assumed to be 24 h/day, 350 d/year, 30 years and 70 years, respectively. The slope factors (SFs) and reference dose (RfD) are documented in Table 1.

Statistical analyses

In addition to descriptive statistics, various other statistical tools have been conducted using SPSS (version 16.0.; SPSS

Table 1 Reference dose and carcinogenic slope factors

Organic compounds	Reference dose (RfD) (mg/kg/day)	Carcinogenic slope factors (SF) (mg/kg/day) ⁻¹
Benzene	8.57 × 10 ⁻³	2.73 × 10 ⁻²
Toluene	1.43	
Ethylbenzene	2.86 × 10 ⁻¹	3.85 × 10 ⁻³
m/p-xylene	2.80 × 10 ⁻²	
o-xylene	2.80 × 10 ⁻²	
Styrene	2.86 × 10 ⁻¹	5.7 × 10 ⁻⁴
1,2,4-TMB	2.00 × 10 ⁻³	
1,3,5-TMB	1.71 × 10 ⁻³	
CHCl ₃	5.7 × 10 ⁻²	8.05 × 10 ⁻²
CCl ₄	5.7 × 10 ⁻³	5.25 × 10 ⁻³
TCE	1.14 × 10 ⁻²	4.0 × 10 ⁻¹
PERC	1.71 × 10 ⁻¹	0.00203

USEPA (1998)

Inc., Chicago, IL, USA) and MATLAB (R2011b; MathWorks, Natick, MA, USA) software. In order to see the seasonal differences of VOCs, O₃, and NO_x, paired-sample *t* test, Wilcoxon rank sum test, Friedman test, and Mann-Whitney test have been carried out. Further, Pearson correlation and principal component analysis were also used to examine the sources of VOCs. A significance value of 0.05 was used in all statistical testing.

Results and discussion

Seasonal and diurnal variability of VOCs

A total number of 84 samples were collected during the entire monitoring period which means 28 samples in each season (sampling begins in May, 2013 and ends in January, 2014). Eight species of aromatics and four halogenated hydrocarbons were measured. The highest mean concentration of ΣVOCs was identified in winter (65.9 ± 28.6 μg/m³) followed by summer (57.2 ± 19.6 μg/m³) and autumn (43.3 ± 16.6 μg/m³). An analysis of variance (ANOVA) test indicated that the observed levels of ΣVOCs were significantly (*p* < 0.05) different during the three seasons. The distinctive feature of the seasonal variations could be an account of factors such as distribution and strength of emission sources, seasonal variability of hydroxyl (OH) radicals, and the prevailing meteorological conditions. Higher temperature and solar radiation in the summer is associated with high losses of VOCs by photochemical degradation which leads to formation of simpler molecules such as CO, CO₂, and other intermediates (Lai et al. 2013). The other reasons for the lower levels in summer could be attributed to well dispersive dilution and mixing of the pollutants (Monod et al. 2001). The higher mixing depth results increased convection phenomenon correspondingly decreases the levels of VOCs during the summer (Filella and Peñuelas 2006). However, the highest VOCs concentration in winter could be due to calm conditions and high atmospheric stability that is commonly encountered during the winter months in the area, restricting the dilution of pollutants (Dumanoglu et al. 2014).

The comparative variability of individual VOC has been displayed in Fig. 2 for the three seasons. It is clearly observed that the levels of aromatics were higher in contrast of halogenated hydrocarbons during the entire studied period. Most of the targeted VOCs were noticed higher in winter with few exceptions whereas lower levels were observed during either autumn or summer (Table 2). Toluene was found to be highest among aromatics as 34.1/19.3/22.8 μg/m³ during summer/autumn/winter, respectively. Next to toluene, the aromatics followed the order as m/p-xylene > benzene > ethylbenzene > styrene > o-xylene > 1,3,5-TMB > 1,2,4-TMB. The levels of m/p-xylene, benzene, ethylbenzene, and styrene were

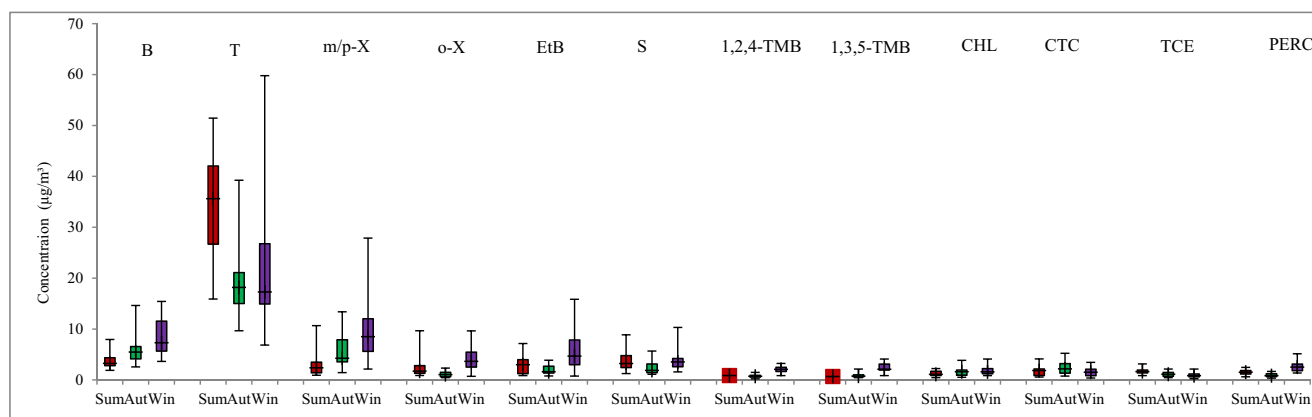


Fig. 2 Seasonal variability of individual VOC shown in box-whisker plot. Boxes show 25th–75th percentile values. The upper and lower whiskers show maxima and minima values. Lines inside the box represent median

observed to be 3.1/5.6/10.2, 3.8/6.0/8.4, 3.0/1.9/5.7, and 3.7/2.4/3.9 $\mu\text{g}/\text{m}^3$ during summer/autumn/winter, respectively. The emitted aromatic VOCs could be emitted from vehicular emissions, solvent usage, and other human activities (Alghamdi et al. 2014; Yan et al. 2017). Specifically, toluene is noticed higher during summer which could be due to transport of pollutants from nearby commercial and industrial activities to rural sampling site. Toluene levels were also reported higher during summer time by Yang et al. (2016), Miller et al. (2012), and Nguyen et al. (2009). On the other hand, the halogenated VOCs showed lower values in the range of nd to 4.11 $\mu\text{g}/\text{m}^3$, nd to 5.24 $\mu\text{g}/\text{m}^3$, nd to 3.15 $\mu\text{g}/\text{m}^3$, and nd to 5.14 $\mu\text{g}/\text{m}^3$ for chloroform, carbon tetrachloride, trichloroethene, and tetrachloroethene, respectively, during the monitoring period. The possible sources of halogenated VOCs are from rural area's own sources like building materials or

products such as chlorine bleach household products, paints and adhesives used in home, industrial solvents, pesticidal fumigants, and chlorinated tap water. Apart from this, the other sources of VOCs could be transported pollutant from the nearby region. Similar results have been also reported by Cai et al. (2010), de Blas et al. (2013), and Zhu et al. (2016). Table 3 compares the observation of the present study with the previous research across the world.

In order to understand the sources, transport, and chemical formation/destruction of the air pollutants, the study of diurnal variability of the pollutants are necessary. Factors such as human activities, nearby local traffic volume, and flow throughout the day and meteorological parameters explain the diurnal variability of the air pollutants. Olumayede and Okuo (2012) stated that it is imperative to know the variability of VOCs at the different times of the day. The average diurnal variation of aromatic and halogenated VOCs at the rural area is depicted in Fig. 3.

The diurnal variability for the aromatic compounds showed similar variation trends with minimal values that appeared in daytime period and higher concentrations in the morning/evening during all seasons. Apart from their primary source strength, their variations mainly corresponded to the diurnal course of meteorological conditions. The accumulation of air pollutants in the morning could be explained by the presence of calm meteorological conditions. However, the elevation of planetary boundary layer (PBL) during daytime enhanced the dispersion and dilution of the pollutants (Zhang et al. 2012). Along with it, photochemical destruction could also be the reason for the lower levels of VOCs in daytime (Tan et al. 2012; Tang et al. 2007). The highest and lowest concentration of OH radicals exhibited during morning/evening and daytime where major sinks of VOCs are its reactions with OH radical. Subsequently, the levels of VOCs generally showed maximum values in morning/evening and minimum in daytime. The higher

Table 2 Mean concentration of individual VOC ($\mu\text{g}/\text{m}^3$) during the three seasons

	Summer	Autumn	Winter
Benzene	3.8 \pm 1.6	6.0 \pm 3.0	8.4 \pm 3.6
Toluene	34.1 \pm 10.4	19.3 \pm 7.6	22.8 \pm 13.5
m/p-xylene	3.1 \pm 2.3	5.6 \pm 3.1	10.2 \pm 6.7
o-xylene	2.7 \pm 2.3	1.1 \pm 0.5	4.2 \pm 2.6
Ethylbenzene	3.0 \pm 1.9	1.9 \pm 1.0	5.7 \pm 3.9
Styrene	3.7 \pm 1.9	2.4 \pm 1.3	3.9 \pm 2.0
1,2,4-TMB	1.0 \pm 0.4	0.8 \pm 0.3	2.1 \pm 0.7
1,3,5-TMB	0.8 \pm 0.4	0.9 \pm 0.5	2.4 \pm 1.0
CHCl ₃	1.3 \pm 0.6	1.7 \pm 0.9	1.9 \pm 0.9
CCl ₄	1.8 \pm 1.0	2.4 \pm 1.3	1.6 \pm 0.9
TCE	1.7 \pm 0.6	1.1 \pm 0.5	1.0 \pm 0.5
PERC	1.5 \pm 0.5	1.0 \pm 0.4	2.7 \pm 1.1

Table 3 Comparison of observed BTEX concentrations ($\mu\text{g}/\text{m}^3$) in the present work with the other studies across the world

Location	Benzene	Toluene	Ethylbenzene	m/p-xylene	o-xylene	Reference
Dariyapur, Delhi	6.06	25.93	3.55	6.27	2.65	Present study
Yucheng, Northern China	1.78	3.44	0.41	0.34	0.29	Zhu et al. (2016)
Quzhou, China	0.81	0.48	–	–	–	Li et al. (2015)
Pearl River Delta, China	3.48	3.43	0.88	0.44	0.22	Zhang et al. (2013)
Tardie` re, France	0.47	1.01	0.17	0.56	0.217	Sauvage et al. (2009)
Dinghu, China	3.73	11.64	2.08	2.86	1.17	Tang et al. (2007)
Navarre, Northern Spain	2.39	5.21	1.17	2.38	1.30	Parra et al. (2006)
Linan, China	2.71	5.76	0.86	1.28	0.84	Wang et al. (2004)

vehicular emissions from the traffic nearby urban areas during the morning/evening rush hours and agricultural vehicles used in agricultural field explain the higher levels of VOCs. On the other hand, the variability of halogenated VOCs does not follow as that of aromatic VOCs.

Seasonal variability of O_3 and NO_x

Figure 4 represents the seasonal and diurnal variability of O_3 and NO_x at the rural site using hourly concentrations averaged over the sampling duration. The meteorological variables, boundary layer processes, and human activities principally influence the variability in the levels of O_3 and NO_x (Reddy et al. 2012). The mean concentration of O_3 was found to be highest in summer ($56.41 \pm 14.21 \mu\text{g}/\text{m}^3$) followed by winter ($43.62 \pm 10.83 \mu\text{g}/\text{m}^3$) and autumn ($35.10 \pm 12.40 \mu\text{g}/\text{m}^3$) for averaging time of 24 h. Higher solar radiation and temperature during summer could be the cause of more photochemical ozone production. Lower O_3 levels were recorded in winter which could be attributed to the shorter daylight hours and larger solar zenith angle (Wang et al. 2013). On the other hand, the levels of NO_x experienced highest levels in winter ($15.85 \pm 2.57 \mu\text{g}/\text{m}^3$) and lowest during autumn ($9.25 \pm 1.56 \mu\text{g}/\text{m}^3$). The suitable meteorological conditions and more use of fossil fuels could be the cause of higher NO_x emissions in winter. However, lower levels of NO_x during summer/autumn might be due to more photo-oxidation reaction and stronger vertical turbulence. Taking into account the adverse health effects, the World Health Organization (WHO) and Central Pollution Control Boards (CPCB), India, have established air

quality guidelines for both O_3 and NO_2 . The permissible limit of O_3 ($100 \mu\text{g}/\text{m}^3$ 8-h average) and NO_2 ($40 \mu\text{g}/\text{m}^3$ annual average) is prescribed by WHO and CPCB, India. The observed values for O_3 and NO_2 during all seasons are lower as compared to the recommended guidelines.

The diurnal variations of O_3 and NO_x during the three seasons were more or less similar with different amplitudes (Fig. 4). It indicates that O_3 concentrations were observed maximum (minimum) during the afternoon (evening or early morning) hours. It is noted that O_3 levels start increasing after the sunrise coinciding with the increasing solar radiation, and it reaches its peak value around 14:00 to 15:00 h. Thereafter, it decreases gradually and reaches minimum values in the night due to absence of solar radiation. This pattern of O_3 and NO_x is universally accepted and also reported in rural areas of previous studies in Indian context (Debaje and Kakade 2009; Hassan et al. 2013; Naja and Lal 2002; Reddy et al. 2012). Duenas et al. (2004) reported that the lower levels of O_3 could also be due to its reaction with NO (sink) present in the atmosphere. However, NO_x showed a more or less opposite diurnal trend to that of O_3 which is characterized by low (high) concentrations during the day (night or early morning).

O_3 photochemical sensitivity

The ratios of mean values of ambient VOCs ($\mu\text{g}/\text{m}^3$) to NO_x ($\mu\text{g}/\text{m}^3$) have been used to examine the O_3 photochemical sensitivity in the rural environment (Cerón-Bretón et al. 2015). The levels of O_3 in the afternoon are dependent on the absolute concentrations and ratios of VOCs and NO_x .

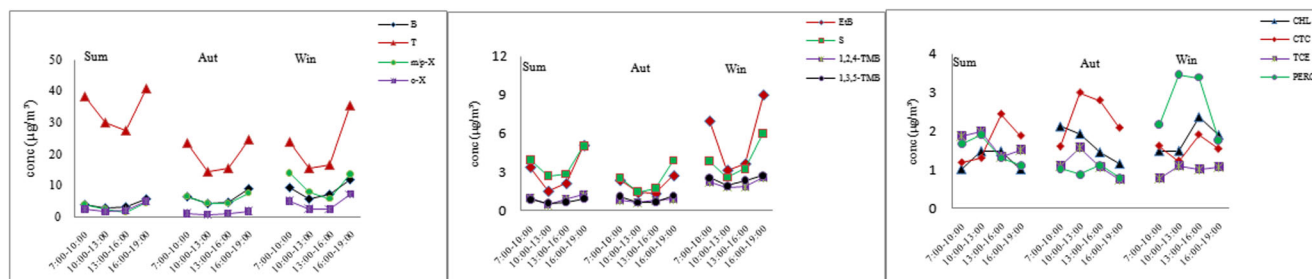
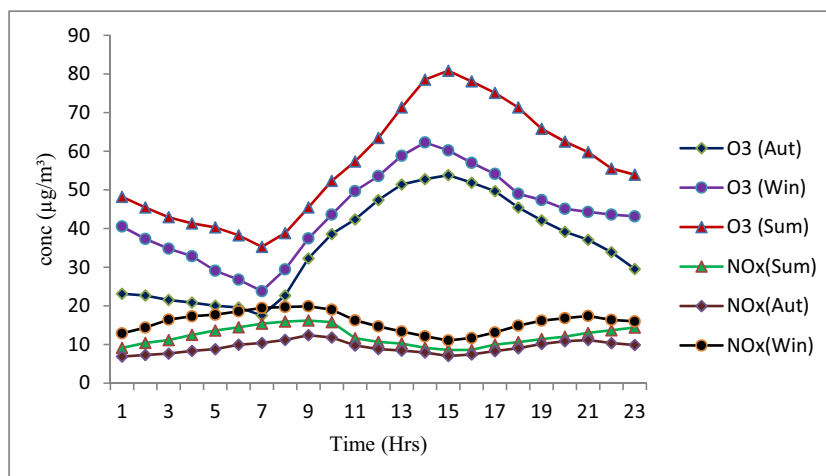
**Fig. 3** Diurnal variability of targeted VOCs during the three seasons at rural area

Fig. 4 Diurnal variability of O₃ and NO_x during the three seasons



Therefore, the estimation of VOCs to NO_x ratios in the morning was used in order to achieve better understanding of effective control strategies of precursors of ozone. The levels of O₃, VOCs, and NO_x are compared during the observation period (Fig. 5). In the present study, VOCs to NO_x ratios were noticed as 3.6, 3.7, and 3.4 for summer, autumn, and winter, respectively. It indicates that the O₃ formation regime in rural areas was VOC-limited during all the three seasons. Since the measurement of all potential VOCs present in the ambient environment has not been carried, the observed VOCs to NO_x ratios can be underestimated. Although, the results indicated that in order to reduce the ozone contamination would result after the control of VOCs emissions (Avery 2006; Cerón-Bretón et al. 2015; Kang et al. 2004).

OFP of VOCs

To estimate the contribution of individual VOC to photochemical O₃ formation, the ozone-forming potential (OFP) has been calculated using maximum incremental reactivity (MIR) values reported by Carter (1994). The OFP is evaluated as the product of the concentration of VOC and the MIR

coefficient (dimensionless, gram of O₃ produced per gram of VOC). Apart from the reactivity of VOC, the other factors viz. levels of NO_x, solar intensity, and meteorological parameters also play a decisive role in the photochemical formation of O₃. Figure 6 illustrates the OFP of aromatic compounds for the rural area during the three seasons. In general, most of the compounds have higher contribution in O₃ formation during winter in contrast to other seasons. Toluene (benzene) contributed the highest (lowest) among the targeted VOCs as 91.9 (1.6), 52.2 (2.5), and 61.5 g O₃ g VOC⁻¹ (3.5) during summer, autumn, and winter, respectively. In addition to this, m/p-xylene and o-xylene have also significant roles in total ozone formation. Many studies reported that BTEX has a significant role for tropospheric ozone formation in ambient atmosphere of Foshan, Yokohama, Beijing, Barcelona, and Jeddah (Alghamdi et al. 2014; Duan et al. 2008; Filella and Peñuelas 2006; Tan et al. 2012; Tiwari et al. 2010).

Sources of VOCs

To estimate the emission sources, two different characteristic ratios of toluene to benzene (T/B) and xylene to benzene

Fig. 5 Comparison of ozone, NO_x, and VOCs during the observation period of three seasons

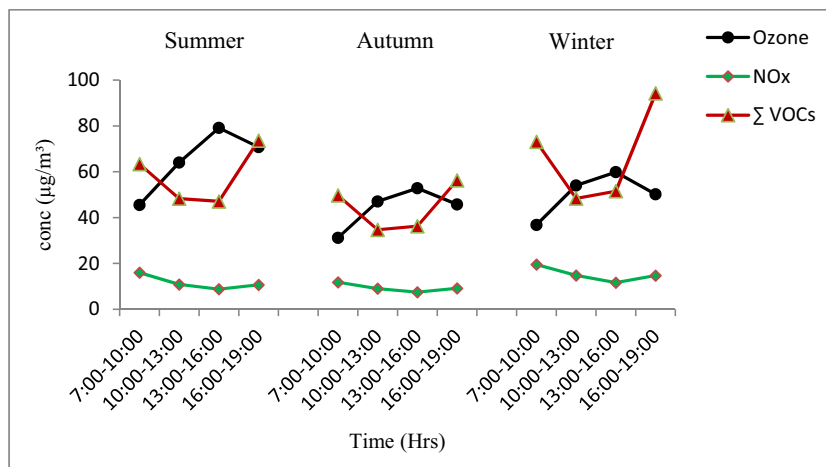
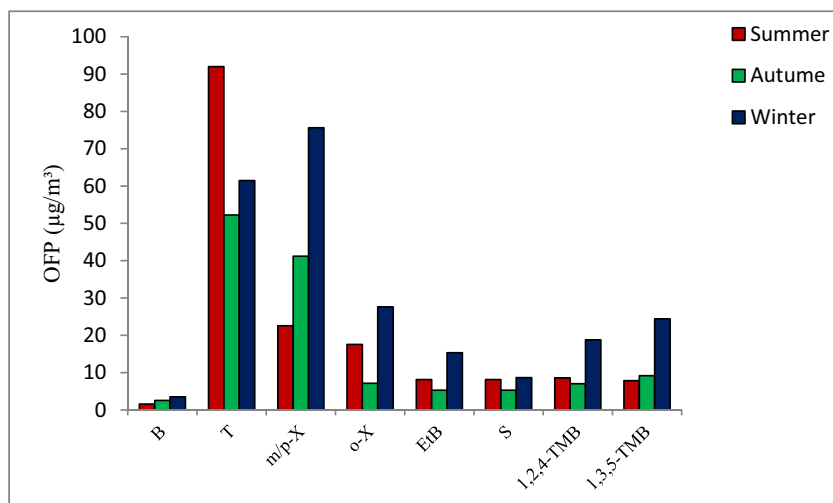


Fig. 6 Ozone-forming potential of aromatic hydrocarbons during the three seasons



(X/B) are used in the present study. The levels of highly reactive organic compounds are decreased due to photochemical degradation during the daytime period while less reactive compounds are accumulated. Benzene and toluene are the stable compounds because of its low reactivity which have 12.5 and 2.0 days of atmospheric lifetime (Prinn et al. 1987). In contrast, xylene has a lifetime of 7.8 h which means they get converted very fast into other atmospheric components. If the ratio of T/B fall in the range of 1.5–4.3, it could be reflected as indicator of vehicular emissions while higher values indicate some additional sources nearby (Alghamdi et al. 2014; Liu et al. 2008, Niu et al. 2012). However, X/B ratio implies the age of air mass and indicates the evidence of transport. The higher values indicate the fresh air mass, local sources, and the low photochemical reactivity of VOCs while lower values signify the old/aged air mass.

Figure 7 illustrates the characteristic ratios of T/B and X/B during the studied seasons. It indicates that the mean T/B ratio during summer is considerably highest at 9.5 which could have some additional sources in contrast to that during autumn (3.4) and winter (2.8). Apart from vehicular emissions, additional sources could be evaporative emissions and painting

and cooking processes. The seasonal variability in values of T/B could be attributed to differences in the emissions, photochemistry, and meteorology. The observed T/B ratios in the current study were nearly similar to those found in several previous studies (Ho et al. 2004; Niu et al. 2012). In addition to this, the mean values of X/B showed lower as 1.4, 1.1, and 1.7 for summer, autumn, and winter, respectively. It reveals the high photochemical reactivity, diffusion, and dispersion of the pollutants to the rural area from nearby sources.

Pearson correlation analysis has also been performed to the targeted compounds in order to identify the possible emission sources (Table 4). Correlation coefficients (r) explain that the majority of aromatic VOCs showed good positive moderate to strong correlation with one other. Except toluene, benzene is significantly positively correlated with other aromatics ($r > 0.60$). In addition to this, the correlation of ethylbenzene with benzene (0.64), m/p-xylene (0.61), o-xylene (0.75), and styrene (0.78) was found to be significantly higher. The other halogenated hydrocarbons did not show any significant correlation with each other and aromatics also. The variability in the correlation among the aromatics could be due to the difference in composition of emission sources (vehicular and

Fig. 7 Seasonal variability of toluene to benzene (T/B) and xylene to benzene (X/B) ratios

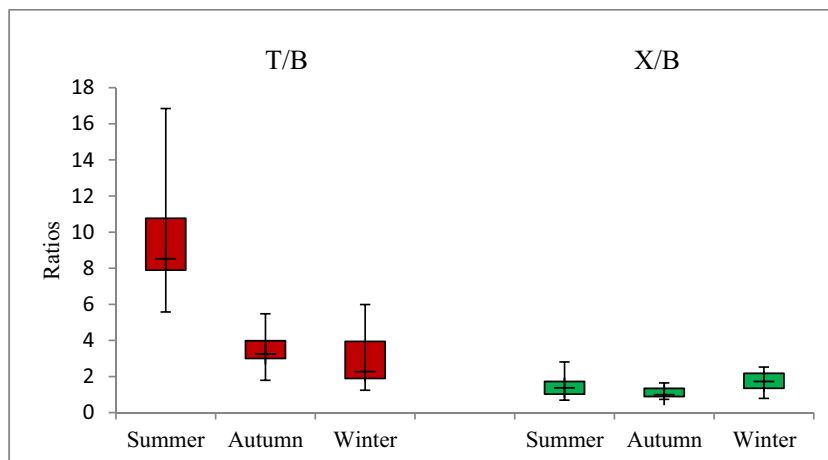


Table 4 Pearson correlation coefficients (r) among studied VOCs at rural site

	1	2	3	4	5	6	7	8	9	10	11	12
1 Benzene	1.00											
2 Toluene	0.22	1.00										
3 m/p-xylene	0.81**	0.24	1.00									
4 o-xylene	0.60**	0.33	0.49**	1.00								
5 Ethylbenzene	0.64**	0.48	0.61**	0.75**	1.00							
6 Styarene	0.60**	0.69**	0.51**	0.70**	0.78**	1.00						
7 1,2,4-TMB	0.71*	0.23	0.73**	0.66**	0.71**	0.52*	1.00					
8 1,3,5-TMB	0.71**	0.20	0.72**	0.54**	0.59*	0.43	0.75**	1.00				
9 CHCl ₃	0.18	0.16	0.17	0.02	0.21	0.27	0.21	0.03	1.00			
10 CCl ₄	0.23	0.05	0.17	0.02	0.01	0.05	0.11	0.01	0.33*	1.00		
11 TCE	-0.16	0.27*	-0.07	-0.09	-0.09	0.07	-0.24	-0.18	0.05	0.22	1.00	
12 PERC	0.31*	0.04	0.34**	0.27*	0.25	0.20	0.51**	0.56*	0.27*	0.13	0.06	1.00

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

solvent usages) and meteorological variables. Further, the differential decay rates of the organic compounds with oxidants such as OH and NO₃ also have a role in correlation variability. This result is highly consistent with the studies performed previously worldwide which stated strong correlation among aromatic hydrocarbons (Choi et al. 2009; Parra et al. 2006; Singh et al. 2015).

PCA, a multivariate statistical tool, has also been performed using varimax rotation to identify the emission sources in the present work. The analysis categorized the huge scattered dataset into clustered groups as principal components (PCs) based on the similarities of the variation of the different VOCs (Lü et al. 2009). Eigenvalues of more than 1.0 are selected for the interpretation. Table 5 documents the

Table 5 Principal component analysis (PCA) of studied VOCs at rural site

	PC-1	PC-2	PC-3	Communality
Benzene	0.82			0.75
Toluene		0.87		0.77
m/p-xylene	0.80			0.71
o-xylene	0.64	0.51		0.70
Ethylbenzene	0.66	0.61		0.81
Styarene		0.81		0.87
1,2,4-TMB	0.89			0.83
1,3,5-TMB	0.87			0.77
CHCl ₃			0.69	0.50
CCl ₄			0.78	0.61
TCE				0.53
PERC				0.51
Eigenvalues	4.47	2.36	1.55	
%age variance	37.28	19.74	12.99	
Cumulative variance	37.28	57.03	70.02	

loading of the factors, fractions of the variance explained by each factor, total variance, and communalities. Three PCs are extracted to explain 70.12% of the total variance where PC-1, PC-2, and PC-3 account for 37.28, 19.74, and 12.99%, respectively. PC-1 comprises with benzene, m/p-xylene, o-xylene, ethylbenzene, 1,2,4-TMB, 1,3,5-TMB, and PERC. However, PC-2 accounted for toluene, o-xylene, ethylbenzene, and styrene while PC-3 is only associated with chloroform and carbon tetrachloride. It may be inferred that vehicle exhaust, solvent usage and degreasing solvents, and industrial sources act as indicators for PC-1, PC-2, and PC-3, respectively.

Exposure assessment

Exposure assessment via inhalation pathway has been evaluated for the two population groups (adults and children) using the USEPA guidelines. The three calculations, namely, chronic daily intake (CDI), hazard quotient (HQ), and lifetime cancer risk (LCR) for each component are documented in Table 6. The order of estimated CDI (mg/kg/day) to observed dataset was found to be in the range from 1.0×10^{-05} to 1.0×10^{-03} . The estimated HQs ranged from 11.76×10^{-04} to 9.36×10^{-02} and from 2.40×10^{-03} to 19.06×10^{-02} for adults and children, respectively, which inferred that none of them exceed the threshold value. Further, hazard indices ($HI = \sum HQs$) also did not exceed the permissible value (1.0) for both population groups. Although, many researchers have reported that values of HQ greater than 0.1 can be considered as potential concern (Kumar et al. 2013). However, the range of estimated LCR is observed to be from 2.24×10^{-07} to 5.98×10^{-05} and from 4.56×10^{-07} to 12.18×10^{-05} for adults and children, respectively. The sum of individual LCR for both population groups were noticed to be higher than the recommended guideline values (1.0×10^{-05}) of WHO; however, it lies in the acceptable range (1.0×10^{-04} to 1.0×10^{-06}) of USEPA (Kumar et al.

Table 6 Exposure assessment in terms of CDI, HQ, and LCR for adults and children

5	Adults			Children		
	CDI	HQ	LCR	CDI	HQ	LCR
Benzene	7.10×10^{-4}	8.28×10^{-2}	19.36×10^{-6}	14.46×10^{-4}	16.86×10^{-2}	3.94×10^{-5}
Toluene	2.96×10^{-3}	2.08×10^{-3}		6.06×10^{-3}	4.24×10^{-3}	
m/p-xylene	7.34×10^{-4}	2.62×10^{-2}		14.96×10^{-4}	5.34×10^{-2}	
o-xylene	3.14×10^{-4}	11.2×10^{-3}		6.40×10^{-4}	2.28×10^{-2}	
Ethylbenzene	4.16×10^{-4}	14.54×10^{-4}	16×10^{-7}	8.48×10^{-4}	2.96×10^{-3}	3.26×10^{-6}
Styrene	3.92×10^{-4}	13.72×10^{-4}	2.24×10^{-7}	8.00×10^{-4}	2.80×10^{-3}	4.56×10^{-7}
1,2,4-TMB	15.24×10^{-5}	7.62×10^{-2}		3.10×10^{-4}	15.54×10^{-2}	
1,3,5-TMB	16.00×10^{-5}	9.36×10^{-2}		3.26×10^{-4}	19.06×10^{-2}	
CHCl ₃	18.88×10^{-5}	3.12×10^{-3}	15.2×10^{-6}	3.84×10^{-4}	6.76×10^{-2}	3.10×10^{-5}
CCl ₄	2.24×10^{-4}	3.94×10^{-2}	11.82×10^{-7}	4.58×10^{-4}	8.04×10^{-2}	2.4×10^{-6}
TCE	14.94×10^{-5}	13.1×10^{-3}	5.98×10^{-5}	3.04×10^{-4}	2.68×10^{-2}	12.18×10^{-5}
PERC	2.02×10^{-4}	11.76×10^{-4}	4.08×10^{-7}	4.10×10^{-4}	2.40×10^{-2}	8.32×10^{-7}
Total		3.52×10^{-1}	9.78×10^{-5}		7.78×10^{-1}	19.92×10^{-5}

Bold values show total sum of LCR and HQ

2014a, 2014b; Ramirez et al. 2012). Results showed that the all estimated risk parameters were higher for children as compared to adults.

Conclusions

Measurement of VOCs, O₃, and NO_x were carried out extensively to see the seasonal and diurnal variability in the rural area of tropical India during 2013–2014. The sum of total targeted VOCs (Σ VOCs) were observed to be $65.9 \pm 28.6/57.2 \pm 19.6/43.3 \pm 16.6 \mu\text{g}/\text{m}^3$ during winter/summer/autumn, respectively, in which variation could be due to distribution of emission sources, seasonal change of OH radicals, and meteorological variability. Toluene had the highest level among the selected VOCs. After examining the diurnal variability, morning/evening and daytime showed the maximum and minimum levels, respectively, for most of the VOCs. In addition to this, O₃ was highest during summer ($56.41 \mu\text{g}/\text{m}^3$) followed by winter ($43.62 \mu\text{g}/\text{m}^3$) and autumn ($35.10 \mu\text{g}/\text{m}^3$) while NO_x followed the order as winter > summer > autumn. The observed ratios of VOC to NO_x clearly indicated the rural area is VOC limited. Toluene to benzene ratios showed an average value of 5.23, concluding that sources are mainly vehicular exhaust, while low xylene-to-benzene ratios explain the old/aged air masses. Significant association has been noticed among aromatic compounds after performing Pearson correlation analysis. Principal component analysis explained the major sources could be vehicle exhaust, solvent usage, and degreasing solvents. Further, toluene and xylene had the highest and lowest contribution in ozone formation. In the concern of lifetime cancer risk and non-cancer risks, the both

population groups (adult and children) lie within the acceptable range of USEPA guidelines.

The present study highlights the seasonal and diurnal variability of VOCs, O₃, and NO_x in the rural ambient air of subtropical India. The observed results for origin of VOCs, its photochemistry and theoretical health risk assessment, are useful in improving the efficiencies and efficacies of future policies to maintain air quality. In order to effectively control measures of VOCs and O₃, some important steps need to be taken which includes minimizing the release of the pollutants at the source itself by using effective and efficient technological measures. In addition to this, the number air quality monitoring networks should be increased to identify the possible sources present in nearby areas as well as implementation of proper land use planning. Indeed, our study is limited to few VOCs; therefore, year-round continuous measurements of more VOCs are required to improve better understanding for atmospheric chemistry in rural areas. Further research is also warranted to gain mutual interaction among trace gases along with various statistical and modeling studies.

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