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

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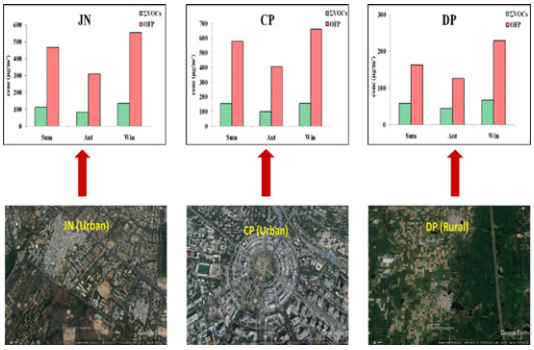
HIGHLIGHTS

- 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 (∑VOC) and total OFP in μg/m^3 at urban and rural sites located in subtropical India.

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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 (∑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 NO*x* 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