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AMBIENT VOLATILE ORGANIC COMPOUNDS (VOCS) AT AN AGRICULTURAL AREA OF KANPUR

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Abstract
The presence of Volatile Organic Compounds (VOC) in air, as defined by the World Health Organization, has in past decades often been associated with adverse health effects. Thus, an investigation of ambient VOCs (benzene, toluene and xylene) was conducted at agricultural area in Kanpur for a span of one year in order to ascertain the contamination levels. Low volume samplers were used for measuring the levels of BTX. The samples were extracted with carbon disulphide by occasional agitation. The aromatic fraction was subjected to GC-FID. The average concentration of total BTX in all samples was 13.9 μg/m^3 and the total range was from 2.08 μg/m^3 to 30.7 μg/m^3 with the median of 9.8 μg/m^3. The maximum concentration of total BTX was found to be 16.8 μg/m^3 in winter season, followed by 10.6 μg/m^3 in summer and 9.6 μg/m^3 in monsoon season. Toluene contributed maximum (68%) followed by benzene (37%) and xylene (3%) and residential site (19%). The concentration of BTX decreased in the order toluene > benzene > xylene. The hazard quotient of benzene, toluene and xylene were 42E-01, 4.8-03 and 1.9E-02 respectively. Integrated lifetime cancer risk for benzene was 7.6E-06.

Keywords:
BTEX, Carcinogenic/Non-carcinogenic risk, Terai zone,

Introduction

With the rapid urbanization and industrialization in the locale, more and more chemicals are introduced into the environment has attracted increasing public and regulatory concerns. Volatile organic compounds (VOCs) are important tropospheric pollutants which are carbon-based compounds that have vapor pressure (0.01 kPa or higher at 20 °C) to significantly vaporize and enter the atmosphere (Marc et al., 2014). The estimated worldwide average emissions of VOCs are about 1,347 million tons/year from biogenic sources and 462 million tons/year from anthropogenic sources. Ambient total concentrations of airborne VOCs in urban and suburban areas have been reported to be in the range of 16.2–1,033 μg/m^3. (Madhoun et al., 2010)

During the recent decades volatile organic compounds (VOCs) such as benzene, toluene and xylene (BTX) have gained interest in the field of indoor and outdoor air quality (Buczynska et al., 2009). These monoaromatic hydrocarbons are the sources of a variety of adverse health effects like asthma, dizziness, fatigue, and eye, nose, and throat irritation. Nausea and nonspecific symptoms have been also associated with BTX (USEPA 2005). Amongst BTX compounds, xylenes are highly reactive and contribute to ozone formation and hence to climate change (Finlayson-Pitts and Pitts, 1993). BTX have been extensively measured worldwide in the last decade due to the rise in health issues (Kerchich, 2012). Benzene's ambient concentration is regulated by guidelines and is limited to 5 mg/m3 as an annual average. Levels of toluene and xylenes, although still not regulated, are suspected to have synergic effects to benzene and their concentrations are usually indicated in the air-monitoring reports (Buczynska et al., 2009). The physical parameters of BTX as given in Table 1.

Humans are exposed to benzene mainly by breathing polluted air (IEH, 1999). Therefore, efforts have been devoted to identify the sources of benzene in both indoor and outdoor air (Duarte-Davidson et al., 2001). Benzene is emitted by vegetation and petroleum reservoirs (CONCAWE, 1997). As benzene is present in crude oil, natural gas, and unleaded gasoline, anthropogenic sources are the main contributors (Masih et al. 2017). Emissions from vehicle exhausts, evaporative loss, and incomplete fuel combustion processes are considered as the main sources of benzene in outdoor air.

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Toluene and xylene are found more in gasoline than benzene. They are also widely used in solvents. Therefore, outdoor levels of these compounds were expected to be higher than that of benzene. Despite the fact that their toxicity is lower than that of benzene, they have the same environmental fate and, when exposed to photochemical reactions in the atmosphere, produce compounds which can provoke adverse effects on human health. Therefore, the analysis of benzene, toluene, and xylene (BTX) concentrations in air is necessary (Gallego et al., 2008).

2. Materials and Methods

Site description, sampling and analysis

Kanpur (26.4499° N, 80.3319° E) is located in the eastern Uttar Pradesh in northern India. The temperature ranges from 1.5°C to 29.5°C with an average of 18.6°C and humidity is 71% during winters. Average temperature was 35.5°C with the range from 20.5°C to 48.5°C having 82% humidity in summer season, whereas in monsoon season the temperature ranges from 12.2°C to 44.6°C with an average of 31.8°C and humidity is 89% as represented in Table 2. Figure 1 illustrates that the prevailing summer and monsoon winds are east-northeast (ENE-30.1% & 26.3%) and west-southwest (WSW-14.9% & 19.5%) with wind speeds of 0.1 to 12.2 and 0.1 to 14.9 meters per second respectively, while during winters, the wind direction are towards east-southeast (ESE-21.9%) and west (W-20.1%) with wind speeds of 0.1 to 10.1 meters per second. Farming lands are very much prevalent in the outskirts of Kanpur city. (Masih et al., 2016).

Air sampling was set up for a span of one year (Nov. 2022 to Oct. 2023) at an agricultural area. Monitoring was performed for 20-24 hours once a week in a scheduled manner and a number of forty eight samples were collected. BTX were sampled and analyzed using a methodology based on National Institute for Occupational Safety and Health (NIOSH) method 1501 (NIOSH, 1994; BIS 2006). BTX were sampled by drawing air through activated coconut shell charcoal tubes (CSC, 8 mm x 110 mm, 600mg) containing two sections of (main section 400 mg, second section 200 mg) separated by a 2 mm urethane foam (SKC Inc.), using a low-flow SKC Model 220 sampling pump (SKC, USA) at the flow rate of 250 ml/min for 20-24 hrs. The suction rate of air was verified weekly using calibrated rotameters with an accuracy of ±1%. Sampled air was then analyzed with an HP 6890 gas chromatography/mass spectrometer and gas chromatography/ flame ionization detector (NIOSH, 1994; Masih et al. 2016).

3. Results and Discussion

Figure 2 represents the seasonal BTX concentrations measured at agricultural sites of Kanpur. The concentration of benzene ranges from 3.6 µg/m^3 to 35.1 µg/m^3 with the mean value of 13.4 µg/m^3. Toluene ranges from 9.9 µg/m^3 to 47.5 µg/m^3 having an average of 22.7 µg/m^3. Xylene has a mean concentration of 1.3 µg/m^3 with the range of 0.5 µg/m^3 to 3.4 µg/m^3. The total mean concentration of BTX was 14.5 µg/m^3 at agricultural area of Kanpur. Figure 3 shows that toluene (63%) had the highest contribution followed by benzene (33%) and xylene (4%) of the total BTX reported from the agricultural area. Information about the characteristics of air at the sampling site is given by the interspecies ratio of VOCs with varying reaction rates against OH. Average VOC relative ratios at Kanpur region with respect to benzene, toluene and xylene (BTX) were studied. Benzene and Toluene. The chief constituents of gasoline emitted into the environment by vehicular exhausts are Benzene and Toluene. Table 3 depicts that the maximum B/T ratio was found during winter season (0.77) followed by summer (0.48) and monsoon seasons (0.49). This indicates that increase in concentration from monsoon to winter and summer to winter is maximum for benzene as compared to toluene and xylene. This fact is also supported by the X/B ratio which was found to be lowest in winter season (0.09) and increases during summer (0.12) and monsoon season (0.13). This may be explained on the account of prevalent usage of cow-dung cakes, charcoal, wood etc. for cooking throughout the year. Additionally, in winter season stubble, brushwood and straw are also used for heating purpose. The weather of Kanpur can be generally classified into three seasons, winter (November-February), summer (March-June) and monsoon (July-October). Figure 4 depicts the seasonal pattern of measured BTX in ambient air at agricultural area of Kanpur. The concentration of benzene in during winter, summer and monsoon seasons are in the order of 17.1, 9.3 and 7.9 µg/m^3 respectively, whereas toluene (23.9, 21.3 and 19.9 µg/m^3), and xylene (1.6, 1.1 and 1.0 µg/m^3). Although the trend of seasonal variation of BTX at agricultural area is similar with nature i.e. maximum concentration of BTX were found to be in winter followed by summer and monsoon seasons. The total BTX ratios for winter to summer (W/S) and winter to monsoon (W/M) were 1.3 and 1.5 at agricultural area indicating significant seasonal variations of BTX. Figure 5 shows the plot of toluene against benzene with R^2 value 0.91, which suggests a linear relationship between toluene and benzene. Thus it can be predicted that the source for benzene and toluene may be same i.e. the biomass fuel (Fan et al., 2014).

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Benzene is classified as carcinogenic substance, whereas toluene, m,p-xylene and o-xylene are classified as non-carcinogenic. Thus, to estimate the hazards on human health by these mono-aromatic pollutants, a risk assessment has been performed in this regard. (Zhang et al, 2012). The present study considers the estimation of the non-cancer hazard and integrated lifetime cancer risk (ILTCR) due to the exposure to BTX at their prevailing levels (Majumdar et al., 2011). The integrated life time cancer risk (ILTCR) was calculated from the equation given as under:

ILTCR = E_L (mg $kg^{-1}day^{-1}$**) × CPF** (mg $kg^{-1}day^{-1}$)

Where, E_L is the effective lifetime exposure and CPF is the carcinogenic potency factor or cancer slope factor. The inhalation cancer slope factor of carcinogenic compounds for benzene was obtained from Risk Assessment Information System (RAIS) as 2.73 x 10^{-2} mg $kg^{-1}day^{-1}$(RAIS, 2010). As per the medical norms, cancer risk of > 10^{-6} was considered "carcinogenic effect of concern" and a value $\leq 10^{-6}$ was considered an "acceptable level" (Zhang et al., 2012). Risk assessment for non-malignant conditions was expressed by hazard quotient (HQ) which is defined as the ratio of yearly average daily concentration received (E_Y) and the reference concentration (RfC) calculated according to equation:

HQ = E_Y/RfC

Where RfC - the inhalation reference concentration of the non carcinogenic compounds toluene and xylene was obtained from the Integrated Risk Information System (IRIS) as 5 and 0.1 mg/m^3, respectively (USEPA-IRIS, 2003; 2005). The RfC of benzene for non-cancer risk is 0.03 (ASTDR 2010). Summation of HQs for individual contaminants gave Hazard Index (HI).Table 4 represents ILTCR and non-cancer (HQ) risks (15 years residing time for an individual). As the estimated cancer risk for benzene exceeded the threshold value of 1E-06 which indicates that more cancer risk is from benzene due its high carcinogenicity. Toluene gives the highest non-cancer HQ followed by benzene and xylene. The individual HQs for BTX did not exceed unity anywhere which indicates that there is no serious threat of chronic non-cancer health effect in pollutant specific target organs for the city population.

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Table 1: Physical parameters of BTX

Compound	Mole weight g mole^{-1}	Density g ml^{-1}	Boiling point °C	Water solubility mg l^{-1}	Vapor pressure mmHg	Log K_{ow}
Benzene	80	0.85	80.1	1780	76	2.13
Toluene	93	0.89	110.8	535	22	2.69
Xylene	116	0.87	140.6	169.3	5.83	3.20

Source: Data from EUGRIS database (http://eugris.info)

Table 2: Meteorological conditions measured during the study period

Meteorological parameter	Mean	S.D.	Range
Summer			
Wind speed (m s^{-1})	2.3	0.33	0.1-12.2
Air temperature (°C)	36.5	3.3	20.5-48.5
Relative humidity (%)	82.6	7.4	27.2-89.6
Monsoon			
Wind speed (m s^{-1})	1.8	0.21	0.1-14.1
Air temperature (°C)	31.8	2.1	18.2-43.8
Relative humidity (%)	87.3	7.8	31.2-97.4
Winter			
Wind speed (m s^{-1})	1.8	0.18	0.1-10.1
Air temperature (°C)	18.8	1.4	3.5-29.5
Relative humidity (%)	72.0	7.1	26.4-83.1

Table 3: Average interspecies ratios (B/T and X/B)

	B/T Ratio	X/B Ratio
Summer	0.445665	0.122056
Monsoon	0.39598	0.130711
Winter	0.773481	0.095906

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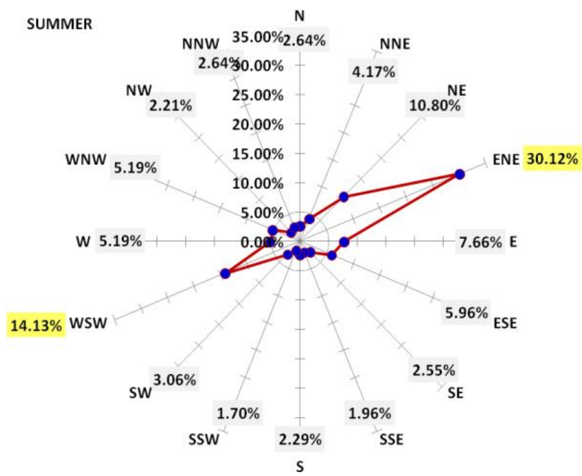
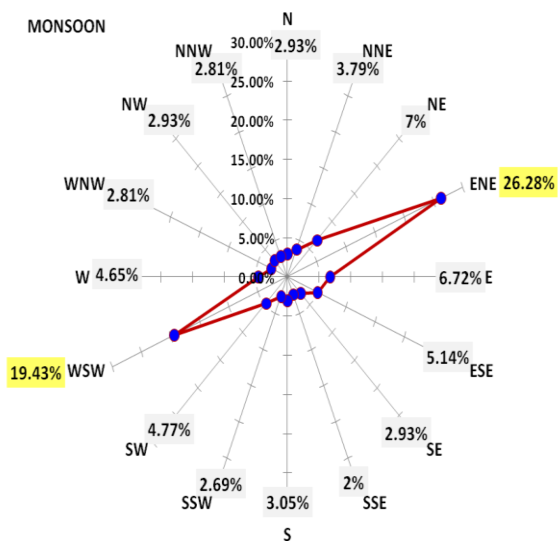
Table 4: Estimate of non-cancer and cancer risk

	HQ	ILTCR
Benzene	3.8E-01	**7.6E-06**
Toluene	4.3E-03	
Xylene	1.3E-02	

HQ: Hazard Quotient
ILTCR: Integrated Life Time Cancer Risk





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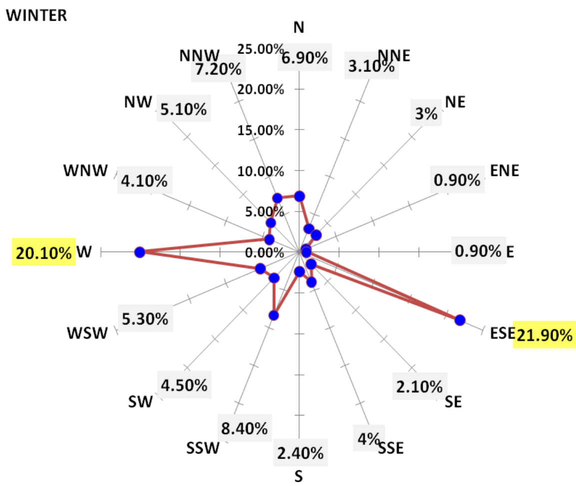

Figure 1: Prevailing wind direction during different seasons

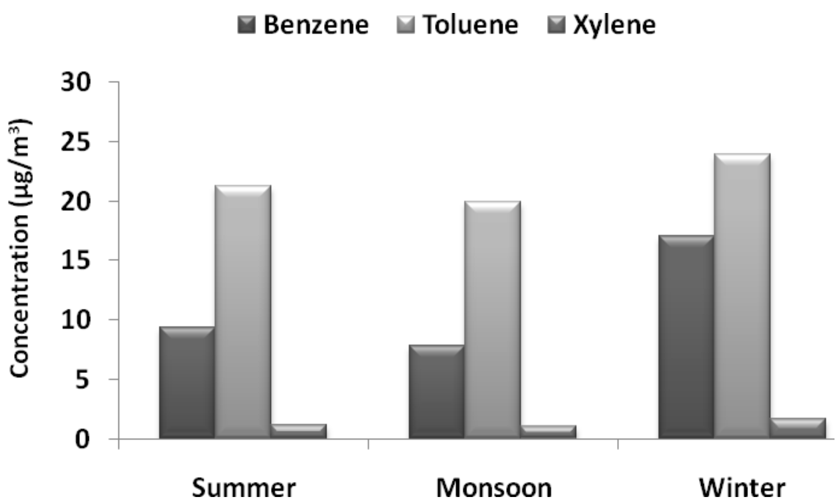

Figure 2: Seasonal BTX concentrations (µg m^{-3})

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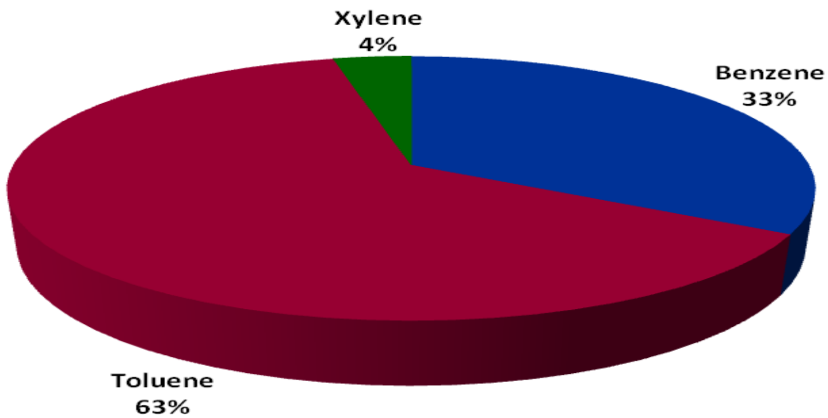

Figure 3: Individual Contribution (%) of BTX

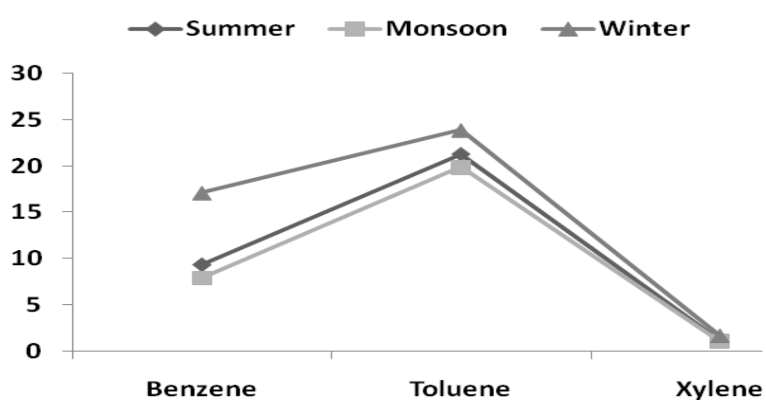

Figure 4: Seasonal BTX pattern at agricultural area

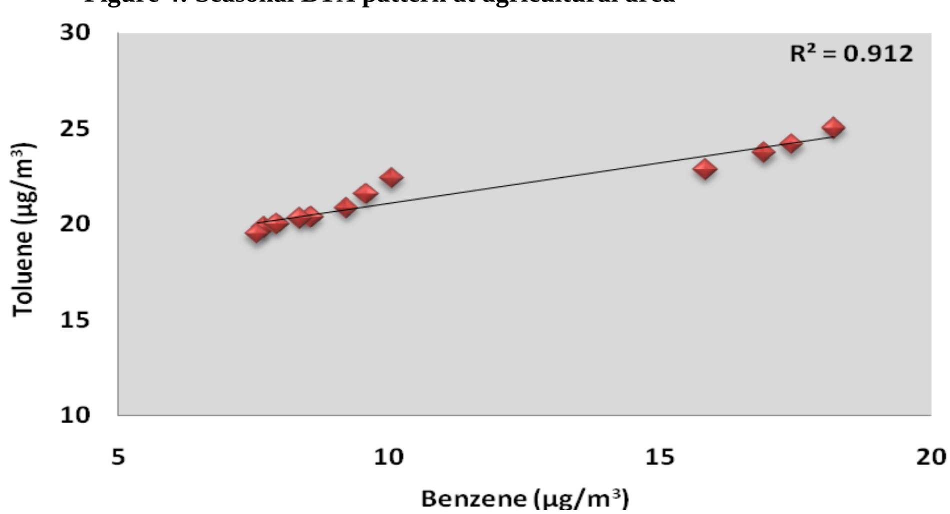

Figure 5: Correlation between Benzene and Toluene