A STUDY OF SEASONAL VARIATION OF BIOGENIC AND ANTHROPOGENIC ISOPRENE EMISSION IN THE AMBIENT AIR OF DELHI

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CERTIFICATE

This is to certify that the thesis entitled "**A study of seasonal variation of biogenic and anthropogenic isoprene emission in the ambient air of Delhi**" submitted to Jawaharlal Nehru University, New Delhi in fulfillment of the requirement for the award of Doctor of Philosophy, embodies original research work carried out by Prabhat Kashyap at School of Environmental Sciences, Jawaharlal Nehru University, New Delhi under the guidance and supervision of Prof. Krishan Kumar and this manuscript has not been submitted in part or full for any degree or diploma in this or any other University.

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It is my genuine gratefulness and warmest regard that

I dedicate this humble piece of work to my beloved

parents for their affection, love and support

And

To my brother who has always been

my greatest inspiration

Acknowledgements

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List of Abbreviations

Average Lifetime	LT
Benzene, Toluene, Ethylbenzene, m/p-Xylene and o-Xylene	BTEX
Biogenic Emission Inventory System	BEIS
Biogenic Volatile Organic Compounds	BVOC
Body Weight	BW
Brunauer-Emmett-Teller	BET
Cancer Risk	CR
Cancer Slope Factor	CSF
Central Pollution Control Board	CPCB
Central Road Research Institute	CRI
Chemical Transport Model	CTM
Chronic Daily Intake	CDI
Cloud Condensation Nuclei	CCN
Compressed Natural Gas	CNG
Delhi Development Authority	DDA
Delhi Pollution Control Committee	DPCC
Delhi Transport Corporation	DTC
Dimethyl allyl pyrophosphate	DMAPP
Emission Factor	EF
Exposed Concentration	EC
Exposure Duration	ED
Exposure Frequency	EF
Exposure Time	ET
Factor Analysis	FA
Gas Chromatograph	GC
Gas Chromatograph-Mass Spectrometry	GC-MS
Gas Chromatograph-Flame Ionization Detector	GC-FID
Global Ozone Monitoring Experiment	GOME
Goddard Earth Observing System global 3-D model of tropospheric chemistry	GEOSCHEM

Hazard Index	HI
Hazard Quotient	HQ
Hydroperoxyl radicals	HO_2
Indian Meteorological Department	IMD
India's Council of Scientific and Industrial Research	CSIR
Inhalation Rate	IR
Inhalation Reference Concentration	RFC
Inhalation Unit Risk	IUR
International Agency for Research on Cancer	IARC
Isopentenyl diphosphate	IPP
Jawaharlal Nehru University	JNU
Maximum Incremental Reactivity	MIR
Methacrolein	MACR
Methyl Vinyl Ketone	MVK
Mevalonic Acid	MVA
Model of Emissions of Gases and Aerosols from Nature	MEGAN
National Ambient Air Quality Standards	NAAQ
National Capital Territory	NCT
National Highway-2	NH-2
Natural Volatile Organic Compound	NVOC
Nitric Oxide	NO
Nitrogen Oxides	NO_X
Non Carcinogenic Risk	NCR
Non-Methane Hydrocarbon	NMHC
Non-Methane Volatile Organic Compounds	NMVOC
Normalized Isoprene Emission Rate	NIER
Number of days in a year	NY
Oxygenated VOCs	OVOC
Ozone	O_3
Ozone Monitoring Instrument	OMI

Ozone Formation Potential	OFP
Particulate Matter	PM
Peroxyacyl nitrates	PAN
Peroxymethacrylic nitric anhydride	MPAN
Peroxyl Radical	RO_2
Photosynthetically Active Radiation	PAR
Pitampura	PTP
Planetary Boundary Layer	PBL
Principal Component Analysis	PCA
Punjabi Bagh	PJB
Quality Assurance	QA
Quality Control	QC
Relative Humidity	RH
Research & Development	R&D
Secondary Organic Aerosol	SOA
Solar Radiation	SR
Standard Temperature and Pressure	STP
Swarn Jayanti Park	SJP
United States Environmental Protection Agency	USEPA
University of Michigan Biological Station	UMBS
Volatile Organic Compounds	VOCs
Wind Speed	WS
World Health Organization	WHO
Yamuna Biodiversity Park	YBP

CHAPTER 1: INTRODUCTION

1. INTRODUCTION

1.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are a heterogeneous group of organic compounds which are present in gaseous or vapour phase, including hydrocarbons (aliphatic and aromatic), aldehydes, alcohols, organic acids, ketones, esters, and halogenated compounds sharing a distinguished trait of having high volatility and low boiling point. VOCs are considered to be significant due to their direct harmful and carcinogenic effects on human beings (Khoder, 2007; Parra et al., 2006) and also for their involvement in the formation of secondary pollutants like smog, photochemical oxidants, secondary organic aerosol etc. (Hoshi et al., 2008; Khoder, 2007).

1.2 Definitions of VOCs

United States Environmental Protection Agency (USEPA) defines VOCs on the basis of its atmospheric effects, as any carbon-containing compound, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in the atmospheric photochemical reactions except compounds having negligible photochemical reactivity i.e. methane (USEPA, 2009). According to European Union Directive 2004/42/CE (EU, 2004), any organic compounds having initial boiling points lower than or equal to 250°C at a standard atmospheric pressure of 101.3 kPa are considered VOCs.

1.3 Sources for VOCs

VOCs emissions sources include biogenic as well as anthropogenic (Atkinson, 2000; Mintz and McWhinney, 2008; Van Langenhove, 2010). Goldstein and Galbally (2007) estimated the global budget of atmospheric VOCs and their fate (Figure 1.1). On a global scale, the total estimated atmospheric VOCs coming from various sources are roughly 1300 teragrams of carbon per year (Tg yr^{-1}, 1 teragram = 10^{12} g). Out of

this, biogenic VOCs are estimated to be around 1150 Tg yr^{-1}, while the anthropogenic emissions are merely 150 Tg yr^{-1} which is roughly one-tenth from its biogenic counterpart (Guenther et al., 1995; Guenther et al., 2006; Talapatra and Srivastava, 2011).
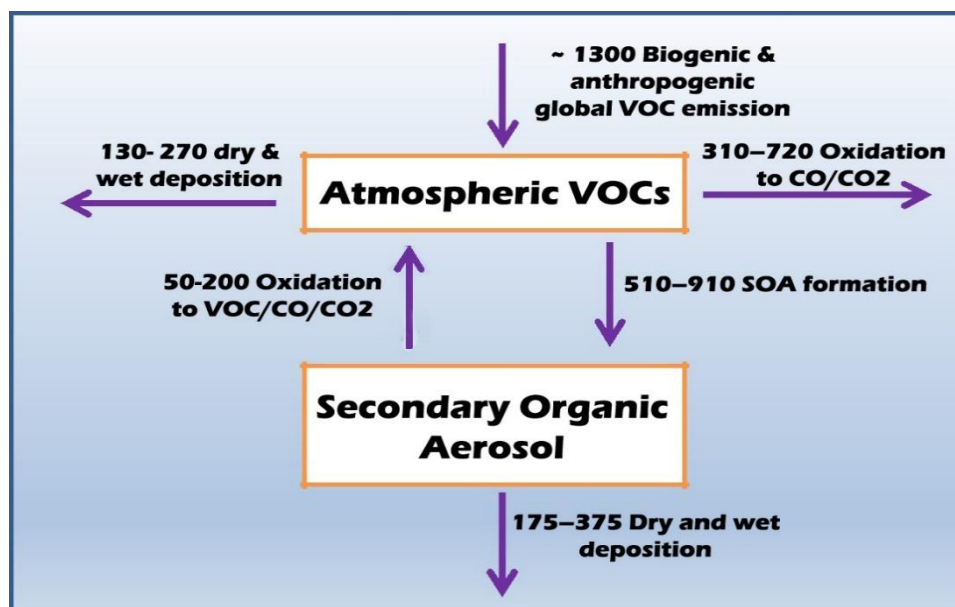
Figure 1.1: Global budget of atmospheric volatile organic compounds; all values are in Tg C/yr (adapted from Goldstein and Galbally, 2007).

1.3.1   Anthropogenic sources:

Anthropogenic emissions of VOCs may include stationary or point sources (largely from industrial activities) and mobile sources (mainly comes from transportation activities). The point sources of emission primarily consist of various industrial activities like petroleum refineries and storage processes, varnish and paint fumes, solvent usage, asphalt concrete factories, etc. (Buczynska et al., 2009; Dumanoglu et al., 2014; Rad et al., 2014). Petrol and diesel-operated motor vehicles are often considered as the key mobile source of ambient VOCs especially in the urban atmosphere (Alghamdi et al., 2014; Theloke and Friedrich, 2007; Guo et al., 2004; Caplain et al., 2006).   Other indoor sources may include perfumes, personal care products, glue, building construction materials, tobacco smoking, and solid waste

decomposition (Demirel et al., 2014; Gaur et al., 2016; Durmusoglu et al., 2010; Marć et al., 2015; Słomińska et al., 2014). Anthropogenic emissions are mostly characterised by saturated compounds with comparatively higher lifetimes from days to months (Atkinson, 1994). As a result, they can affect the atmospheric chemistry from regional to hemispheric level.

1.3.2   Natural sources:

Natural or biogenic sources of ambient VOCs mainly consist of the emissions from the vegetation which include large number of tree species especially from the forested areas, marine and freshwater system, geological reservoirs, phytoplanktons, decomposition of organic matter by microorganisms, soil microbes, animals, humans beings (Guenther, 1999; Guenther et al., 1995; Sahu, 2012). The maximum biogenic emissions occur from 23 N to 23 S in the tropical region of the globe because of the presence of diverse tree species (Karl et al., 2007). Among various sources, the major portion of natural or biogenic VOCs is contributed by terrestrial vegetation. Biogenic emissions mainly consist of unsaturated and highly reactive species having a very short lifetime (a few minutes to a few hours) (Guenther et al., 1999). Hence, they cause a local effect on tropospheric chemistry.

The biogenic volatile organic compounds (BVOCs) are released from different parts of plant organs (Laothawornkitkul et al., 2009). Leaves emit maximum amount of BVOC due to the high mass emission rate rather than flowers and fruits, which release a comparatively low but wide variety of BVOCs with maximum emission rates during maturity (Dixon and Hewett, 2000; Knudsen et al., 2006; Soares et al., 2007). Further, the vegetative part emits several types of BVOCs, such as monoterpenes, sesquiterpenes, isoprene, and diterpenes (Laothawornkitkul et al., 2009; Owen et al., 2001). More than thousands of BVOCs have been identified so far
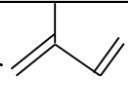
(Fall, 1999), but the isoprene and methane are the most prominent VOC species in terms of global annual flux.

1.4 Isoprene

Out of biogenic emissions, isoprene (2-methyl 1,3-butadiene, C_5H_8) emitted in high amount and has the capability to influence the global atmospheric chemistry. It is the single most abundant, highly reactive, colourless BVOC in our earth system. Isoprene was first discovered in the year 1950 by Sanadze & Kursunov in the form of volatile cell-metabolite emitted from plant leaves (Sanadze, 2004; Sharkey and Yeh, 2001).

Table 1.1: Chemical and physical properties of isoprene.

Isoprene (2-methyl-1,3-butadiene)	
Chemical Structure	C=C(C)C=C or
Molecular formula	C_5H_8
Molar mass	68.11 g mol^{-1}
Density	0.681 g cm^{-3} at 20 °C
Boiling Point	34.067 °C
Melting Point	-145.95 °C
Flash Point	-48 °C

Sources: (Bekkedahl et al., 1937; Lide, 2004)

The molecular formula of isoprene consists of five carbon atoms having two double bonds (C_5H_8). This structure of isoprene was identified in 1882 (Tilden, 1882). Isoprenoid species are derived from the biological precursors, mainly isopentenyl pyrophosphate (IPP) and its isomeric form dimethylallyl pyrophosphate (DMAPP). These precursors are together known as active isoprenes (Sharkey and Yeh, 2001). Physical properties of isoprene include, it is a highly volatile, colourless, and flammable liquid at room temperature, which readily reacts with other atmospheric compounds. It is readily soluble in organic solvents like methanol but not soluble in water. Other important chemical and physical properties are presented in Table 1.1.

1.4.1   Isoprene synthesis in plants

After methane (CH_4), isoprene is the most dominated hydrocarbon emitted from the vegetation (Telford et al., 2010). In plants, isoprene is synthesised by two different metabolic pathways occurring in the cells, the "mevalonic acid" (MVA), and "non-mevalonate" pathway. Both these pathways present in the photosynthetic cells of various plant species form isoprene, and they operate independently of each other (Laule et al., 2003). Isoprene emissions are detected in the leaves of various tree species such as poplar, oak, acacia, eucalyptus, willow, some legumes, etc. but no phylogenetic patterns have been observed among the isoprene emitting tree species (Harley et al., 1999). It has been estimated that around 30% of plant species are isoprene emitters (Tiiva et al., 2008). It was observed that the majority of isoprene-emitting tree species are woody angiosperms (Harley et al., 1999).

1.4.2   Isoprene emissions in the atmosphere

The global annual isoprene emission is estimated around 503 Tg C/yr, which is approximately 44% of the global biogenic emissions (1150 Tg C/yr) by various terrestrial tree species (Guenther et al., 1995). The share of other BVOCs like monoterpenes is 11%, other reactive hydrocarbons and non-reactive hydrocarbons are both 22.5% (Kansal, 2009; Guenther et al., 1995). This makes isoprene the most abundant BVOCs in the earth system. Isoprene thus plays an important role by affecting both gas phase and heterogeneous chemistry of the atmosphere regionally as well as globally. Isoprene is highly reactive BVOC having a rate of reaction ($1.00 \pm 0.15) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} with OH radicals in the gases phase, so it has very small atmospheric life (Medeiros et al., 2018; Guenther et al., 2006). Due to its high abundance along with water molecules and solar radiation in tropics, it disproportionately causes a major impact in tropical photochemistry (Sahu, 2012). At

regional level too, isoprene has been given same importance as other anthropogenic VOCs because it also has various anthropogenic sources as well along with biogenic sources (Borbon et al., 2001; Reimann et al., 2000).

1.4.3   Factors affecting isoprene emission

*Solar radiation***:** The biosynthesis of isoprene emission that occurs in the chloroplast of plant cells is closely connected with the photosynthesis, especially with the Calvin-Benson-Bassham cycle (Sharkey and Yeh, 2001). Many investigators studied the effect of light on the emissions rate of isoprene derived from plants, and it was found that its emission follows a similar pattern as that of photosynthesis (Rasmussen and Jones, 1973). The emission increases with light intensity and illumination until a saturation level of photosynthesis is reached (Guenther et al., 1993; Rasmussen and Jones, 1973). Therefore, the isoprene emissions are highly dependent on the light intensity; high illumination boosts up its emission rate while, low light intensity rapidly decreases isoprene emissions (Monson et al., 1991).

*Temperature***:** The role of temperature in isoprene emissions is important and differs from that of photosynthesis. At 30˚C or above, the process of photosynthesis becomes stable, or in declining phase while, isoprene emission is positively correlated with the temperature (Sharkey and Yeh, 2001). The emissions of isoprene from plants react almost instantaneously with a slight change in temperature. At 30˚C, merely 2% of carbon is emitted in the form of isoprene by the plants; however, 10˚C rise in temperature increases its value to 15% (Sharkey et al., 1996). Above 40˚C, the emission rate of isoprene becomes constant and goes down with a further increase in temperature (Harley et al., 1999).

Carbon dioxide: The change in ambient carbon dioxide concentrations can affect the rate of isoprene emissions by the plants. Various studies have demonstrated that

increased levels of CO_2 in the atmosphere decrease the isoprene emission rate (Tingey et al., 1981; Jones and Rasmussen, 1975). At low CO_2, isoprene emission depends on the atmospheric oxygen (O_2). In CO_2 free air, O_2 concentration determines the isoprene emission, and if in case the O_2 supply stops, the isoprene formation is also terminated (Loreto and Sharkey, 1990).

*Nitrogen***:** The emission of isoprene from various tree species is enhanced by the availability of nitrogenous nutrients whose effects are modulated by the sunlight (Litvak et al., 1996; Harley et al., 1994). Under good sunlight, a plant growing with low nitrogenous nutrient condition emits isoprene at a rate similar to that from the same plant when it grows under the shade with a similar amount of nitrogen nutrient (Sharkey et al., 2007).

*Other factors***:** Tingey et al., (1981) reported that in water stress conditions when the rate of photosynthesis and leaf conductance declined by more than 90%, the rate of isoprene emission remains almost constant. However, isoprene emission rate increased to five times from its pre-stress rate upon re-watering, when photosynthesis recovered to its pre-stress level (Sharkey and Loreto, 1993).

Isoprene emission at a certain part of the plant is affected by the wounds on any other part of the same plant. Wounds (puncturing, cutting, burning, etc.) transmit signals to the unaffected leaves of the plant and affect the isoprene emission ability of nearby leaves (Loreto and Sharkey, 1993). The isoprene emission rate is linearly related to the distance from the damaged leaves (Loreto and Sharkey, 1993).

1.4.4   Role of isoprene in Plants

Various terpenoid species are emitted by the plants for different roles. For example, they may help the plant in deterring herbivores, attracting pollinators for pollination and defence against pathogens, in addition to their role as mating pheromones, visual pigments, reproductive hormones and components for plant communication (Holopainen,

2004; Peñuelas and Munné-Bosch, 2005; Sacchettini and Poulter, 1997). Moreover, isoprene acts as a flowering hormone (Terry et al., 1995), as an antioxidant by quenching ozone from the atmosphere, and as a metabolite which serves the plant by getting rid of excess carbon or energy. In addition to these functions, the most important role of isoprene is the photo-protection (Sharkey et al., 2007; Peñuelas and Munné-Bosch, 2005). Isoprene act as a photoprotective agent, which protect the plants from intense solar radiation. Isoprene by acting as an antioxidant, which provides thermo-tolerance to the plant. According to the thermo-tolerance hypothesis, isoprene emissions protect the plant from the damage caused by high temperature to the photosynthesis (Sharkey and Singsaas, 1995). Isoprene serves as one of the most effective antioxidants in leaves because of its rapid reaction with ozone (Sharkey and Yeh, 2001).

1.4.5 Atmospheric role of isoprene

Isoprene plays a significant role in the atmosphere due to its huge annual global emission rate and its fast reactivity towards several chemical species present in the atmosphere (Palmer and Shaw, 2005). The isoprene chemistry is complex to understand because of its highly reactive nature that involves numerous interactions with the different constituents of the atmosphere. In the atmosphere, OH radicals work as a strong oxidant and are often referred as "detergent of the atmosphere" (Comes, 1994), because they oxidize majority of pollutants including isoprene from the atmosphere and clean it up. They combine with isoprene molecules present in the atmosphere to form the double bond followed by immediate addition of oxygen to form a series of peroxy radicals (ISOPOO; $HOC_5H_8OO^.$) (Paulson et al., 1992; Jenkin et al., 1998) (Figure 1.2).

Further, the chemistry of these newly formed peroxy radicals (ISOPOO$^.$) depends upon the atmospheric conditions. According to their atmospheric behaviour, these

radicals can proceed through the following pathways: (a) react with nitric oxide (NO) to form ozone in NOx dominated atmosphere (Tuazon and Atkinson, 1990; Liu et al., 2013), (b) react with hydroperoxyl radicals (HO_2) to form organic hydroperoxides (ISOPOOH; HOC_5H_8OOH) or alkoxy radicals (ISOPO, $HOC_5H_8O^.$) (Paulot et al., 2009), (c) react with self and cross peroxyl radicals (RO_2) to form alkoxy radicals (Jenkin et al., 1998), and (d) involve in other uni-molecular isomerization reactions (Da Silva et al., 2009; Crounse et al., 2011). Alkoxy radicals rapidly decompose to form different products like formaldehyde, hydroxyl radical, and carbonyl compounds (Gu et al., 1985; Killus and Whitten, 1984). Carbonyl compounds such as methyl vinyl ketone (MVK, C_4H_6O) and methacrolein (MACR, C_4H_6O) are formed by the decomposition of ISOPBO and ISOPDO isomeric forms (Figure 1.2).

$$\text{ISOPBO} + O_2 \rightarrow \textbf{MVK} + \textbf{HCHO} + \textbf{HO}_2 \qquad\qquad (1.1)$$
$$\text{ISOPBO} + O_2 \rightarrow \textbf{MACR} + \textbf{HCHO} + \textbf{HO}_2 \qquad\qquad (1.2)$$
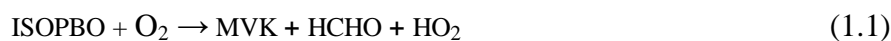
First two pathways, i.e. reaction with NO and HO_2 are the major determining pathways for $ISOPOO^.$ radicals (Crounse et al., 2011). Most of the isoprene dominated regions; particularly tropical forests are having less NOx (Lelieveld et al., 2008) and hence, HO_2 pathway determines the fate of $ISOPOO^.$ Radicals (Crounse et al., 2011). However, NO pathway dominates in NOx rich urban polluted areas where isoprene significantly influences the tropospheric chemistry (Liu et al., 2013).
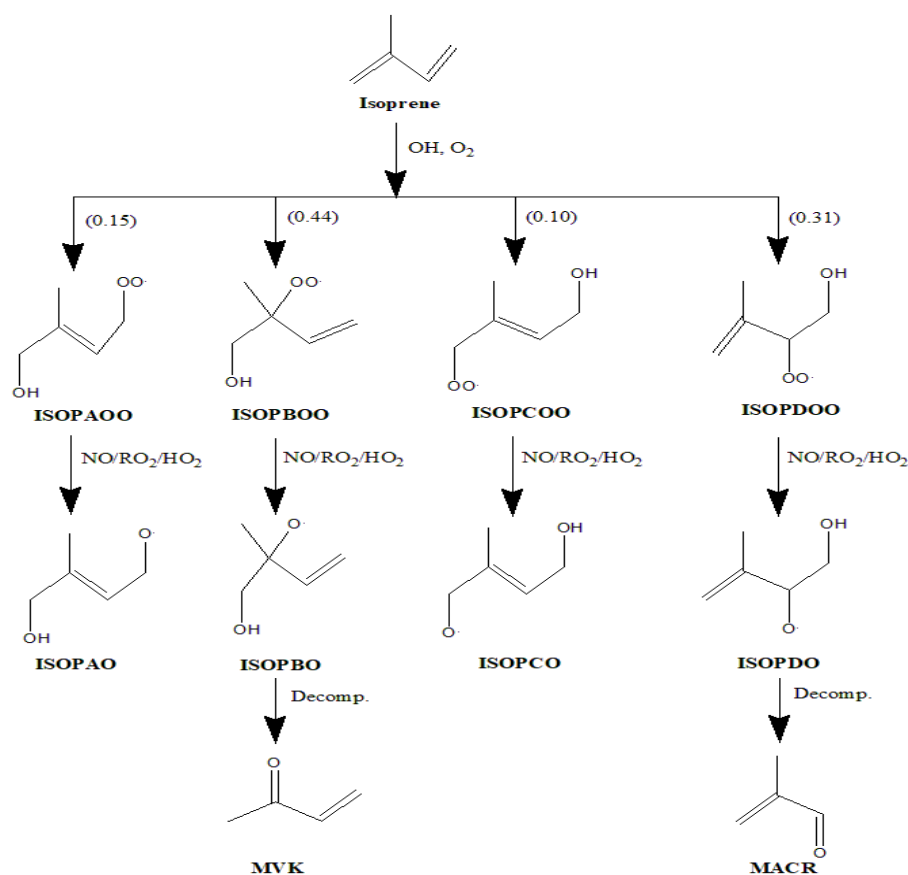
Figure 1.2: Isoprene oxidation mechanism and formation of MVK and MACR after decomposition of ISOPBO and ISOPDO (adapted from Liu et al., 2013).

1.4.5.1 Formation and destruction of ozone in the troposphere

In the urban area where NOx levels are high, isoprene oxidized to form peroxy radicals and combine with NO to generate alkoxy radicals and nitrogen dioxide (NO_2). Further, NO_2 undergoes photolysis and leads to the formation of ozone molecule with NO. The NO and NO_2 cycle determines the amount of O_3 produced in the atmosphere, and one O_3 molecule is produced per NO_2 (Jacob, 1999). Further, reactions generate HO_2 radicals that can again convert NO to NO_2 and produced OH radical. Following reactions describe the formation of O_3 from isoprene.

$$\text{Isoprene (C}_5\text{H}_8\text{)} + OH + O_2 \rightarrow ISOPOO^. + H_2O \qquad (1.3)$$

$$ISOPOO^. + NO \rightarrow ISOPO^. + NO_2 \qquad (1.4)$$

$$ISOPO^. + O_2 \rightarrow HCHO + HO_2 \qquad (1.5)$$

$$HO_2 + NO \rightarrow OH + NO_2 \qquad (1.6)$$

$$2(NO_2 + O_2 \rightarrow NO + O_3) \tag{1.7}$$

$$\text{Net: Isoprene} + 4O_2 + NO \rightarrow HCHO + 2O_3 + H_2O \tag{1.8}$$

When NOx levels are high, one molecule of isoprene forms many molecules of ozone but at low NOx, isoprene directly combines with ozone that results in ozone destruction (Sharkey et al., 2007). A simplified diagram is shown in Figure 1.3 for the production and destruction of O_3 in the atmosphere.

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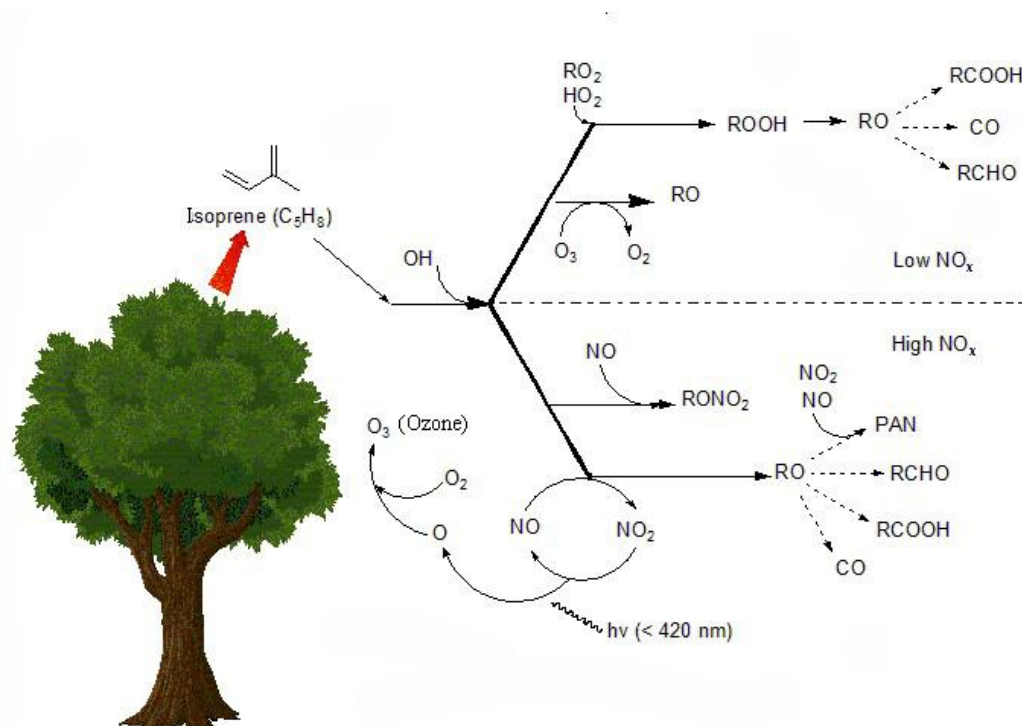
Figure 1.3: Atmospheric reactions of isoprene in high and low NOx levels and other potential products forming from its oxidation (adapted from Harley et al., 1999).

1.4.5.2   Formation of Organic nitrates and PANs

In the atmosphere, nitrogen oxides (NOx) are emitted from various sources, primarily in the form of NO that is instantly converted into a steady-state, NO_2. The major loss of NOx from the atmosphere is the reaction producing nitric acid (HNO_3) from hydroxyl radical (OH) (Fisher et al., 2016). However, different reactions dominate in the presence of isoprene or other VOCs. NOx readily reacts with organic peroxy

radicals (RO$_2$) and forms different types of nitrates, i.e. peroxy nitrates (RO$_2$NO$_2$), alkyl nitrates (RONO) and multifunctional organic nitrates (RONO$_2$) (O'Brien et al., 1995). Further, these organic nitrates are lost as dry and wet depositions, which provide an efficient mechanism of removing NOx from the atmosphere. Photo-oxidation of isoprene with NOx also forms peroxyacylnitrates (PANs) which are phytotoxic and eye irritants, and which readily dissolve in water (Taylor, 1969). At high temperature, they decompose and release NOx. Hydroxyl and nitrate initiated oxidation of methacrolein (MACR), which is the main product of isoprene oxidation, produces peroxymethacrylic nitric anhydride (MPAN) which is a harmful product (Orlando et al., 2002). Figure 1.4 shows the reactions taking place in the formation of MPAN.
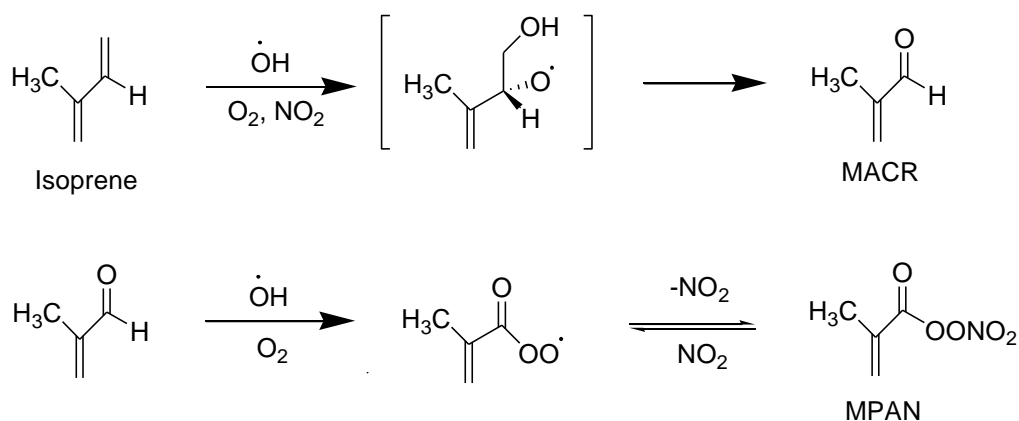
Figure 1.4: Formation of peroxymethacrylic nitric anhydride (MPAN) from the oxidation of methacrolein (MACR) (adapted from Bertman and Roberts, 1991).

1.4.5.3 *Formation of organic acids*

Oxidation of isoprene in the interstitial spaces of cloud or fog leads to the formation of water-soluble aldehydes. Because of the presence of an elevated concentration of OH radicals in the cloud's interstitial spaces (Mauldin et al., 1997), these water-soluble organic compounds are further oxidised to form weak organic acids (such as formic, oxalic, glycolic and acetic acid) (Lim et al., 2005). These less volatile organic

acids contribute a major fraction of acidity in rainwater, which might be very high in comparison to the contribution of sulphuric and nitric acid (Sun et al., 2016) Figure 1.5 shows the isoprene cloud chemistry and formation of various organic acids.
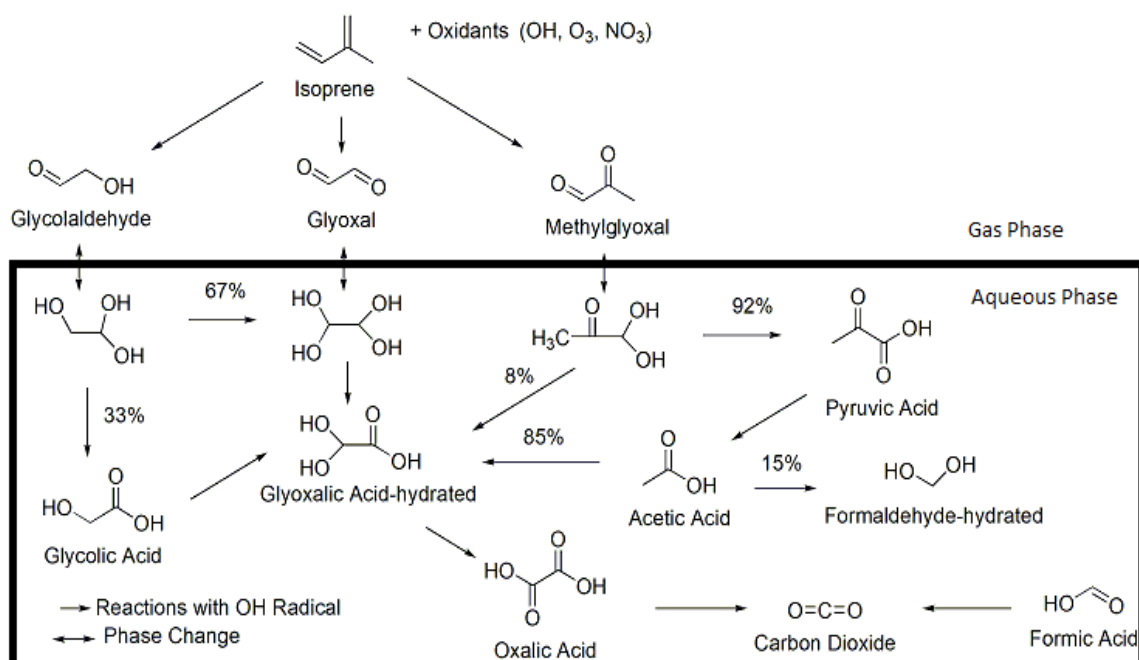
Figure 1.5: Isoprene cloud chemistry and formation of various organic acids. (Adapted from Lim et al., 2005).

1.4.5.4   Role in particulate matter formation

The global emission of isoprene is very high as compared to other biogenic or anthropogenic VOCs. Many researchers reported that isoprene might be involved in the formation of Secondary Organic Aerosol (SOA) through numerous heterogeneous reactions. Kroll et al. (2005) proposed the possibility that the gas phase oxidation of isoprene, leading to the formation of SOA. It was also observed that water-soluble volatile aldehydes produced from the isoprene photo-oxidation, undergo various heterogeneous reactions like polymerization, hydration, acetyl formation in the presence of an atmospheric acid catalyst such as sulphuric acid and contribute to the formation of SOA (Jang and Kamens, 2001). Sometimes these particles may act as cloud condensation nuclei (CCN), that may take part in the formation of raindrop. The organic aerosols play

an important role in maintaining the radiation balance of earth by scattering and absorbing the light. These aerosols act as CCN in the atmosphere (Andreae and Crutzen, 1997) and have drawn the attention of investigators across the globe in understanding the role of isoprene in aerosol formation and its associated chemistry (Claeys et al., 2004; Griffin et al., 1999; Hoffmann et al., 1997; Kroll et al., 2006; Pandis et al., 1992).

1.4.5.5   *Role in Global Warming*
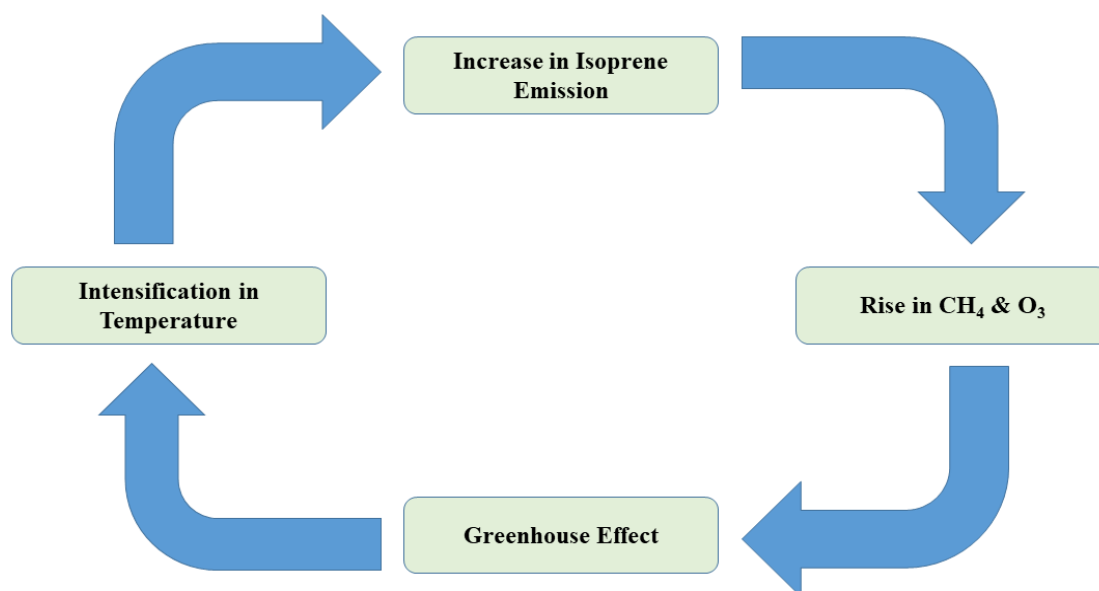
Figure 1.6: Role of isoprene in global warming.

One of the secondary implications of increasing levels of isoprene in the atmosphere is that it enhances the effect of global warming for biospheric habitability (Turner et al., 1991). Isoprene affects the growth rates and abundance of various greenhouse gases like O_3, CH_4, and HFCs by influencing the abundance of OH radicals in the lower atmosphere (Bell et al., 2003). Ozone formation from the oxidation of isoprene in the presence of NOx and UV radiation has been well established (Atkinson, 2000). In turn, O_3 also acts as a significant source of carbon monoxide (CO), which again plays an indirect role in global warming (Fishman and Crutzen, 1978). Isoprene emissions are strongly linked with the ambient temperature of the atmosphere (Loreto and Sharkey, 1990; Monson and Fall, 1989). Rise in global temperature because of

greenhouse gases further increases the isoprene concentrations. As a result, isoprene may have less potential to remove methane in the troposphere further resulting in global warming (Turner et al., 1991). This makes a feedback loop shown in Figure 1.6, in which levels of isoprene along with methane and ozone increase with each other. This indirect role of isoprene in contributing to global warming is significant, as methane has a higher global warming potential as compared to CO_2 (Ali et al., 2013). Thus, the role of isoprene in the contribution of global warming cannot be ignored.

1.5   Literature Review

1.5.1   International Scenario

Given the significant role isoprene plays in the tropospheric chemistry, a number of studies have been conducted worldwide at the local, regional and global levels to monitor its emissions and examine its influence on the photochemistry of the lower atmosphere.

Rasmussen and Khalil (1988) measured the isoprene variations at different altitudes (150 m, 360 m, 710 m, 1520 m, 3700 m) from the ground over the Amazon Basin and found that the concentration of isoprene declined rapidly with altitude, with the minima occurring at the boundary layer. The study also reported that maximum concentrations of isoprene occurred during mid-day time and lowest during night-time. In the Amazon forest area, concentrations of isoprene were found to increase to its highest at the level of the canopy.

Tuazon and Atkinson (1990) investigated the reaction of isoprene with OH radicals in the presence of NOx and identified the products formed by this reaction. They found that MVK, MACR, and HCHO were the main products, and 3-methylfuran was the minor product obtained with this reaction. Previously, Gu et al. (1985) also studied

the same reaction and reported that 3-methylfuran was the major product along with methyl vinyl ketone, methacrolein, and formaldehyde.

Guenther et al. (1991) measured the variability of isoprene in the leaves of *Eucalyptus globulus* with the help of laboratory-based gas exchange system under constant environmental conditions. They observed that the short-term fluctuations in isoprene emission rate were very low as compared to the day-to-day fluctuations. The leaf-to-leaf variation was much higher (~ 60 %), possibly due to the variation in the leaf ages. Temperature and light dependency were also examined. Isoprene emissions from tree species at leaf level were better described by the relationships based on both photosynthetically active radiation (PAR) and leaf temperature. On the basis of it, they developed an isoprene emission rate model. The model predicted the isoprene variations within the 10 % range with the observed emission rate. Later, Guenther et al. (1993) modified these algorithms and developed a model which can simulate isoprene emission rates more precisely. Further, Guenther et al. (1995) developed a global model for estimating natural volatile organic compounds (NVOCs) emissions. They estimated that the total annual global flux of VOC was 1150 TgC which mainly consisted of isoprene (44%), monoterpenes (11%), other reactive VOCs (22.5%) and nonreactive VOCs (22.5%).

Pierce and Waldruff (1991) used the Personal Computer adapted Biogenic Emission Inventory System (PC-BEIS) model developed by the United States Environmental Protection Agency (USEPA) to estimate hourly isoprene emissions along with other biogenic hydrocarbons based on input information on meteorological parameters such as temperature, cloud cover, wind speed, and relative humidity. They found the model to be useful but also reported various uncertainties in the data.

Jobson et al. (1994) investigated the seasonal variation in the isoprene, alkanes (C_2 to C_5) and acetylene levels over a period of more than 2 years at a remote boreal site of

Canada. Their results showed that levels of isoprene were found to be high from July to August. On the other hand, the concentrations of alkanes (C_2 to C_5) and acetylene showed different pattern as their concentrations were minimal during summers (July to August) and higher during winters (December to February).

McLaren et al. (1996) conducted a study on isoprene over the Amazon basin, and for the first time, they observed isoprene concentrations at roadside sites. They observed that variable temporal traffic patterns influenced the isoprene levels in the urban atmosphere. During morning rush hour, peaks of isoprene from the urban area indicated that the isoprene was emitted mainly from the vehicular exhaust.

Hagerman et al. (1997) investigated the biogenic hydrocarbons consisting mainly of isoprene and terpenes, which showed a seasonal trend with higher concentration during summer and minimum during winter at the Southeast United States. However, isoprene was virtually negligible in winters at almost all the sites, whereas its value varied from 9.8 ppbC to 2l.15 ppbC during the summer.

Keller and Lerdau (1999) screened 51 different tree species for determining the isoprene emission rates at the canopy top of the semi-deciduous forest in the Republic of Panama. Out of these, 15 isoprene-emitting trees had the emission rates of more than 0.8 nmol m^2 s^{-1}. Isoprene emission showed a hyperbolic response against the light and exponential response with respect to temperature. With these results, they modified the algorithms suggested by Guenther et al. (1995) for light responses and compared the new results with the previous results obtained by using a global model for temperate plants in estimating isoprene emissions. Comparison of results suggested that the model underestimated the isoprene emissions for the tropical plants by using algorithms developed for temperate plants because of the presence of intense light and high temperature.

He et al. (2000) measured the isoprene and monoterpene emissions in fifteen Eucalyptus species in Australia using air exchange chamber technique. The combined emission rate of isoprene and monoterpene from Eucalyptus species were very high, and most of the species were found to be high emitters except *E. cladocalyx, E. botryoides* and *E. wandoo* (as they were moderate emitters). It was also found that isoprene was the most dominant species emitted by the Eucalyptus tree.

Reimann et al. (2000) monitored isoprene along with 1,3-butadiene concentrations at the rural region of Taenikon, Switzerland. They used the molar ratio of isoprene and 1,3-butadiene to calculate the anthropogenic portion of isoprene. It was observed that the anthropogenic portion of isoprene was close to 100 % during winters whereas the biogenic portion was dominant during summers. These results revealed that a major portion of isoprene was anthropogenic in nature during winters.

Borbon et al. (2001) measured isoprene along with 30 other VOCs at an urban location in France. Emissions of these hydrocarbons were also determined in passenger vehicles with the help of chassis dynamometer to investigate the double origin of isoprene. For the estimation of the anthropogenic isoprene, several traffic tracers were used. Out of various traffic tracers, 1,3-butadiene suited well for the estimation of the anthropogenic fraction of isoprene. Their results showed that traffic was the chief source of isoprene during winter with a contribution of 50%. However, it constituted a non-negligible source of isoprene in summer.

Petron et al. (2001) studied the impact of temperature variation on isoprene emission rate on bur oak leaves (*Quercus macrocarpa*) under controlled conditions. The whole tree was grown under growth chamber and was exposed to a series of temperature for 3-4 weeks. It was observed that the emission capacity of the tree leaves doubled when the temperature increased by 5°C and decreased to 50% when temperature was decreased to 20°C.

Apel et al. (2002) measured the mixing ratios of isoprene and its oxidation products, i.e. methyl vinyl ketone (MVK), and methacrolein (MACR) during summer of 1998 from a tower at the rural forested area located inside the campus of University of Michigan Biological Station (UMBS). Isoprene flux was also estimated with the help of BEIS-3 model by taking 1 km of emission resolution with a radius of 60 km from the tower. Estimated isoprene emission from the model was compared well with the measured isoprene flux. They also observed a rapid decrease in the concentration of isoprene after sunset. They suggested that vertical diffusion and advection of air could be the possible reason for this rapid decrease in the isoprene concentration after sunset.

Sanderson et al. (2003) investigated the effect of climate change on isoprene emission, vegetation, and ground-level ozone by using a 3D general circulation model, which was coupled with dynamic vegetation and chemistry models. Based on the model, they performed iterations for the years 1990 and 2090 and found that the isoprene emission would increase to 736 Tg yr^{-1} in the year 2090 from the value of 549 Tg yr^{-1} in the 1990s due to climate change in a fixed vegetation scenario. While, if changes in vegetation were included, the isoprene emission would increase only up to 697 Tg yr^{-1}. Similarly, ozone levels would increase by 20 to 30 ppbv with fixed vegetation and only by 10–20 ppbv if the changes in vegetation were accounted for.

Lim et al. (2005) developed a photochemical model to study the role of isoprene in the formation of SOA through cloud processing. They suggested that oxidation of isoprene in the interstitial spaces of cloud or fog lead to the formation of water-soluble aldehydes. These aldehydes further formed weak acids after reacting with OH radicals present in the interstitial spaces of clouds and form SOA during cloud evaporation.

Lee and Wang (2006) measured isoprene along with other hydrocarbons at two different suburban and urban locations of Taiwan to understand their possible role in ozone formation. Hourly measurements of isoprene along with other meteorological parameters were taken at both the sites in order to interpret the seasonal and diurnal pattern of isoprene. Their results revealed that isoprene levels were highly synchronous with solar radiation during summer. On the other hand, during winter, the mixing ratio of isoprene showed little concurrency with solar irradiation, and anthropogenic sources of isoprene were dominant at the urban site. Further, isoprene was higher during the mid hours of the day and largely involved in the photochemical process, which leads to the forming of tropospheric ozone.

Guenther et al. (2006) developed a Model of Emissions of gases and aerosols and used it to quantify the biogenic emissions, especially, isoprene at both global and regional level. The model had global coverage with a spatial resolution of nearly 1 km^2. The variables required for the model were derived from satellite observations. Model estimated global annual isoprene emissions were 500 to 750 Tg. They also compared the isoprene emission estimates with the satellite-derived HCHO measurements and found a reasonable agreement among them.

Müller et al. (2008) calculated the inter-annual variability of global isoprene emission from 1995 to 2006 by using Model of Emissions of Gases and Aerosols from Nature (MEGAN) model developed by Guenther et al. (2006) at a resolution of 0.5° x 0.5°. The estimated global isoprene emission by the model ranged from 374 Tg in 1996 to 449 Tg in 2005 with an average value of 410 Tg year^{-1}. The results of the model were also compared with the field measurements and the isoprene estimates computed from the Goddard Earth Observing System global 3-D model of tropospheric chemistry (GEOS-CHEM) tropospheric chemical/transport model (CTM) based on HCHO

column data obtained from Global Ozone Monitoring Experiment (GOME). Results showed that the model could capture the short-term variability in isoprene concentrations well, but it overestimated the isoprene fluxes during the rainy season.

Millet et al. (2008) studied the measurements of HCHO column by the Ozone Monitoring Instrument (OMI) having a daily global coverage with 13 x 24 km^2 nadir footprint to estimate the biogenic isoprene emissions over North America. They compared the OMI derived estimates of isoprene with the other isoprene emission inventories especially MEGAN derived isoprene emissions. They obtained a better fit (R^2 = 0.73) with MEGAN when using uniform isoprene emission factors for the broadleaf trees. However, in the case of high isoprene emission factor, the model may overestimate the emissions. Therefore, they further optimized the MEGAN emission factors for the broadleaf trees, which act as a major isoprene emission source.

Warneke et al. (2010) performed airborne measurements of biogenic VOCs mainly isoprene and monoterpenes over Eastern USA and Texas. Results obtained from the measurements were used to assess the biogenic emission inventories (BEIS3.12, BEIS3.13, MEGAN2, and WM2001). Assessment of inventories was done in two ways: Firstly, direct comparison of the measured results with the inventories. Secondly, comparison of airborne measurements with the isoprene and monoterpenes emissions calculated from BEIS3.12 coupled with transport model FLEXPART. The uncertainty lied within a factor of 2 for all inventories for isoprene. Comparison results suggested that the BEIS inventories underestimated the isoprene emissions while MEGAN overestimated the emissions from the actual measurements.

Hellén et al. (2012) studied the seasonal variation of isoprene and its effect on local air quality of Helsinki, Finland. The highest concentration of monoterpenes and isoprene were observed during summer as compared to winter seasons. But, during winter the highest concentration of isoprene was reported in the urban area as

compared to the forested site, which indicated towards the traffic or other anthropogenic emission sources. A significant concentration of isoprene was also observed in July and October month due to biogenic emission. The study also explained the high OH-radical reactivity and ozone formation, which affected local air chemistry and quality due to isoprene emission.

Chang et al. (2014) studied the isoprene emissions in the Taipei and observed that isoprene emissions were dominant during wintertime because of anthropogenic sources. On the other hand, isoprene in the ambient air was mainly because of biogenic sources in summer.

Wagner and Kuttler (2014) compared isoprene concentration with benzene and toluene and found that the diurnal variation in isoprene concentration depended on the temperature and was mainly from the biogenic emissions in summer. It was found to be more as compared to benzene and toluene concentrations during day time.

Franco et al. (2015) monitored VOCs in ambient air at three different sites of Bogota, Colombia using Synstech Spectra portable gas chromatograph. Mean VOC concentrations were observed to be higher at the industrial sites and the sites where commercial activity and vehicular activity were high. The diurnal trend of total VOCs showed that concentrations were high during morning and evening time. The study also reported that road traffic activities influenced the concentrations of VOC. Role of each VOC in ozone formation was calculated using a maximum incremental reactivity method. It was concluded that most of VOCs were emitted from road traffic and were responsible for ozone formation.

Salameh et al. (2015) measured C_2-C_{16} non-methane hydrocarbons (NMHCs) at a suburban site in Beirut during field campaign in summer 2011 and winter 2012. Toluene, isopentane, butane, m/p-xylenes, propane, and ethylene were the most

abundant NMHCs in both seasons. Petrol evaporation and vehicular exhaust were the main emission sources. It was observed that maximum concentrations occurred in summer and minimum during winter. Further, they investigated the duality of the biogenic and vehicle exhaust origin of isoprene. Their results showed biogenic isoprene concentration was more during daytime in summer however vehicular exhaust emission was dominant during night in winter.

Temporal variability and sources of VOCs were monitored by Kaltsonoudis et al. (2016) in different urban areas of Athens and Patras in Greece. It was concluded that the high concentration of VOCs during summer was due to emission from traffic and biogenic sources, while isoprene emitted mainly from the vegetation. It was also noticed that the wintertime emissions of VOCs were mainly due to biomass burning used for the residential heating and biogenic factors.

Dunn-Johnston et al. (2016) studied the isoprene emission rates of *Xanthostemon chrysanthus, Buckinghamia celsissima, Harpullia pendula* and substituted those rates in their model to extrapolate and quantify the isoprene emissions in the target regions. Their study showed that care needed to be taken while extrapolating the individual species emissions over a larger community scale.

Tani et al. (2017) studied the effects of ozone on the isoprene emissions by two *Quericus* species and showed a decrease in the isoprene emissions and added that though the response is similar, the underlying molecular mechanism involved may not be identical.

Hantson et al. (2017) studied the global isoprene and monoterpene emissions with respect to land use as well as climate change and showed that the anthropogenic land-use change was responsible for the global decrease in isoprene emissions and

demonstrated that the isoprene emissions could remain stable or further decrease depending on the underlying land-use scenario.

Chen et al. (2018) studied the patterns of biogenic emissions of isoprene at a global level with the help of satellite tree coverage data and modeled it using the MEGAN model which maps the isoprene emissions based on the land cover/land use patterns. The data though had systematic error due to overestimation of tree cover at sparse regions and underestimation at dense regions yet it was still sufficient to infer to the gain of isoprene emissions in response to afforestation and loss in response to deforestation, thereby confirming that the isoprene emissions could be used as a parameter to make qualitative inferences on the change in land use.

Panopoulou et al. (2018) investigated the role of traffic, and heating in non-methane hydrocarbon (NMHC) variability, ozone, and secondary organic aerosol formation during wintertime, in Athens, Greece. They reported the high level of NMHC during winter by 4 times as compared to autumn, which could be due to domestic heating along with traffic sources. It was also concluded that high level of NMHC in the morning was due to traffic while night peak was due to heating. Among the NMHCs which they also studied isoprene had the lowest concentration and showed similar patterns of monthly variability as other NMHCs.   Meteorological factors such as wind speed and planetary boundary layer (PBL) affect significantly the concentration of NMHC. Their study had the highest concentrations of the NMHCs reported in the Mediterranean region.

1.5.2   Indian Scenario

In the Indian context, numerous enclosure based measurement studies have been conducted to examine the normalized isoprene emission rate (NIER) from different types of plants.

Varshney and Singh (2003) carried out a detailed study of isoprene emission from 43 tropical Indian trees through enclosure chamber technique and classified these plant species on the basis of isoprene emissions into four categories, i.e. negligible (BDL), low, moderate and high isoprene emitting varieties of plants species. They found the eleven plant species as high isoprene emitting (25 mg g^{-1} h^{-1}), five as moderate (10 to <25 mg g^{-1} h^{-1}), six as low emitting (1 to <10 mg g^{-1} h^{-1}), and eighteen as negligible (<1 mg g^{-1} h^{-1}) isoprene emitting. They also reported maximum isoprene emission in *Dalbergia sissoo* (81.5 mg g^{-1} h^{-1}) while negligible in case of citrus species.

Padhy and Varshney (2005a) measured VOC emissions from 51 common plant species of Delhi, India and provided detailed information about hourly, diurnal, and seasonal emission patterns of VOC. In this study, they noticed no VOC emission from fifteen plant species, while thirty-two plant species were reported as moderate to low emitters. Out of these 51 plant species, they reported four plant species as very high VOC emitters. They also reported maximum value (87 lg g^{-1} dry leaf h^{-1}) of VOC emission in *Lantana camara*, and minimum (<1 lg g^{-1} dry leaf h^{-1}) in *Ficus infectoria*.

Padhy and Varshney (2005b) measured the diurnal and seasonal variation of foliar isoprene emission in nine common plant species of Delhi during 1998-99. They collected samples using Tenax-GC cartridges by Dynamic flow enclosure technique. In this study, they reported no isoprene emission in three plant species (*Azadirachta indica, Alstonia scholaris, and Cassia fistula*) while isoprene emission was found in six other plant species viz. *Ficus religiosa, Mangifera indica, Ficus benghalensis, Melia azedarach, Eucalyptus sp., and Syzygium jambolanum*. No isoprene emission was reported during the night time.

Singh et al. (2007) studied the seasonal and monthly variations in isoprene emission from four deciduous plant species (*Ficus infectoria, Ficus relegiosa, Pongamia*

pinnata, and Morus alba) during 2002-03. Significant seasonal variation of isoprene emission rate was noticed with maximum and minimum values during summer and winter, respectively for all plant species. Maximum isoprene emission was reported in *Ficus relegiosa.*

Singh et al. (2008) examined isoprene emission of 40 Indian plant species through enclosure chamber technique, where maximum isoprene emission rate was found in *Madhuca latifolia* (69.5 μ g g^{-1} h^{-1}). They also experimented on 80 common Indian plants for suitability for afforestation and plantation program. In this experiment, they reported that about 50% of plant species fell in the categories of moderate to high (10 to $\leq$25 μ g g^{-1} h^{-1}), and low isoprene emitters (1 to $\leq$10 μ g g^{-1} h^{-1}) while remaining were in the non-isoprene emitter category. They also suggested that VOC emission potential of plants species should be taken into account while afforestation and plantation programs because of their adverse impact on air quality by changing atmospheric chemistry.

Sinha et al. (2014) studied VOCs over IGP region and makes use of an atmospheric chemistry facility combining high sensitivity proton transfer, ambient air quality station and meteorological station making the study first of its kind on the Indian region and giving an insight VOC emitting sources. They studied isoprene and its correlation with other VOCs. They concurred with other studies attributing high concentrations of Isoprene with biogenic emissions from nearby forests and parks in the urban areas.

Sahu and Saxena (2015) studied the VOCs concentrations in Ahmadabad, India, during the winter of 2013. They noticed clear diurnal variation in the concentration of VOCs, with maximum emission in the morning and evening hours, while lowest during the afternoon. Aromatic VOCs were reported in the range of 0.85–23 ppbv,

where OVOCs constituted up to 80% of total measured VOCs. They reported the isoprene concentration of 1.6 ± 0.55 ppb in the ambient air. They also concluded that the local meteorological conditions and the height of the planetary boundary layer (PBL) also influenced the pattern of VOCs emission.

Seasonal variation of isoprene emissions rate from two plant species (*Dalbergia sissoo* and *Nerium oleander*) were examined by Saxena (2015) with the help of the bag enclosure technique in Delhi. The result showed high isoprene emission from *Dalbergia sissoo* (84.67 ± 3.87 μg/g/h) as compared to *Nerium oleander* (0.001 ± 0.17 μg/g/h) during summer. The minimum emission rate of isoprene was found during the monsoon season.

Saxena and Ghosh (2019) studied the correlation between abiotic stress and isoprene emission potential of two selected plant species viz. *Dalbergia sissoo* and *Nerium oleander* grown near traffic site. In this study, temperature and photosynthetic active radiation (PAR) dependence of isoprene emission in *Dalbergia Sisso* were studied. It was found that the value of isoprene emission rate increases with the increase in temperature and PAR, while no such relationship had been reported for *Nerium oleander* species. They divided *Dalbergia sissoo* and *Nerium oleander* into the categories of high and low isoprene emitting plant species.

The review of existing literature reveals that despite the significance of isoprene in the tropospheric photochemistry, only a limited number of studies have been conducted on it in the Indian context. Most of these studies have been focussed at estimating the isoprene emission from selected plant species. Very few studies (Sahu and Saxena, 2015; Sinha et al., 2014) in India have reported the concentration of isoprene in the ambient atmosphere. To the best of our knowledge, no study in India has attempted to evaluate the biogenic and anthropogenic fractions of the total ambient isoprene levels. Delhi, the capital city of India is amongst the most polluted cities in the world. A number of studies in the context of air quality of Delhi have reported very high levels of ozone in its ambient air (Jain et al., 2005; Prakash et al., 2011). Given the high reactivity of isoprene and the important role it plays in the ozone chemistry, it is important to examine the isoprene levels and their association with ozone in Delhi's ambient air. Thus, the present study has been conducted with the following objectives:

1.6   OBJECTIVES

1. To study the seasonal and intraday variations of isoprene with other selected traffic tracers in the ambient air of Delhi.

2. To study the isoprene emission in the exhaust of different types of vehicles.

3. To evaluate the relationship of isoprene with ozone (O_3), NOx and other meteorological parameters.

1.7   SIGNIFICANCE OF THE STUDY

As increasing number of vehicles are plying on the roads of Delhi. Its vehicular population has reached 10 million in 2018 (Economic Survey of Delhi, 2018-19), which is the highest among all the metropolitan cities of India. Large amounts of VOCs are emitted from these vehicles, which degrade the air quality of Delhi significantly. Not surprisingly, Delhi is placed among the top polluted cities of the world in terms of air quality. Isoprene is one of the important VOC species emitted from both biogenic and anthropogenic (especially traffic) sources. Because of high reactivity and ozone-forming potential of isoprene, it influences atmospheric chemistry significantly. The present study will help to gain insight into the role of biogenic and anthropogenic sources of isoprene in influencing the air quality of Delhi.

CHAPTER 2: MATERIALS AND METHODS

2 MATERIALS AND METHODS

2.1 Study Area

Delhi, the capital of India, is considered as one of the rapidly developing cities of the world. It lies at a latitude of 28°23′17″–28°53′00″ N and longitude of 76°50′24″–77°20′37″ E with ~ 216 m elevation above mean sea level (Pandey et al., 2012). Its population is growing at an exponential rate. According to the Indian Census 2011, Delhi's population was 16.79 million (Census of India, 2011). Assuming the population growth rate between 2001 and 2011, the present population is projected to have increased at a level of 19.58 million and which makes it the most populous city of India and considered as the 3rd largest urban agglomeration of the world (Demographia World Urban Areas, 2019). Calculating the population density of Delhi from the above figures, then it is 13,202.97 people per square kilometre, which is one of the highest in the world. The city encompasses a geographical area of 1483 km^2 with 51.9 km in length and 48.48 km in width (Srivastava et al., 2005). Delhi is bordered by Gangetic plains of Uttar Pradesh in the East and Haryana on other three sides. Delhi has a typical semi-arid subtropical climate with continental air leading to relatively dry and hot summer. Being a sub-tropical area, Delhi shows extreme climatic patterns with very hot summers where the maximum temperature ranges from 41 to 45°C in the month of May-June and a very cold winter where the minimum temperature goes down up to 3 to 6°C (December-February) (Mohan and Bhati, 2011). The mean annual rainfall in Delhi is 714 mm, the majority of which occurs in the months of monsoon (July-September) (Kumar and Goyal, 2011). Geographically, the city's mainland is chiefly divided into three major parts, the Yamuna flood plain, the plains, and the ridges part of Aravali hills (Gupta and Mohan, 2013).

Despite being an urban area, National Capital Territory (NCT) Delhi region is having a total of 192.41 Km^2 of forest which is 12.97 % of the total area of Delhi (State of Forest Report, 2017). However, the green cover of Delhi is almost double, i.e. 20.6% (Economic Survey of Delhi, 2018-19) which includes all parks and gardens. The vegetation of Delhi is Northern Tropical Thorn Forest Type (Champion and Seth, 1968) with floral diversity of 551 species in 90 angiosperm families. The most dominant species consist of herbs followed by shrubs, trees, grasses, climbers, and parasites (Mishra et al., 2015). Species of various genera found here are isoprene-emitting species like *Ficus religiosa, Ficus virens, Dalbergia sisoo, Eucalyptus globules, Mangifera indica, Butea monosperma,* etc.(Padhy and Varshney, 2005a).

Due to rapid industrialization, urbanization, and opportunities for better education and health, Delhi attracts people from all parts of India. This directly affects its population and the vehicle load on roads. The total number of registered vehicles in the city is now more than 10 million (Economic Survey of Delhi, 2018-19). The rate of increase in the number of registered motor vehicles in Delhi was proportional to the population growth until 1990. After this, the growth of vehicles was spectacular, which has now increased manifold. Table 2.1 shows the increase in the number of vehicles with the population in Delhi.

Table 2.1: Growth of human population and number of vehicles in Delhi.

	1991	2001	2011	2021 (projected)
Population of Delhi (in millions)	9.4	13.8	16.7	22
Number of vehicles in Delhi (in millions)	1.8	3.6	6.9	10

Source: Economic Survey of Delhi (2012-13)

2.2 Site Description

In this study, six different sites were selected for the monitoring of isoprene along with Benzene, Toluene, Ethylbenzene, m/p-Xylene and o-Xylene (BTEX) in the ambient air of Delhi in four major seasons (post-monsoon, winter, summer, and monsoon) from October 2017 to September 2018. Sampling was conducted in October - November 2017 for the post-monsoon, December 2017 to February 2018 for the winter, April - June 2018 for the summer and July - September 2018 for the monsoon seasons respectively. These seasons were divided on the basis of climatic condition and the analysis of air trajectories reported by many researchers (Kumar and Yadav, 2016; Jain et al., 2005).

Table 2.2: Details of representatives monitoring sites.

Sampling sites	Lat/Long	Site type	Abbreviation
Jawaharlal Nehru University	28.540 N, 77.169 E	Vegetative	JNU
Yamuna Biodiversity Park	28.730 N, 77.219 E	Vegetative	YBP
Swarn Jayanti Park	28.719 N, 77.120 E	Vegetative	SJP
Punjabi Bagh	28.673 N, 77.139 E	Traffic	PJB
Central Road Research Institute	28.551 N,77.274 E	Traffic	CRI
Pitampura	28.699 N, 77.152 E	Traffic	PTB

The sampling locations were divided into two groups based on the abundance of vegetation and traffic density at the site. The first group - 'the vegetative sites' consisted of three locations, namely; Jawaharlal Nehru University (JNU), Yamuna Biodiversity Park (YBP) and Swarn Jayanti Park (SJP). The other group categorized as 'the traffic sites' also included three locations viz. Punjabi Bagh (PJB) traffic intersection, Central Road Research Institute (CRI) traffic intersection and Pitampura

(PTP) traffic intersection. The spatial distribution of the sampling sites is shown in Figure 2.1, and their specific locations (latitude/longitude) are given in Table 2.2.
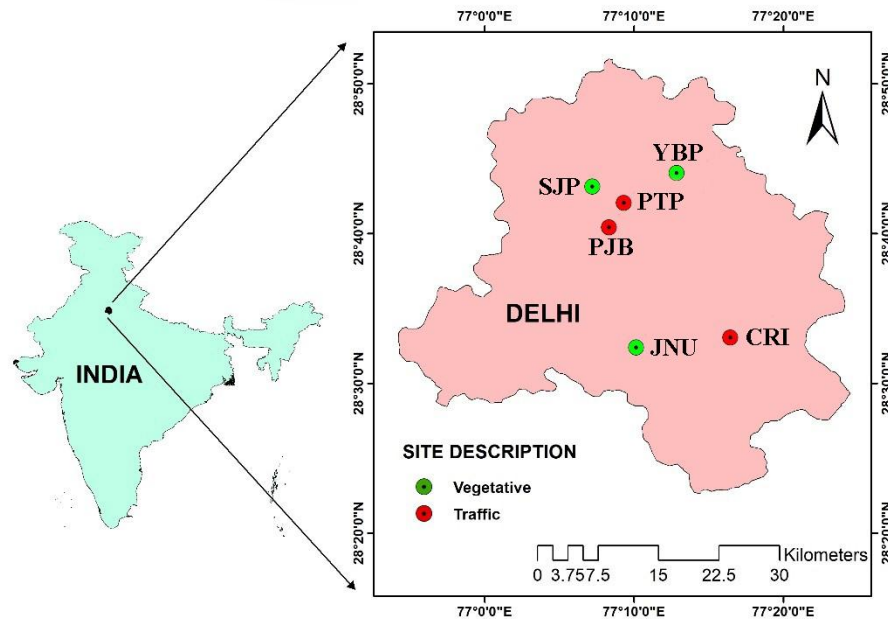
Figure 2.1: Delhi map showing different sampling locations.

A brief description of each sampling location is given below.

Jawaharlal Nehru University (JNU): JNU is the central university spread in an area of more than 1000 acres on the southern Aravali range. It is an institutional cum residential site having a vast green cover. Sampling was done at a site near (within 100m) the library building with a dense green cover. This area is completely surrounded by green vegetation having different varieties of isoprene emitting trees such as Peepal (*F. religiosa*), Banyan (*F. Bengalensis*), Babul (*Acacia sp.)*, Neem (*Azadirachta indica*), Jamun (*Syzygium cumini) and* Pilkhan (*Ficus virens*). The campus of this university is good example of native biodiversity conservation in an urban ecosystem.

Yamuna Biodiversity Park (YBP): The Park spreads over an area of roughly 457 acres near Wazirabad village on the flat alluvial plains of the Yamuna. This park has

been created and maintained by the Delhi Development Authority (DDA). The park is rich in its floral biodiversity having grassland, wetland, various species of fruits and medicinal plants. Sampling was done in a public park, which was freely accessible inside YBP. The sampling area is surrounded by various tree species including isoprene emitting species like Peepal (*F. religiosa*), *Eucalyptus* species (*Eucalyptus globulus*), and flowering plants like *Nerium* (*Nerium oleander*) and *Bauhinia (Bauhinia blakeana*).

Swarn Jayanti Park (SJP): Swarn Jayanti Park is present in the vicinity of a major residential area (Rohini) in the north-west district of Delhi and is popularly known as the Japanese Park. The Park is spread in 250 acres of area, which was planned as a leisure retreat for the local residents of the nearby area. Rich greenery having a wide variety of plant species and lakes with colourful boats make it a perfect picnic spot for the residents from the nearby localities. The park is having several isoprene emitting tree species like Pilkhan (*Ficus virens*), Sheesham (*Dalbergia sissoo),* Indian Elm *(Holoptelea intergrifolia), Eucalyptus* species etc. Sampling location was around 100 m away from the main gate of the park.

Central Road research Institute (CRI): Central Road Research Institute is a premier national laboratory of the Council of Scientific and Industrial Research (CSIR), India. It acts as a research and developmental unit. It is situated on the Delhi-Mathura Road National Highway-2 (NH-2) that connects Delhi to Mathura. Sampling was carried out at the traffic intersection present at the main gate of this institute. This being an intercity road, the density of traffic throughout the day is very high. Vehicles plying during daytime mainly consist of bikes, autos, buses, and cars, while heavy trucks dominate the traffic composition at night. This sampling location is situated near the

Okhla Industrial Area. Besides, there is also a waste dumping site and a sewage treatment plant within 10 kilometers of the location.

Punjabi Bagh (PJB): This sampling site was located at the cross-intersection of Rohtak road and Mahatma Gandhi road near Punjabi Bagh Metro Station. There is an underpass on Rohtak road and a flyover on Mahatma Gandhi road, and above that flyover Delhi Metro's green line is present. At the cross intersection, round circle for smooth flow of traffic is provided. This location also witnesses high traffic density as vehicles from within the city and from Delhi's adjoining state of Haryana pass from here.

Pitampura (PTP): Pitampura sampling site is located at the traffic intersection near Pitampura TV Tower opposite to the Guru Govind Singh College of Delhi University. Although here the traffic density of heavy vehicles is relatively low as compared to other traffic sites because only a few DTC bus routes are defined along this route, the traffic density of small vehicles such as cars and 2-wheelers here is high.

2.3   Methodology

2.3.1   Sampling Method for Isoprene and BTEX Compounds

For sampling the selected compounds in Delhi, samples were collected from all locations for post-monsoon, winter, summer and monsoon seasons. From each site, a total of nine samples were collected in each season on three different days and at three different time intervals during the day i.e. morning (8:00 hrs to 11:00 hrs), afternoon (12:00 hrs to 15:00 hrs) and evening (17:00 hrs to 20:00 hrs).

Air samples were collected using preconditioned FLM carbopack X deactivated stainless steel thermal desorption tubes (TD tubes) (brought from Supelco Inc., USA) with the help of portable VOC sampler (used for pumping the ambient air through the tubes) at a flow rate of around 100 ml/min for 3 hours. Carbopack X is one of the

strongest adsorbent (graphitized carbon black) with a BET (Brunauer-Emmett-Teller) surface area of 240 m^2/g and a mean pore volume of 100 Å. TD tubes and VOC sampler are shown in Figure 2.2.
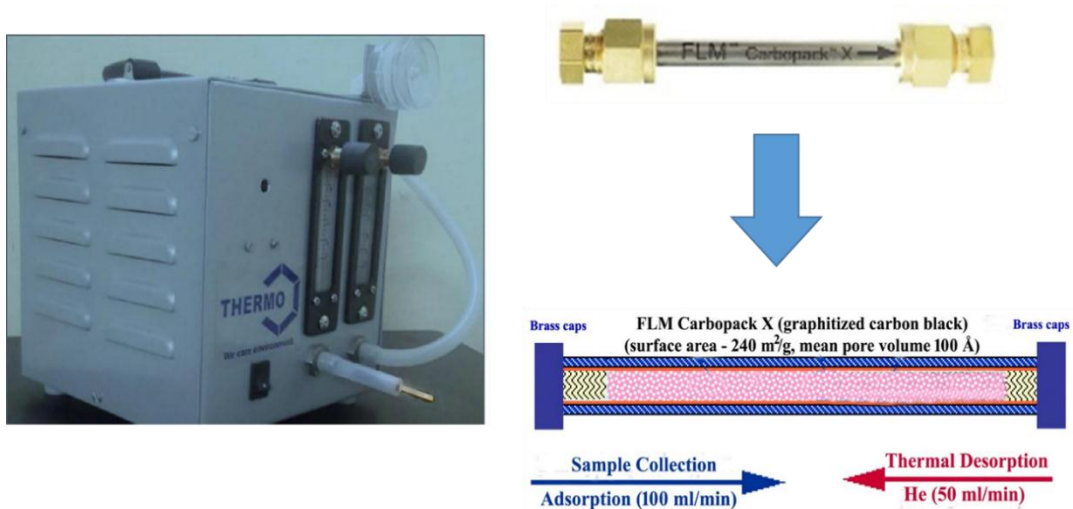
Figure 2.2: Portable VOC sampler along with FLM Carbopack X (graphitized carbon black) TD tubes.

Figure 2.3: Gas Chromatograph coupled with Mass Spectrometry and Thermal Desorption Unit.

After sampling, the outlets of the tubes were sealed using the brass end-cap to prevent any contamination. Then, these tubes were wrapped in the aluminum foil after labeling and immediately stored at a temperature $< 4°C$. Finally, these TD tubes were transferred to the laboratory for further analysis within 24 hours after sampling. All collected samples were analysed using Gas Chromatograph coupled with Mass Spectrometry (GC-MS) (Shimadzu QP-2010 Plus). Samples containing tubes were desorbed thermally with the help of a thermal desorption unit (TD-20, Shimadzu). Figure 2.3 represents GC-MS coupled with thermal desorption unit.

2.3.2   Sampling Analysis for Isoprene and BTEX Compounds

Analysis of targeted compounds such as isoprene and BTEX were performed according to the thermal desorption, EPA TO-17 method. After sampling, targeted compounds were trapped in carbopack X present in thermal desorption tubes. For thermal desorption, TD tubes were directly put on thermal desorption unit connected with GC-MS. Desorption was done in the direction opposite to the sampling direction to avoid retention of heavy analytes deep inside the tube. Highly pure Helium (He) was used as carrier gas with a flow rate of 50 ml/min.

Table 2.3: Illustrates the oven properties for isoprene and BTEX compounds analysis.

Rate (^{o}C/min)	Temperature (^{o}C)	Time (min)	Total (min)
Initial	40	5	5
15	200	5	21.67
		Total runtime	21.67
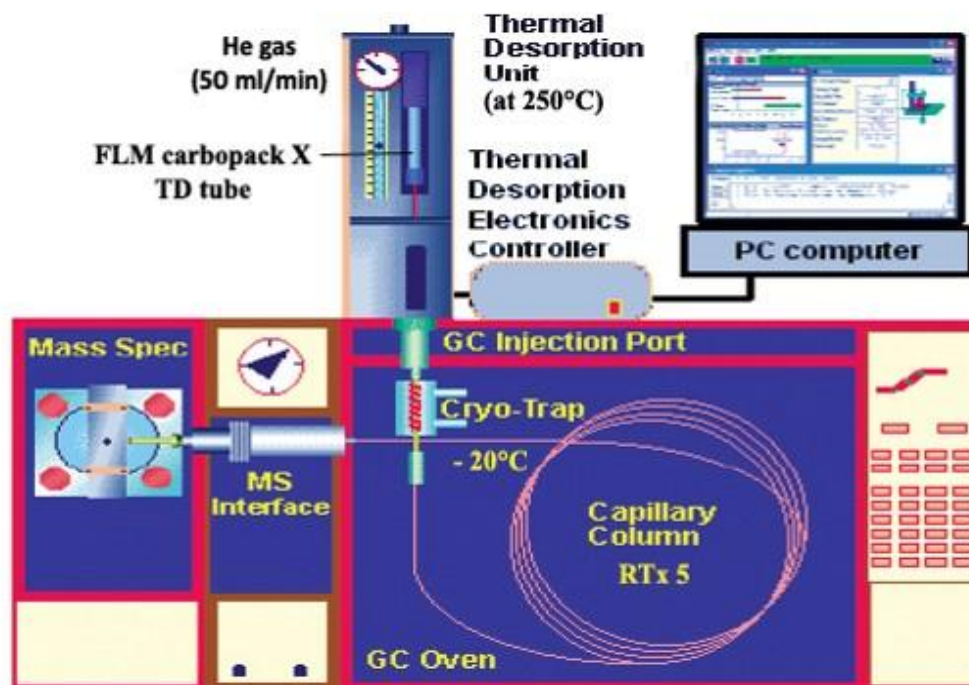
Figure 2.4: Schematic representation of the analytical process involved in the quantification of selected hydrocarbons.

Desorption was done for 5 minutes at 250°C and after desorption, analytes were moved to cold trap, which was maintained at -20°C. All desorbed analytes were then injected into GC coupled with capillary column Rtx 5 MS having a thickness of 0.25 μm, internal diameter 0.25 mm and a length of 30 m. GC column was then connected to MS, where the ion source temperature was maintained at 200°C. The oven was programmed with an initial temperature of 40°C, kept for 5 minutes and then, gradually increased the temperature until it attained 200°C at the rate of 15° C/min to be held for 5 minutes. Oven properties for the analysis of compounds are shown in Table 2.3. After analysis, all the TD tubes were reconditioned using the conditioning mode of the thermal desorber at a temperature 280°C again with He gas at a flow of 50 ml/min for further reuse of the tubes. The schematic representation of the analysis process is shown in Figure 2.4.

2.3.3   Vehicular Exhaust Sampling

For the estimation of isoprene and other VOC compounds present in the exhaust of different motor vehicles, sampling of vehicular exhausts of different types of vehicles was conducted. These vehicles included 2-wheelers (mainly bikes, scooters), 3-wheelers (autos and lower transport vehicles), cars, Delhi Transport Corporation (DTC) buses, and tempos. All vehicles were segregated on the basis of the type of fuel used, i.e. diesel/petrol/CNG. A minimum of 30 (approximately) vehicles were selected from each category. The vehicular exhaust was directly collected from the tailpipe of the vehicle in idling mode after 5 to 10 minutes of engine start in 1-liter Tedlar bags using squeezer pump. After sampling, Tedlar bags were labeled and kept in black colour bags to prevent any photochemical reactions in the presence of sunlight. These samples were analyzed within 24 hours of sample collection and Gas Chromatograph (450 GC, Bruker) was used for the analysis of collected samples. The diagram for vehicular exhaust sampling technique is shown in Figure 2.5.
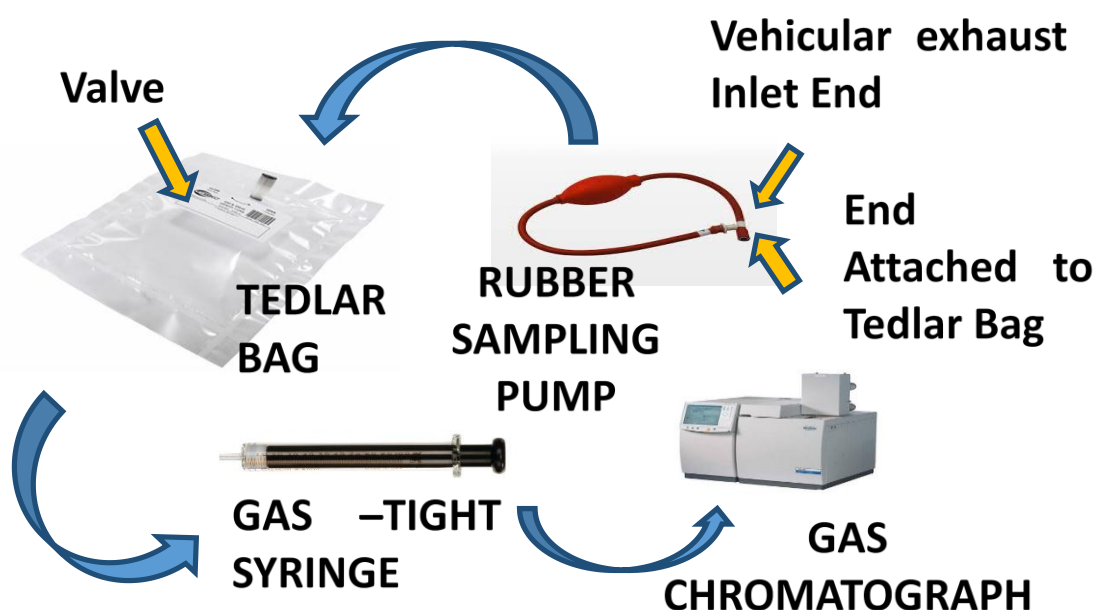
Figure 2.5: The diagram for vehicular exhaust sampling technique.

2.3.4 Vehicular Exhaust Analysis

1-2 ml volume of air at Standard Temperature and Pressure (STP) from the collected vehicular exhaust sample was taken using a gas-tight syringe, which is specially designed for extracting gas without any sample contamination with local air. This sample was further diluted with pure nitrogen gas and injected directly into the Gas Chromatograph-Flame Ionization Detector (GC-FID) system with the help of gas-tight syringe. The temperature for injector was kept at $250^{o}C$ and detector at $301^{o}C$. Rt-Alumina BOND/KCl Column (fused silica PLOT) purchased from Restek was used for the analysis. Gas Chromatograph (GC) oven temperature program was started initially at $35^{o}C$ for 1.2 min, then increased gradually at the rate of $12^{o}C$/min and then kept at $65^{o}C$ for 1min. Further, the rate of temperature increase was programmed for 15 ^{o}C/min rise from $65^{o}C$ to $150^{o}C$ and kept at $150^{o}C$ for 2 min, so that proper separation of different compounds takes place. Highly pure (99%) nitrogen (N_2) gas was used as a carrier gas with a flow rate of 25ml/min. GC oven properties for analyzing these compounds are described in Table 2.4.

Table 2.4: Illustrates the oven properties for the analysis of vehicular exhaust.

Rate (^{o}C/min)	Temperature (^{o}C)	Time (min)	Total (min)
Initial	35	1.2	1.2
12	65	1	4.7
15	150	2	12.37
		Total runtime	12.37

2.4 Quality Assurance/ Quality Control (QA/QC)

The quantification of ambient air samples was accomplished by their peak area in comparison to a standard calibration curve prepared with the standard of pure isoprene (>99.5%) and a mixture of BTEX compounds purchased from Supelco Inc.,

USA (BTEX mix, 2000 µg/ml each in methanol) by spiking in TD tubes. The calibration curves for each compound were constructed according to the 325B method of US Environmental Protection Agency (USEPA) guidelines. From the original liquid standards, multiple standards of different concentrations (0 ppm, 1 ppm, 100 ppm, 500 ppm, 1000 ppm) were prepared and spiked exactly with 1 µl of an aliquot from each liquid standard to the separate TD tubes. Further, the mass of each compound was theoretically calculated in µg for each standard tube. The calibration curves were prepared between mass and area under the curve and fitted linearly with R² >0.99 for each compound. The concentrations (C_m) in µg/m^3 of targeted compounds were calculated with the following equation:

$$C_m = \frac{M_c \; X \; 10^6}{T_s \; X \; F_r}$$ (2.1)

Where M_c is the mass of targeted compounds computed from the calibration curve in µg, T_s is the total time of sampling in minutes, and F_r is the flow rate of the sampler in ml/min Before sampling, a breakthrough test was also performed in order to know the safe sampling volume for the TD tubes. For this test, two identical TD tubes were placed in series, and sampling was conducted. Both these tubes were analysed in a similar way as other sampled tubes and no breakthrough was observed for the selected compounds. Field blanks were also analyzed where no targeted compounds were observed. For the reliability of results, analytical precision was also calculated from the relative difference between the absolute values of the two identical samples taken together in the same environmental conditions with the same flow rate and sampling duration. The precision results gave the variation within 10% and it was also found that the high concentration values had more precision as compared to low concentration values. The performance of GC was checked on a regular basis by

analysing the graph obtained by running GC for the mid-range compound from the calibration standard.

Similarly, for vehicular exhaust quantification, the standard gas mixture containing all targeted compounds, each having 1 ppm concentration purchased by CHEMIX Speciality Gases, Bangalore, India was utilized for the calibration of GC. The standard gas mixture was diluted with nitrogen gas to obtain lower concentrations. The standard gas mixture was analyzed with the same GC temperature program, which was used to run for the vehicular exhaust samples. Three concentration levels of gases like isoprene, benzene, toluene, ethylbenzene, m/p-xylene, o-xylene standard mixture in nitrogen were used to achieve a calibration curve for the different VOC compounds. 2 ml of gases standard mixture were taken using gas-tight syringe and injected into the GC through injection point, and GC was run with pre-defined conditioned program. After running program for three standards, the GC was calibrated with a good linear fit line for all compounds ($R^2 > 0.99$). Calibration curve so obtained from both the standard mixtures were evaluated and re-checked weekly for better results.

2.5 Meteorological Data

Data regarding meteorological variables such as solar radiation, temperature, wind speed, and wind direction were also taken during the sampling time. While temperature data was recorded with the help of thermometer and data for other parameters were collected from the nearby weather stations around each site. Air quality data of ozone and NOx were collected from the nearby monitoring stations of Delhi Pollution Control Committee (DPCC), Central Pollution Control Board (CPCB), and Indian Meteorological Department (IMD) around selected sampling

sites. Data were directly downloaded from their respective websites. Data collected from different monitoring stations for corresponding sites are presented in Table 2.5.

Table 2.5: Data Collection from monitoring stations in Delhi.

Monitoring stations	Managing Agency	Sites
R. K. Puram	DPCC	JNU
Burari Crossing	IMD	YBP
Rohini	DPCC	SJP
Punjabi Bagh	DPCC	PJB
CRRI	IMD	CRI
Wazirpur	DPCC	PTP

2.6   Segregation of Biogenic and Anthropogenic Isoprene

In urban settings, isoprene in the ambient atmosphere may be due to contributions from both anthropogenic and biogenic sources (Borbon et al., 2001). In the study on biogenic isoprene emissions in Taipei, Wang et al. (2013) suggest that comparison between the ratios of ambient isoprene/tracers and the ratios of isoprene/tracers that are characteristic of vehicle exhaust could be used for the estimation of anthropogenic contribution to ambient isoprene levels. For this purpose, they suggest that the characteristic ratio of isoprene/exhaust tracer could be obtained either (i) by using the ratios from traffic dominated site or (ii) by using the minimum ratio observed among urban sites. In this study, the minimum isoprene/benzene ratio at the traffic sites has been used to estimate the traffic contributions to ambient isoprene, and then separate biogenic isoprene from traffic emissions. Here, benzene is used as a traffic tracer as the burning of fossil fuels in motor vehicles is considered to be its most dominating source and merely 5-10% of its emissions in the ambient air, are from non-mobile sources (Bolden et al., 2015). The anthropogenic contribution to ambient isoprene was estimated using the following equation:

$$I_{anthro} = \left(\frac{I}{B}\right)_{min\_traffic} \times B \qquad\qquad (2.2)$$

Where, I_{anthro} is the anthropogenic isoprene, $\left(\frac{I}{B}\right)_{min\_traffic}$ represents the minimum

isoprene/benzene ratio among the traffic sites and B is the benzene concentration at

any given site. Subtracting I_{anthro} from the total ambient isoprene at a given site gave

the biogenic isoprene (I_{bio}).

2.7   Propene Equivalent and Ozone Forming Potential (OFP) Assessment

To scale the relative reactivity of selected VOCs with hydroxyl radical (OH), each

VOC compound was normalized to the reactivity of propene concentration. In this

study, Propene Equivalent (Prop-Equiv) concentration method was used, which was

proposed by (Chameides et al., 1992). The Prop-Equiv concentration was derived by

normalizing the ambient concentration of selected VOC species to the propene

concentration based on corresponding OH reaction rate coefficients. The values of

OH reaction rate coefficients of individual VOC species were adopted from Atkinson

(1990). The equation 2.3 was used to calculate the Prop-Equiv of individual VOC

compound (i) as:

$$Prop - Equiv_{(i)} = Conc._{(i)} \, x \, \frac{K_{OH(i)}}{K_{OH(C_3H_6)}} \qquad\qquad (2.3)$$

Where, $Conc._{(i)}$ is the concentration of individual VOC_i (µg/m³) species, $K_{OH(i)}$ is the

OH reaction rate coefficient for the individual VOC_i. While $K_{OH(C_3H_6)}$ is the reaction

rate coefficient of propene with OH radical.

This study also deals with the estimation of ozone formation potential (OFP) of the

studied VOCs (isoprene and other BTEX compounds) at different sites. The

maximum incremental reactivity (MIR) method proposed by Carter (1994) was used

for calculating OFP of individual VOC (*i*) by using the following equation 2.4:

$$OFP_{(i)} = Conc._{(i)} \, x \, MIR \, coefficient_{(i)} \qquad\qquad (2.4)$$

Where, $OFP_{(i)}$ describes the ozone formation potential of individual VOC (i) and MIR coefficient$_{(i)}$ (dimensionless, gram of O_3 per gram of VOC) infers maximum incremental reactivity of compound i.

Table 2.6: Photochemical properties of measured VOCs

Compounds	$K_{OH} \times 10^{12}$ (cm^3 molecule^{-1}s^{-1}) at 298 K	MIR Values (g of O_3/g VOCs)
Isoprene	101	10.61
Benzene	1.23	0.72
Toluene	5.96	4.0
Ethylbenzene	7.1	3.04
m/p-Xylene	18.95	7.79
o-Xylene	13.7	7.64

Source: (Carter, 2009; Atkinson, 1990)

The values of MIR coefficients used for OFP calculation were obtained from Carter (2009). MIR method for comparing the OFP of individual VOCs is just used as an indicator. However, apart from VOCs reactivity towards OH radical, other meteorological parameters such as solar intensity, temperature, and concentration of NOx also play a crucial role in the formation of tropospheric ozone. The values of MIR coefficients and OH reaction rate coefficients are shown in table 2.6.

2.8   Health Risk Calculation

Many volatile organic compounds (especially BTEX) are considered as hazardous because of their harmful effects on human beings. Various adverse health impacts on respiratory, cardiovascular, and endocrine systems of humans are associated with chronic exposure of BTEX (Bolden et al., 2015). Therefore, this study evaluates the health risk assessment in terms of cancer and non-cancer risk. Humans can be exposed to these compounds by three different routes viz., inhalation, ingestion, and dermal exposure. In this study, only the exposure through inhalation pathway was

considered for the calculation of chronic daily intake (CDI) because ingestion and dermal exposure routes are considered less efficient (Durmusoglu et al., 2010). CDI is calculated using the following equation 2.5:

$$CDI = \frac{(EC \times IR \times ET \times EF \times ED)}{(BW \times LT \times NY)}$$ (2.5)

Where, EC is the exposed concentration of targeted compound ($\mu g/m^3$) in the ambient air; IR is the inhalation rate (m^3/hour) of adult human being; ET is the exposure time (hours/day); EF is the exposure frequency (days/year); ED denotes exposure duration (years); BW is the body weight (kg), LT is the averaging lifetime (years), and NY indicates the number of days in a year. The IR value was taken as 0.667 m^3/hour for a normal adult of 70 kg and 30 years of age, as recommended in the Exposure Factor Handbook of US Environmental Protection Agency 2011(USEPA, 2011). Other values of BW, ET, EF, LT, NY, and ED were taken as 70 kg (average body weight of the human body), 8 hours/day (per day exposure), 365 days/year (exposure throughout year), 70 years (average life expectancy of humans), 365 days/year (number of days in a year) and 15 years (average exposure duration) respectively (Masih et al., 2016; Massolo et al., 2010; Miri et al., 2016; Garg and Gupta, 2019; Kashyap et al., 2019). A tabular presentation of these parameters is shown in Table. 2.7.

Table 2.7: Parameters used for the calculation of chronic daily intake (CDI).

Parameters	Adults
Inhalation Rates (IR)	0.667 m^3/h
Body Weight (BW)	70 kg
Per Day Exposure Time (ET)	8 h/day
Exposure Frequency (EF)	365 days/year
Average life expectancy of humans (LT)	70 years
Number of Days in a Year (NY)	365 days
Average Exposure Duration (ED)	15 years

Further, CDI was used to calculate cancer risk (CR) associated with benzene by multiplying chronic daily intake (CDI) with cancer slope factor (CSF) as suggested by the United States Environmental Protection Agency (USEPA) in equation 2.6 (USEPA, 2010).

$$CR = CDI \times \text{CSF} \qquad (2.6)$$

Where, CDI represents the chronic daily intake for benzene in μg/kg/day, and CSF is the slope factor or carcinogenic potency factor for benzene $(\mu g/kg/day)^{-1}$. The value for CSF was taken as 27.3 $(\mu g/kg/day)^{-1}$ in the case of benzene (Masih et al., 2016; Garg and Gupta, 2019).

For all BTEX compounds, non-carcinogenic risks were determined in terms of Hazard Quotient (HQ), which is defined as the ratio of chronic daily intake (CDI) (mg/kg-day) to the inhalation reference concentration (RfC) (mg/kg-day) as shown in equation 2.7.

$$HQ = \frac{CDI}{RfC} \qquad (2.7)$$

The inhalation reference concentrations of all the BTEX compounds were calculated using inhalation unit risk (IUR) obtained from https://cfpub.epa.gov/ncea/iris/search / index.cfm (USEPA, 2016) using the following equation 2.8:

$$\frac{IUR\left(\frac{mg}{m^3}\right) x IR\left(\frac{m^3}{day}\right)}{BW(Kg)} = RfC\left(\frac{mg}{Kg.day}\right) \qquad (2.8)$$

The Inhalation Unit Risk (IUR) and Carcinogenic Slope Factors used for the study are shown in Table 2.8.

The HQ value greater than one (>1) is an indicator of potential health hazard for human beings while its value less than one or equal to one ($\leq$1) is considered acceptable as the dose level is less than RfC (Dehghani et al., 2018; Demirel et al., 2014; Miri et al., 2016; Tunsaringkarn et al., 2012). Further, the Hazard Index (HI) is

computed by the summation of HQs of individual pollutants (equation 2.9).

$$HI = \sum_{i=1}^{n} HQ_i \qquad\qquad (2.9)$$

Where HQ_i is the HQ of ith pollutant.

Table 2.8: Inhalation Unit Risk (IUR) and Carcinogenic Slope Factors.

Organic Compounds	Inhalation Unit Risk (IUR) (mg/m^3)	Carcinogenic slope factors (SF) (kg-day/mg)
Benzene	0.3	2.73×10^{-2}
Toluene	5	
Ethylbenzene	1	3.85×10^{-3}
m/p-Xylene	0.1	
o-Xylene	0.1	

CHAPTER 3: RESULTS AND DISCUSSION

3   RESULTS AND DISCUSSION

In the urban environment, isoprene is the most influential species, which determines various atmospheric phenomenon occurring in the lower troposphere and largely influences the oxidative chemistry of the atmosphere (Beerling et al., 2007). Many researchers have studied the role of isoprene and other VOCs in the formation of tropospheric chemistry (Atkinson, 2000; Shirley et al., 2006; Li et al., 2015). This study deals with the measurements of isoprene along with BTEX (benzene, toluene, ethylbenzene, m/p-xylene, and o-xylene) compounds at six different locations in Delhi during four seasons. This chapter discusses the quantification and statistical summary of the data obtained from the sampling of studied compounds.

3.1   Variability of Isoprene and BTEX Compounds

Measurements of isoprene and other BTEX compounds were made at six different locations divided into two broad categories viz. traffic and vegetative. The mean levels and overall variability of each compound are shown in Figures 3.1 and 3.2 for traffic and vegetative sites, respectively. A comparative examination of the figures shows the mean levels of all the compounds except the isoprene are greater at the traffic sites as compared to the vegetative sites. The mean concentrations of isoprene, however, were found to be higher at the vegetative sites. The error bars given in the box plots represent the overall variability in the concentrations of all the compounds. It is seen that the overall variability of each compound was more at traffic sites as compared to the vegetative sites except for isoprene, which was more variable at vegetative sites. Figure 3.1 depicts that among all the compounds at traffic sites, toluene has the maximum mean concentration (52.78 ± 22.14 μg/m^3) followed by m/p-xylene (38.28 ± 18.73 μg/m^3), benzene (20.22 ± 10.71 μg/m^3), o-xylene (15.35 ± 8.65 μg/m^3) and ethylbenzene (11.65 ± 7.10 μg/m^3), whereas, isoprene was found to

be minimum (0.51 ± 0.21 μg/m³). Conversely, at vegetative sites (figure 3.2), the mean concentration of isoprene (4.56 ± 3.29 μg/m³) was higher than o-xylene (4.24 ± 2.83 μg/m³) and ethylbenzene (2.51 ± 1.37 μg/m³). However, like traffic sites, toluene (21.82 ± 10.87 μg/m³), m/p-xylene (9.17 ± 5.84 μg/m³) and benzene (7.17 ± 4.16 μg/m³) follow the similar order at vegetative sites also. Tables 3.1 and 3.2 show the description statistics at traffic and vegetative sites, respectively.
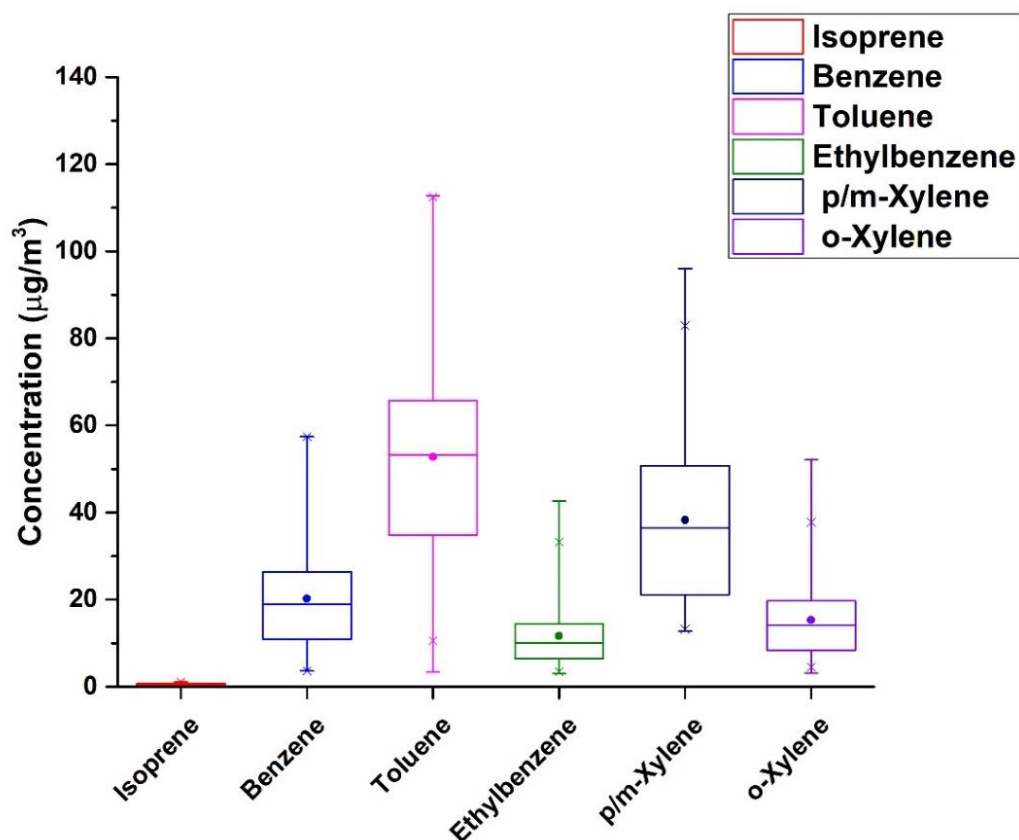
Figure 3.1: Boxplot of all compounds at traffic sites. The solid dot inside the box represents the mean concentrations. While the box shows the interquartile range. The bottom and top of the box indicate the 25th (the first quartile) and the 75th (the third quartile) percentile respectively. The upper end of whisker represents the maximum value, and its lower end corresponds to the minimum value.

Table 3.1: Descriptive statistics at traffic sites.

	N total	Mean	Standard Deviation	Sum	Min	Median	Max
Isoprene	108	0.51	0.21	52.06	0.22	0.50	1.13
Benzene	108	20.22	10.71	1961.41	3.61	18.90	57.40
Toluene	108	52.78	22.14	5383.92	3.40	53.20	112.73
Ethyl benzene	108	11.65	7.10	1188.59	2.96	10.05	42.67
p/m- Xylene	108	38.28	18.73	3904.52	12.75	36.41	96.02
o-Xylene	108	15.35	8.61	1565.40	3.18	14.20	52.15
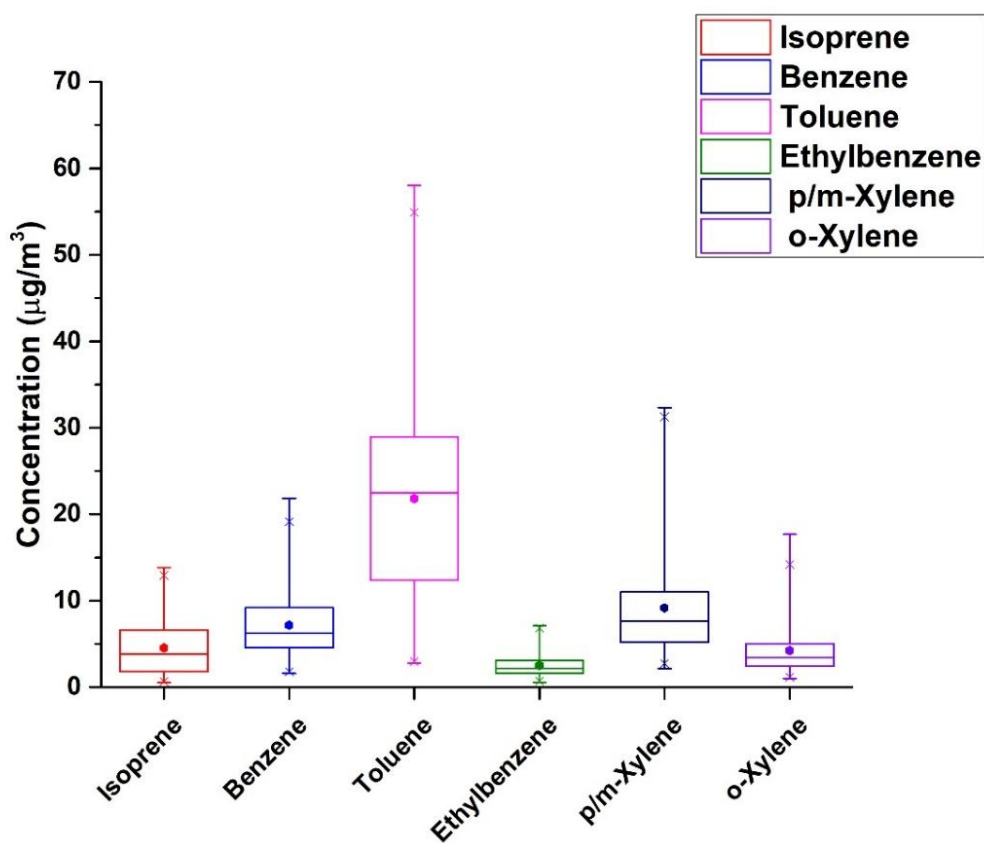
Figure 3.2: Boxplot of all compounds at vegetative sites. Boxplot of all compounds at vegetative sites. The solid dot inside the box denotes the mean concentrations. While the box shows the interquartile range. The bottom and top of the box indicate the 25th (the first quartile) and the 75th (the third quartile) percentile. The upper end of

whisker represents the maximum value, and its lower end corresponds to the minimum value.

Table 3.2: Descriptive statistics at vegetative sites.

	N total	Mean	Standard Deviation	Sum	Min	Median	Max
Isoprene	108	4.56	3.29	492.07	0.53	3.85	13.82
Benzene	108	7.17	4.16	759.50	1.59	6.25	21.86
Toluene	108	21.82	10.87	2312.60	2.80	22.46	58.03
Ethyl benzene	108	2.51	1.37	271.00	0.53	2.19	7.12
p/m-Xylene	108	9.17	5.84	990.42	2.15	7.66	32.33
o-Xylene	108	4.24	2.83	457.57	0.98	3.44	17.69
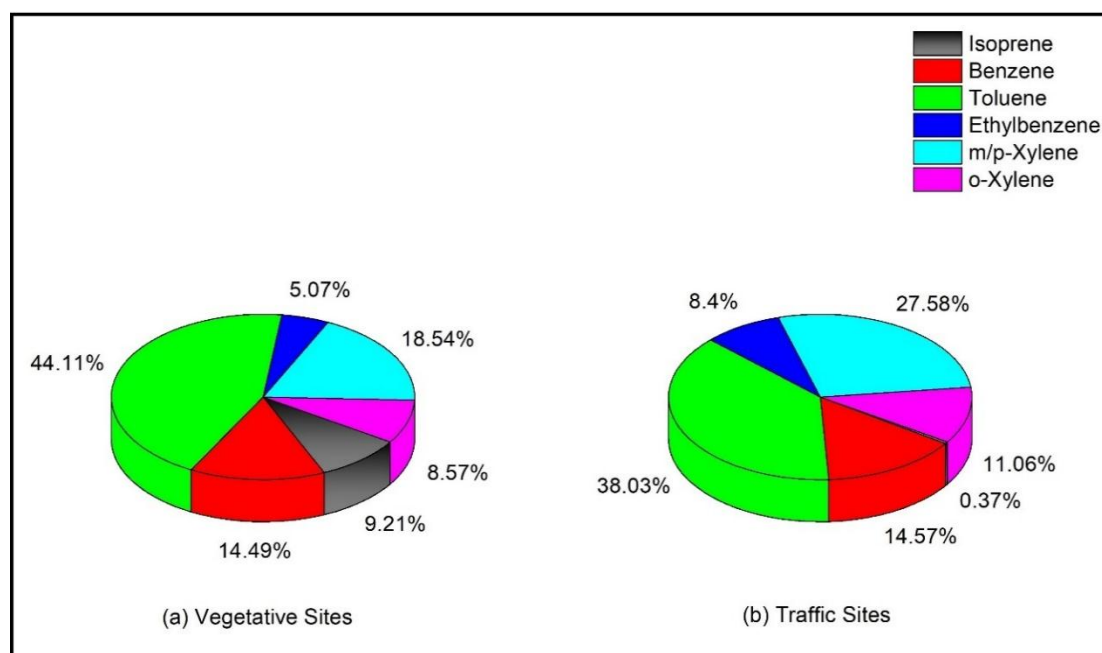
Figure 3.3: Overall contribution of each compound at (a) Vegetative sites, (b) Traffic sites.

The results show that toluene is the most dominant species among studied compounds at both the sites and accounts for approximately 44.1 % and 38.0 % from the total selected compounds at traffic and vegetative sites respectively (Figure 3.3). The

percentage contribution of m/p-xylene, benzene, o-xylene and ethylbenzene at the traffic/vegetative sites accounted for 27.6/18.5, 14.6/14.5, 11.1/8.6 and 8.4/5.1 percent respectively, of the total concentration of the selected VOCs. Isoprene's contribution to the total concentration of selected VOCs was observed to be 0.4 % and 9.2 % traffic and vegetative sites respectively. The contributions of toluene, m/p-xylene and benzene are higher among all the selected compounds because they are the most dominant species in the vehicular exhaust. The concentration of isoprene is found to be very low at traffic sites, but significantly high at the vegetative sites, which indicates that contribution to isoprene in the ambient atmosphere comes mainly from biogenic sources.

In the present study, the average concentrations of BTEX followed a pattern similar to that reported in some earlier studies (Shuai et al., 2018; McKenzie et al., 2012; Miller et al., 2011; Khoder, 2007), with toluene being the highest, followed by m/p-xylene, benzene, o-xylene, and ethylbenzene. Though a very limited number of studies have reported measuring BTEX with isoprene, most of these studies report that isoprene concentrations were observed to be lower than other BTEX compounds (Panopoulou et al., 2018; Martins et al., 2015; Salameh et al., 2015).

3.1.1 Variability of compounds among different sites

The site-wise box plots of each studied compound are shown in Figure 3.4. It is seen that isoprene levels were significantly higher at the vegetative sites as compared to the traffic sites (Figure 3.4 (a)). The mean concentration of isoprene at vegetative sites were found to be 6.49 ± 3.48, 4.49 ± 2.93 and 2.69 ± 2.23 μg/m^3 at YBP, JNU and SJP, respectively while its values at traffic sites were found to be 0.59 ± 0.22, 0.51 ± 0.21 and 0.43 ± 0.18 μg/m^3 for CRI, PJB, and PTP, respectively.   Among the vegetative sites, the YBP site was dominated by trees like *Ficus religiosa* and

Eucalyptus globulus, which are reported to be isoprene emitting plant species (Padhy and Varshney, 2005a). The JNU site is dominated with trees species like *Ficus religiosa, Ficus benghalensis, Ficus virens*, and *Syzygium cumini* while the SJP site is abundant with species like *Ficus virens* and *Eucalyptus globulus* with a few species of *Dalbergia sissoo* which are also known to be isoprene emitting (Varshney and Singh, 2003). In the case of traffic sites, the most plausible source of isoprene emission was vehicular exhaust (Borbon et al., 2001; Reimann et al., 2000).

The mean concentrations of benzene at different sites are represented in Figure 3.4 (b). It shows that mean benzene levels and their variability at the traffic sites were significantly higher as compared to those over the vegetative sites. The mean concentrations of benzene were found to be the highest at CRI (24.19 ± 12.25 $\mu g/m^3$), followed by PJB (21.93 ± 10.08 $\mu g/m^3$) and PTP (14.78 ± 7.28 $\mu g/m^3$). Among the vegetative sites, the mean concentrations of benzene were in the order JNU (8.86 ± 5.33 $\mu g/m^3$) >SJP (7.05 ± 3.74 $\mu g/m^3$) >YBP (5.59 ± 2.26 $\mu g/m^3$). It is also noteworthy to mention here that the benzene levels at all the sites in all seasons were higher than the National Ambient Air Quality Standards (NAAQS) (5 $\mu g/m^3$) limit prescribed by Central Pollution Control Board (CPCB, 2009). Similarly, the mean concentrations of toluene, ethylbenzene, m/p-xylene, and o-xylene at traffic sites were also observed to be higher than that over the vegetative sites (Figure 3.4 (c, d, e, f)).

Among the traffic sites, the highest mean concentrations of toluene, ethylbenzene, m/p-xylene and o-xylene were observed at CRI as 58.96 ± 22.97, 15.22 ± 8.81, 46.43 ± 19.35 and 19.87 ± 10.20 $\mu g/m^3$ respectively, followed by PJB (52.5 ± 22.15, 12.25 ± 6.22, 42.21 ± 18.69 and 15.96 ± 7.45 $\mu g/m^3$) and PTP (47.38 ± 20.41, 7.83 ± 3.42, 27.21 ± 12.13 and 10.64 ± 5.04 $\mu g/m^3$) respectively.

The higher mean levels of BTEX at traffic sites could be explained by the high traffic density at these sites. In comparison, the values of mean concentrations of these hydrocarbons at vegetative sites were observed to be relatively low. Here, the maximum mean concentrations of toluene, ethylbenzene, m/p-xylene, and o-xylene were found at JNU (23.49 ± 10.18, 3.16 ± 1.76, 11.28 ± 7.19 and 5.06 ± 3.27 $\mu g/m^3$) followed by SJP (22.49 ± 12.53, 2.52 ± 1.17, 9.33 ± 5.85 and 4.51 ± 3.13 $\mu g/m^3$) and then YBP (19.54 ± 9.63, 1.84 ± 0.63, 6.90 ± 2.93 and 3.14 ± 1.42 $\mu g/m^3$), respectively.

Various researchers have studied isoprene and other BTEX compounds under different physical conditions across the world. Many of such studies are listed in Table 3.3. From the table, it is observed that the levels of isoprene and BTEX in the present study are comparable to those reported in other studies. In particular, the concentrations of isoprene in this study were found to be lower than those in other Indian cities i.e. Mohali (Sinha et al., 2014) and Ahmedabad (Sahu and Saxena, 2015). However, much lower values were observed for isoprene in other major cities of the world (Salameh et al., 2015; Panopoulou et al., 2018; Baudic et al., 2016; Franco et al., 2015; Christensen et al., 1999; Wang et al., 2013).
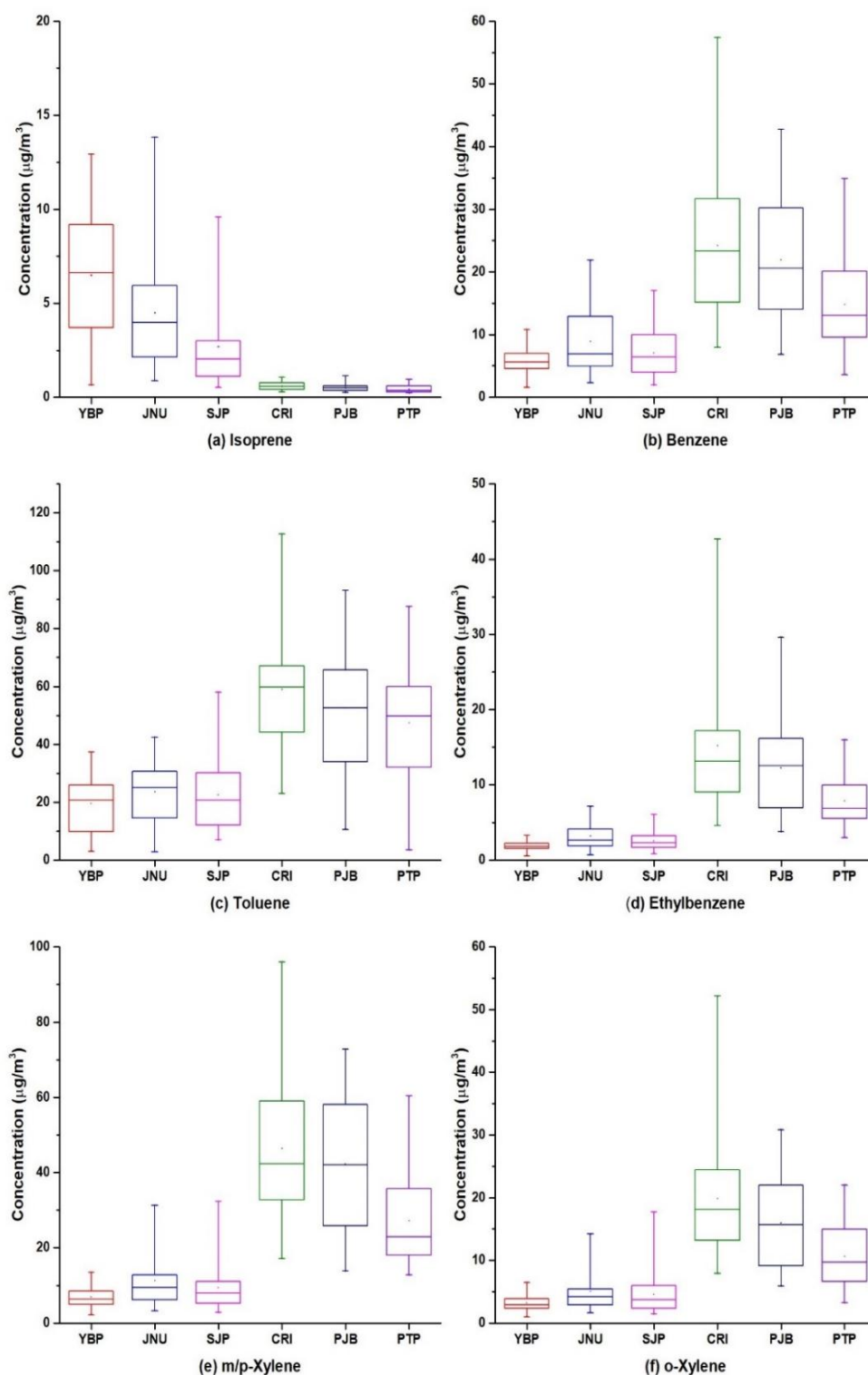
Figure 3.4: Boxplot of studied compounds at different sites. The solid dot inside the box denotes the mean concentrations. While the box shows the interquartile range. The bottom and top of the box indicate the 25th (the first quartile) and the 75th (the third quartile) percentile. The upper end of whisker represents the maximum value, and its lower end corresponds to the minimum value.

Table 3.3: Comparisons of estimated VOCs concentrations ($\mu g/m^3$) in present study with the various other studies.

City	Isoprene	Ethylbenzene	Toluene	Benzene	m/p-Xylene	o-Xylene	References
Delhi (India)	2.59	6.95	37.00	13.40	23.31	9.63	Present study
Delhi (India)		5.90	19.19	7.07	13.30[a]		Garg and Gupta (2019)
Delhi (India)		-	73.21	44.03	67.22	53.01	Kumar et al. (2019)
Athens (Greece)	0.28	1.74	3.01	7.03	5.21	1.74	Panopoulou et al. (2018)
Daegu Dyeing (South Korea)		2.34	161.37	3.54	10.48	1.73	Shuai et al. (2018)
Patras (Greece)	2.81		1.06	0.38	0.65[a]		Kaltsonoudis et al. (2016)
Paris city (France)	0.25		1.05	3.29			Baudic et al. (2016)
Beirut (Lebanon)	0.19	1.30	11.34	1.86	1.74	1.30	Salameh et al. (2015)
Ahmedabad (India)	4.46		27.51	8.31			Sahu and Saxena (2015)
Rio de Janeiro (Brazil)	1.39	4.79	17.74	12.42	9.5	8.13	Martins et al. (2015)
Bogota 3 sites (Colombia)	0.98			1.71			Franco et al. (2015)
Mohali (India)	5.29		10.17	5.43			Sinha et al. (2014)
Eskişehir (Turkey)		0.26	6.11	1.23	0.47	0.38	Demirel et al. (2014)
Tczew (Poland)		1.30	2.9	0.87	5.9[a]		Marć et al. (2014)
Taipei (Taiwan)	1.31	1.30	7.91	1.37	3.26	1.52	Wang et al. (2013)
Mohali (India)			150.7	51			Sarkar et al. (2013)
Logos (Nigeria)		9.38	12.38	15.02	33.1	23.05	Ojiodu (2013)
Algiers (Algeria)		6.8	40.5	16.7	12.2	3.1	Kerchich and Kerbachi

						(2012)
Haicang (China)		9.63	108	10.25	8.47	10.88	**Niu et al. (2012)**
Mumbai (India)		19.1	15.45	46.99	9.11	9.11	**Pandit et al. (2011)**
Windsor (Canada)		0.49	2.87	0.79	1.54	0.53	**Miller et al. (2011)**
Xujiahui (China)		5.6	17.4	5.6	5.9	2.4	**Cai et al. (2010)**
Delhi (India)		17	167	87	66	34.25	**Hoque et al. (2008)**
Greater Cairo-Ramsis (Egypt)		22.86	111.03	46.41	73.18	37.47	**Khoder (2007)**
Hanoi (Vietnam)		16	62.33	72.67	41.67	21.67	**Truc and Oanh (2007)**
Greater Cairo-Ramsis (Egypt)		42.5	213.8	87.2	140.44	72.38	
Guangzhou (China)		9.4	51.8	28.8	19.2	5.6	**Tang et al. (2005)**
Central &Tsuen Wan (Hong Kong)		1.27	13.45	2.31	1.66	0.57	**Guo et al. (2004)**
Berlin (Germany)		3.4	14.5	6.7	4.3	3.3	**Monod et al. (2001)**
USA		4.3	3.8	3.4	4.1	4.3	**Pankow et al. (2003)**
Seoul (Korea)		1.69	147.8	39.8	8.87	9.12	**Son et al. (2003)**
Copenhagen (Denmark)	0.56	8.25	38.43	10.86	23.88	11.29	**Christensen et al. (1999)**

a: average conc. of m/p-Xylene and o-Xylene

3.2   Temporal Variation of Isoprene and BTEX

3.2.1   Seasonal Variations

The mean concentrations of each compound at vegetative sites in different seasons are shown in Figure 3.5. At vegetative sites, maximum mean concentrations for isoprene were observed during the summer season (6.51 ± 3.56 µg/m^3) followed by monsoon (5.1 ± 3.06 µg/m^3), post-monsoon (4.8 ± 3.18 µg/m^3) and winter (1.82 ± 0.57 µg/m^3). High temperature and intense solar radiation enhance the isoprene emissions from the plants during summer, monsoon, and post-monsoon seasons (Reimann et al., 2000). On the contrary, low values of these parameters during winter retarded the isoprene emission rate from the trees and thus decreases the isoprene levels. The isoprene levels observed in this study during different seasons are comparable to the levels observed in the other major subtropical metropolis cities of the world (Chang et al., 2014; Park et al., 2011; So and Wang, 2004; Wiedinmyer et al., 2001). However, much lower isoprene concentrations were reported in various temperate cities (Borbon et al., 2001; von Schneidemesser et al., 2011; Hellén et al., 2012). The BTEX concentrations showed the opposite pattern having maximum ambient concentrations during wintertime. The ambient mean concentrations of BTEX observed during winter were 9.72 ± 5.28 µg/m^3, 25.91 ± 9.75 µg/m^3, 3.21 ± 1.63 µg/m^3, 13.44 ± 7.6 µg/m^3 and 6.31 ± 3.38 µg/m^3, respectively. The higher concentrations in winter can possibly be explained on the basis of lower mixing height of the atmosphere during winter as compared to other seasons. After winter, the higher mean concentrations of benzene and toluene were found during summer (7.38 ± 2.82 µg/m^3) and (25.31 ± 5.96 µg/m^3), respectively. For ethylbenzene, m/p-xylene and o-xylene, the high winter concentrations were followed by their post-monsoon season concentrations i.e. (2.49 ± 1.43 µg/m^3), (9.23 ± 6.31 µg/m^3) and (4.54 ± 3.4 µg/m^3) respectively. During

monsoon season, all compounds were found to have low concentrations possibly due to washout of pollutants (Srivastava et al., 2006). The mean concentration values for BTEX obtained during monsoon were 5.1 ± 1.97 µg/m^3, 13.12 ± 4.8 µg/m^3, 1.96 ± 0.82 µg/m^3, 6.8 ± 2.79 µg/m^3 and 2.95 ± 1.22 µg/m^3, respectively.
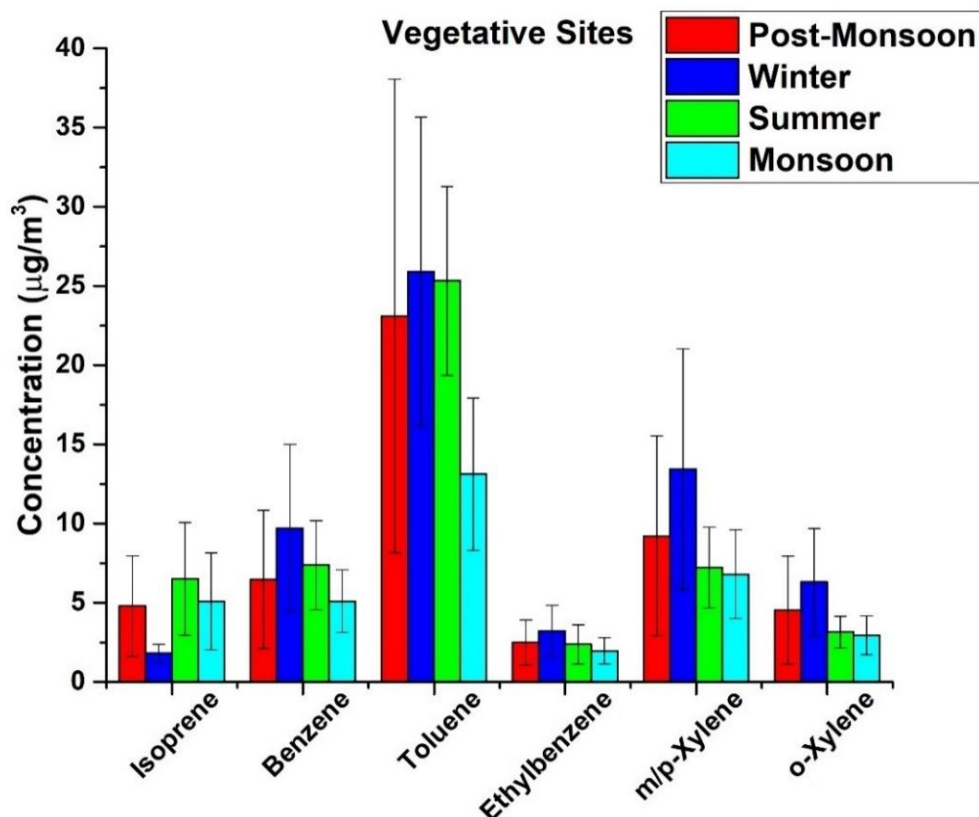
Figure 3.5: Mean concentrations of selected compounds during different seasons at vegetative sites.

Figure 3.6 illustrates the bar chart representation of mean concentrations of selected compounds in different seasons at traffic sites. In contrast to the vegetative sites, no significant seasonal variation in isoprene concentrations was observed at traffic sites, and very low isoprene concentrations were observed at these sites during all the seasons. The measured mean isoprene concentrations at traffic sites during winter, summer, post-monsoon and monsoon were 0.56 ± 0.21 µg/m^3, 0.56 ± 0.19 µg/m^3, 0.57 ± 0.26 µg/m^3 and 0.36 ± 0.07 µg/m^3 respectively. However, benzene, ethylbenzene m/p-xylene and o-xylene species followed similar seasonal pattern to

that over the vegetative sites, with highest concentrations during the winter (25.76 ±

10.2/ 17.06 ± 8.55/ 51.17 ± 19.01/ 20.5 ± 9.67 µg/m^3), followed by summer (23.65 ±

7.34/ 12.48 ± 3.54/ 45.92 ± 14.19/ 17.34 ± 5.86 µg/m^3) post-monsoon (19.39 ± 14.95/

11.1 ± 8.11/ 33.41 ± 18.66/ 15.18 ± 9.98 µg/m^3) and monsoon (12.45 ± 4.35/ 6.51 ±

2.17/ 23.51 ± 8.43/ 23.51 ± 8.43 8.93 ± 3.32 µg/m^3), respectively. A different trend

was observed in case of toluene whose concentrations were the highest during post-

monsoon (66.69 ± 17.54 µg/m^3) followed by winter (60.49 ± 24.66 µg/m^3), summer

(55.24 ± 17.64 µg/m^3) and monsoon (31.12 ± 7.4 µg/m^3) season.
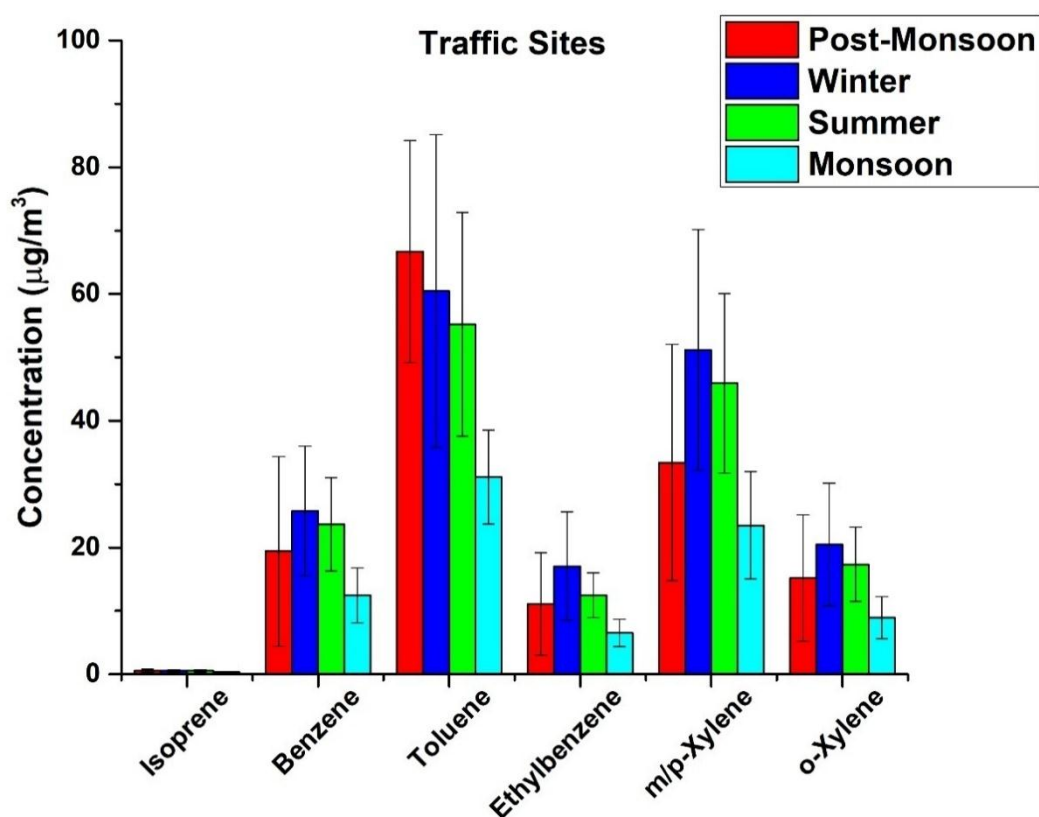
Figure 3.6: Mean concentrations of selected compounds during different seasons at traffic sites.

3.2.2 Intraday Variations

To examine the variability of selected pollutants at three different points of time, i.e.

morning, afternoon and evening (intra-day) during the day, the average concentrations

for individual compounds were computed by averaging the respective intra-day values

across the three sites belonging to each category (vegetative and traffic). The average

intra-day variation of selected VOCs at vegetative and traffic sites are depicted in

Figures 3.7 and 3.8, respectively.
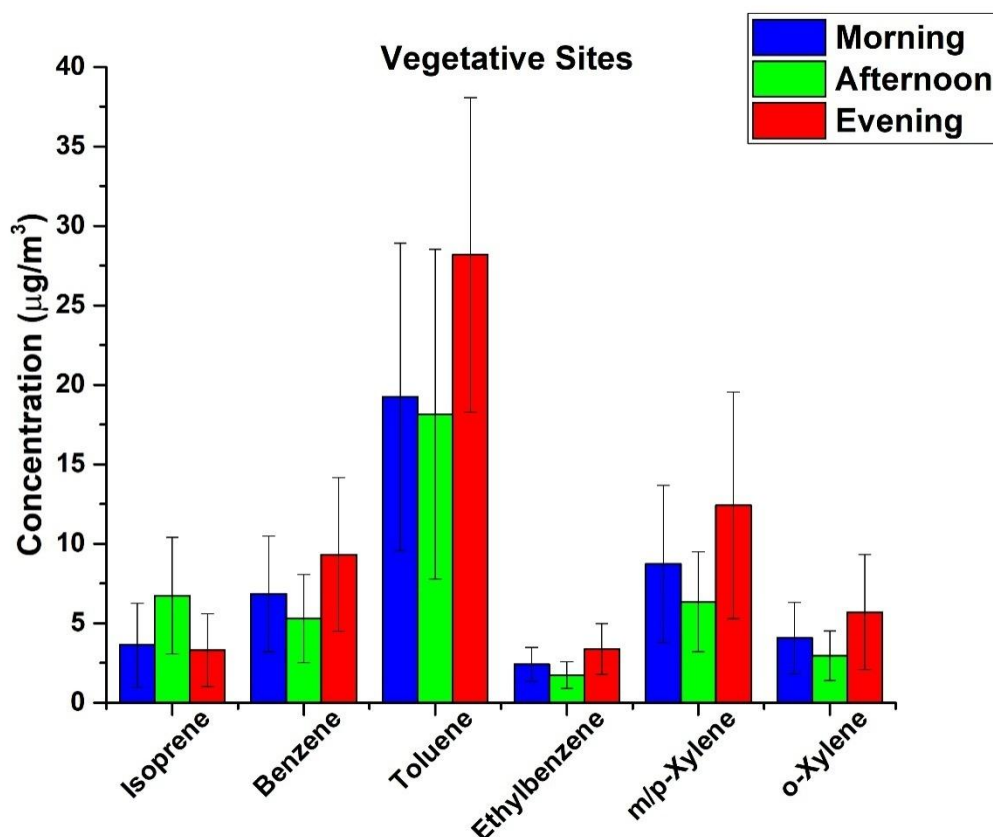
Figure 3.7: Intra-day variation of all selected compounds at vegetative sites.

Figure 3.7 shows similar variation trends for all BTEX compounds at vegetative sites,

with maximum values observed during morning and evening period and minimal

values during the afternoon time. However, isoprene levels at vegetative sites were

notably higher in the afternoon (6.74 ± 3.67 µg/m^3) as compared to morning/evening

($3.63 \pm 2.64/3.31 \pm 2.3$ µg/m^3). This kind of intra-day variation at vegetative sites

presumably occurs because biogenic isoprene emissions are primarily governed by

solar irradiance and ambient temperature (Guenther et al., 1993; Niinemets et al.,

2010; Sharkey and Singsaas, 1995). In contrast, the average concentrations of each

BTEX compound at vegetative sites were found to be the highest ($9.32 \pm 4.83/ 28.17$

± 9.91/ 3.37 ± 1.6/ 12.42 ± 7.13/ 5.7 ± 3.62 µg/m^3) during evening and lowest (5.31 ±

2.77/ 18.14 ± 10.37/ 1.74 ± 0.84/ 6.35 ± 3.14/ 2.95 ± 1.56 µg/m^3) during the afternoon

time.
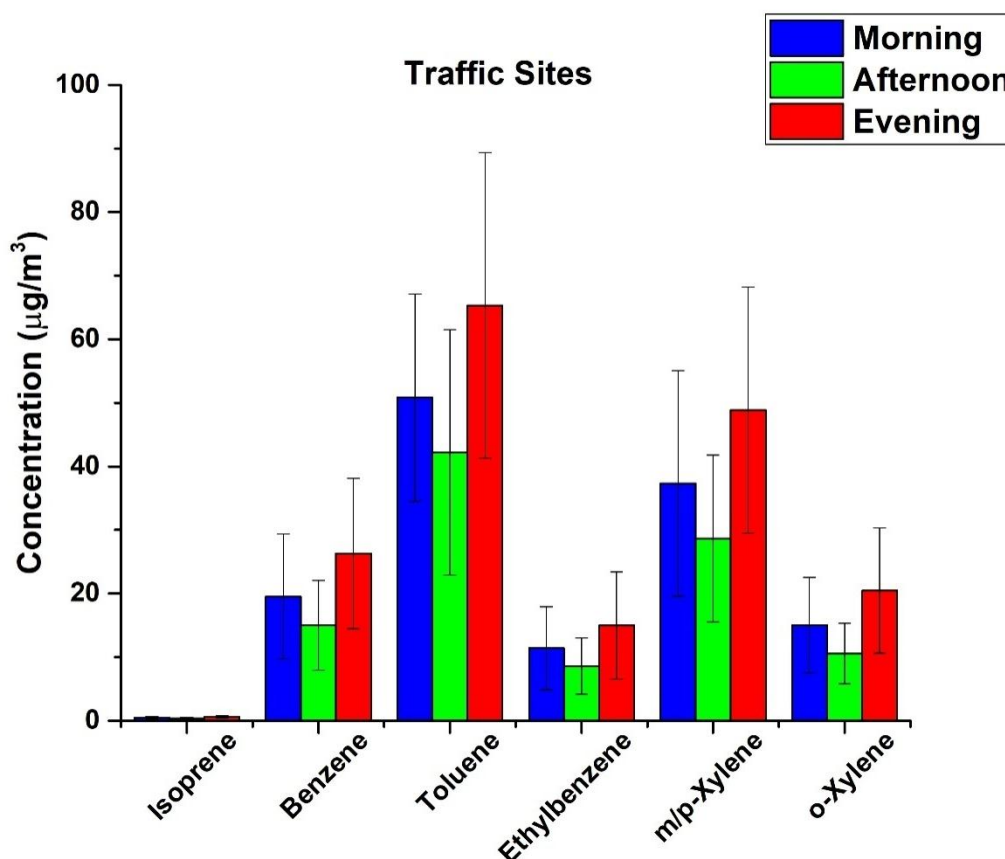
Figure 3.8: Intra-day variation of all selected compounds at traffic sites.

At the traffic sites, however, isoprene did not show any specific pattern in intra-day

variation, as the isoprene concentrations remained low at these sites during the entire

day (Figure 3.8). Irregular pattern and extremely low values for isoprene indicate the

non-biogenic source of emissions. However, the maximum concentration of BTEX

compounds were measured during peak traffic hours i.e. morning and evening and

lowest during the afternoon. Thus, the observed intra-day variation for BTEX

compounds was possibly due to the intraday variation in vehicular activity at these

sites. The lower values for all selected VOCs during mid-day time could also be

attributed to the dilution effect caused by the rising of the boundary layer during the afternoon (Chang et al., 2014).

3.3   Exhaust Emission from Vehicles

In urban cities, vehicular emissions are considered as the major source of air pollution and cause several health hazards (Poorfakhraei et al., 2017). The exhaust emitted from the automobiles is discharged into the atmosphere via the exhaust pipe. The amount and composition of exhaust gases released depend on the type of engine and the fuel consumed. Prior research on vehicular exhaust observed a significant concentration of BTEX compounds in the vehicular exhaust (Lan and Minh, 2013; Macedo et al., 2017). To combat vehicular pollution, the Government of India took several legislative measures in the form of fixing the emission limits for the vehicles and has updated these emission norms from time to time. However, the vehicular emission norms in India pertain to only a few chemical species such as particulate matter (PM), nitrogen oxides (NOX), carbon monoxide (CO), and total hydrocarbons (HC) (Sood, 2012; Adamović et al., 2018). Other species such as the BTEX compounds, though emitted in large amounts by the vehicles, are not specifically targeted. Another important chemical species that has been reported to be present in the vehicular exhaust is isoprene (Reimann et al., 2000; Borbon et al., 2001). The megacity of Delhi, with a large vehicular population and significant vegetation cover, is expected to have both the anthropogenic and biogenic sources of isoprene. Therefore, examining the isoprene levels along with BTEX compounds in the vehicular exhaust was one of the objectives in this study. Samples of exhaust were collected from different types of vehicles run on petrol, diesel and CNG, and the concentrations of isoprene and BTEX compounds were estimated on GC. The mean concentrations of

isoprene and BTEX compounds observed in the exhaust from different types of vehicles are shown in Table 3.4.

Table 3.4: Mean concentrations of targeted compounds in the exhaust of different types of vehicles within each fuel category.

		Isoprene	Benzene	Toluene	Ethyl benzene	m/p-Xylene	o-Xylene
Petrol	Bikes	3820.86	29296.15	170424.99	79705.30	224408.03	143867.78
	Scooters	5212.81	42353.55	234347.95	70185.69	179388.43	76948.91
	Cars	2220.49	20155.08	108045.31	86812.70	258381.95	123381.11
CNG	DTC buses		291.23	1674.67	1197.46	4086.63	870.07
	Cars		505.28	3798.43	2502.12	6976.17	1545.27
	Autos		362.05	1620.65	847.97	2865.91	1115.68
	Tempos		696.65	7505.60	4613.71	8487.08	1618.56
Diesel	Cars		1557.79	3584.70	3469.76	8366.69	3952.00

(All values are in $\mu g/m^3$)

Table 3.5: Mean concentration of targeted compounds in different types of vehicular exhaust.

Compounds	Petrol		CNG		Diesel	
	Mean	SD	Mean	SD	Mean	SD
Isoprene	3923.50	3171.08				
Benzene	31495.10	21608.17	451.84	273.10	1557.79	1068.17
Toluene	177478.64	140396.49	3418.14	2757.83	3584.70	2032.07
Ethylbenzene	78195.40	57950.15	2158.34	1122.66	3469.76	2020.79
m/p-Xylene	217343.73	170107.87	5509.52	5863.97	8366.68	4288.98
o-Xylene	118422.50	108619.70	1282.82	562.62	3952.00	1728.16

All values are in $\mu g/m^3$, SD stands for standard deviation

It may be observed that among the petrol-driven vehicles, isoprene, benzene, and toluene are emitted in higher concentrations from bikes and scooters as compared to cars. On the other hand, ethylbenzene and xylene isomers are found to be emitted in

higher concentrations from cars as compared to bikes and scooters. In the case of CNG vehicles, Tempos are found to have higher concentrations of BTEX compounds followed by cars, DTC buses, and autos. The diesel-driven cars are found to emit most of the BTEX compounds in higher concentrations than CNG driven vehicles, but their emission is far less than that from the petrol-driven vehicles.

Mean values of targeted compounds computed by taking their average concentrations across all categories of vehicles for a given fuel type, i.e. Petrol, CNG, and Diesel are presented in Table 3.5.

3.3.1   Exhaust from Petrol Driven Vehicles

The levels of VOCs emissions from vehicles run on petrol have been shown in Figure 3.9. In this study, we found that the emission of xylene is more from the vehicles run on petrol. The emission of m/p-xylene (217343.7 $\pm$ 170107.87 $\mu g/m^3$) was observed to be the maximum followed by toluene (177478.64 $\pm$ 140396.49 $\mu g/m^3$). Along with these compounds, high emission levels of o-xylene (118422.50 $\pm$ 108619.70 $\mu g/m^3$), and ethylbenzene (78195.40 $\pm$ 57950.15 $\mu g/m^3$), were also observed. Benzene, which is a major carcinogenic compound (Group 1 Carcinogen) was also emitted by the petrol-driven vehicles in a significant amount (31495.10 $\pm$ 21608.17 $\mu g/m^3$). Further, isoprene also was found in significant amounts in the exhaust of petrol-driven vehicles (3923.50 $\pm$ 3171.08 $\mu g/m^3$). The study clearly signifies that the vehicles run on petrol are the major source of isoprene and BTEX compounds.
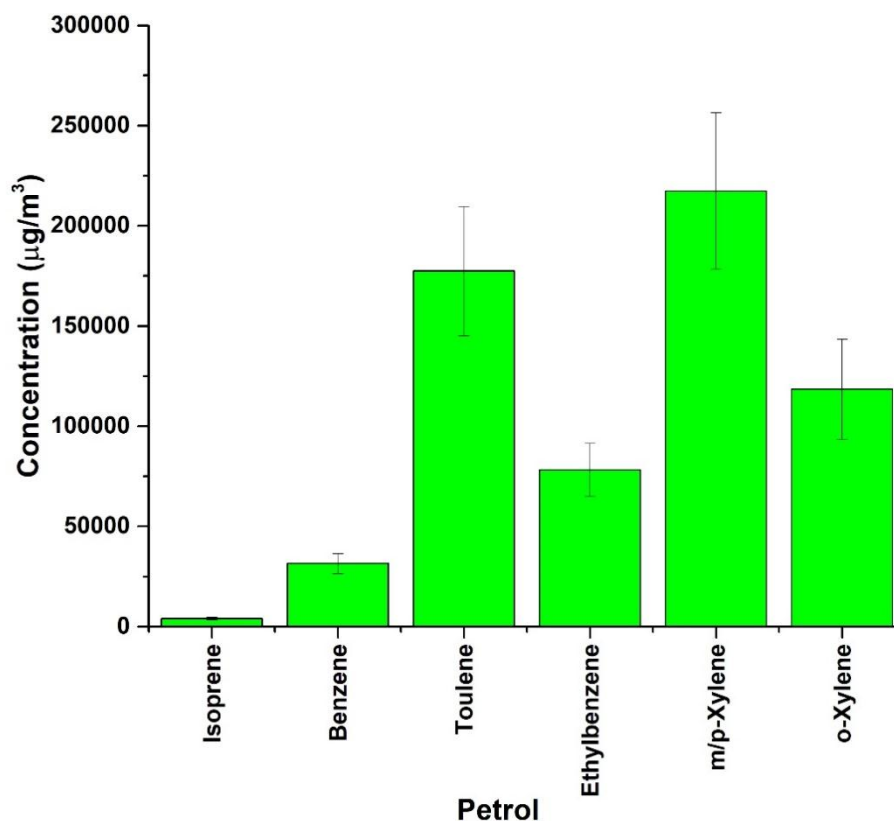
Figure 3.9: Emission of VOCs from the vehicles runs on petrol.

3.3.2   Exhaust from Diesel Driven Vehicles

The levels of VOCs emissions from diesel exhaust have been represented in Figure 3.10. It is clear from the figure that the emissions from diesel driven vehicles are less than the vehicles run on petrol. Among the BTEX compounds, the maximum concentration in the diesel vehicles exhaust was that of m/p-xylene (8366.68 $\pm$ 4288.98 $\mu g/m^3$) followed by toluene (3584.70 $\pm$ 2032.07 $\mu g/m^3$)   and o-xylene (3952.00 $\pm$ 1728.16 $\mu g/m^3$). It is also noteworthy to mention here that no isoprene was detected in the exhaust coming from diesel-operated vehicles.
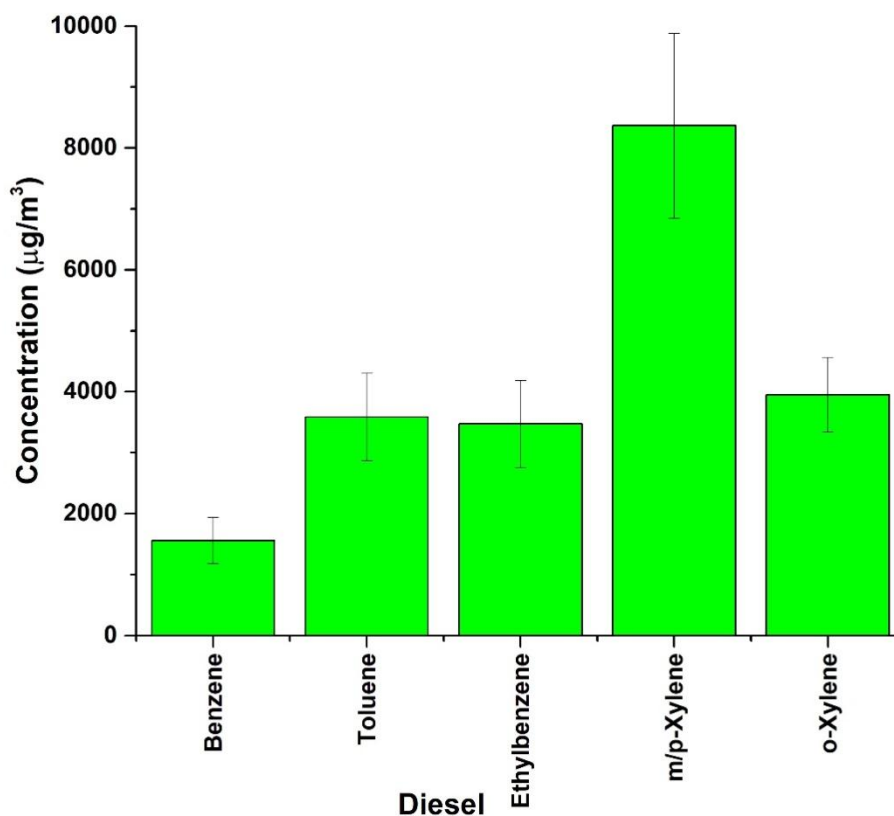
Figure 3.10: Emission of VOCs from the vehicles runs on diesel.

3.3.3 Exhaust from CNG Driven Vehicles

The levels of VOCs emissions from CNG vehicle's exhaust have been represented in Figure 3.11. It is seen that emissions of m/p-xylene (5509.52 $\pm$ 5863.97 $\mu g/m^3$), toluene (3418.14 $\pm$ 21608.17 $\mu g/m^3$), benzene (451.84 $\pm$ 273.10 $\mu g/m^3$) and o-xylene (1282.82 $\pm$ 562.62 $\mu g/m^3$) are comparable but lower than their levels in the exhaust from diesel vehicles**.** Further, like the diesel vehicles, isoprene was also not observed in any of the exhaust samples of CNG vehicles. It is also observed that emissions of BTEX compounds in diesel and CNG vehicles are significantly lower as compared to their emission from petrol vehicles.
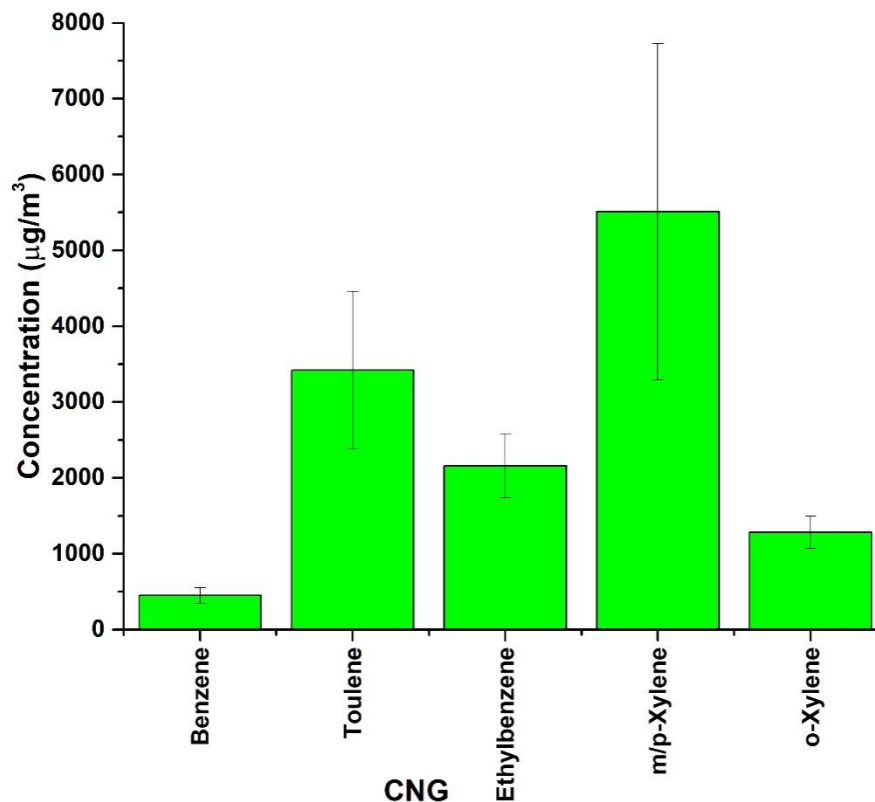
Figure 3.11: Emission of VOCs from the vehicles runs on CNG.

3.4   Anthropogenic and Biogenic Fractions of Isoprene

In the urban settings, where the vehicular population is high and govern the concentrations of various pollutants in the ambient air, they may also affect the isoprene concentrations as well. Isoprene enters into the ambient atmosphere from both anthropogenic as well as biogenic sources (Borbon et al., 2001; Reimann et al., 2000; Chang et al., 2014; Wang et al., 2013). Various studies measured isoprene levels in the tailpipe emissions of different vehicles (Duffy et al., 1999; Borbon et al., 2001). To estimate the anthropogenic portion of isoprene from the ambient measured isoprene, Wang et al. (2013) suggested that the comparison of the lower ambient ratio of isoprene/tracers at traffic dominated area with the measured ambient isoprene/tracers ratio can be used in the estimation of the anthropogenic isoprene. In the present study, we used benzene, as a suitable traffic tracer because its most

dominant source in the ambient atmosphere is traffic exhaust and merely 5-10 % of its emissions in the outdoor air, are from non-mobile sources (Bolden et al., 2015). Moreover, we obtained a strong positive correlation (correlation coefficient, r = 0.81) between isoprene and benzene in the ambient air at traffic sites. We have also measured the isoprene and benzene species in the traffic exhaust and observed a good correlation between isoprene and benzene with a correlation coefficient of 0.73. However, the measurements of isoprene and benzene in pure vehicular exhaust revealed that isoprene is only emitted from the petrol-driven vehicles, but benzene is present in the exhaust of all types of vehicles including petrol, CNG and diesel. Further, isoprene is highly reactive with an atmospheric lifetime of 30-40 minutes as compared to benzene having an atmospheric lifetime of around 12 days. Hence, isoprene/benzene ratios from pure vehicular exhaust would overestimate the anthropogenic portion of isoprene in the ambient atmosphere. For this purpose, we used the minimum isoprene/benzene ratio $(I/B)_{min\_traffic}$ at traffic sites for the estimation of anthropogenic and biogenic contribution to ambient isoprene. The minimum isoprene/benzene ratio (0.01594) was observed at PJB site in evening time during the winter season and was used for the computation of anthropogenic fraction. This ratio most likely represents the isoprene emissions present in the ambient atmosphere during that time because of the vehicular exhaust. Any higher isoprene/benzene ratio from this may lead to the addition of biogenic contribution in isoprene emissions.

Table 3.6 shows the anthropogenic and biogenic isoprene with their percentage contributions at different sites. It is seen that anthropogenic isoprene (I_{anthro}) and biogenic isoprene (I_{bio}) averaged over all the seasons, were observed to lie in the range of 0.089 to 0.142 µg/m^3 and 2.471 to 6.390 µg/m^3, respectively at the vegetative

sites. In comparison, the I_{anthro} and I_{bio} at traffic, sites lied in the range 0.230 to 0.399 µg/m³ and 0.177 to 0.198 µg/m³, respectively. Overall, the contributions of I_{anthro} and I_{bio} to total ambient isoprene were found to be 2.50% and 97.50% at vegetative sites and 63.53% and 36.47% at traffic sites, respectively.

Table 3.6: Anthropogenic and biogenic fraction estimation of isoprene (µg/m³) at the sampling sites.

	Sites	Average Estimated Anthropogenic Isoprene	Average Estimated Biogenic Isoprene	Average Total Estimated Anthropogenic Isoprene	Average Total Estimated Biogenic Isoprene
Vegetative	YBP	0.089 (2.78%)*	6.390 (97.22%)	0.11 (2.50%)	4.46 (97.50%)
	JNU	0.142 (5.24%)	4.512 (94.76%)		
	SJP	0.112 (8.05%)	2.471 (91.95%)		
Traffic	PTP	0.230 (58.38 %)	0.186 (43.62%)	0.33 (63.53%)	0.19 (36.47%)
	CRI	0.399 (65.73%)	0.198 (34.27%)		
	PJB	0.349 (66.01%)	0.177 (33.99%)		

*Values in the parenthesis represent the percentage contribution.

Season wise estimation of anthropogenic isoprene and biogenic isoprene is shown in Figure 3.12. It was found that the biogenic isoprene dominates its anthropogenic counterpart in all the seasons at vegetative sites. However, the maximum contribution from biogenic sources was found at vegetative sites during summer followed by monsoon and post-monsoon seasons. On the contrary, isoprene levels were found to be low at the traffic sites and the estimated I_{anthro} was the dominant source during all

the seasons. The contribution of I_{anthro} was found to be maximum during winters but a non-negligible fraction to biogenic isoprene was also observed.

The percentage contributions of both I_{anthro} and I_{bio} across different seasons are shown in Figure 3.13. During all the seasons more than 90% of the contribution of ambient isoprene at the vegetative sites was estimated to be released from the biogenic sources. Among the sites, YBP contributed (> 99%) maximum for I_{bio} followed by JNU (> 94%) and SJP (> 90%) during post-monsoon, summer and monsoon seasons. During winter season also, these sites contributed more than 90% to biogenic isoprene emissions.
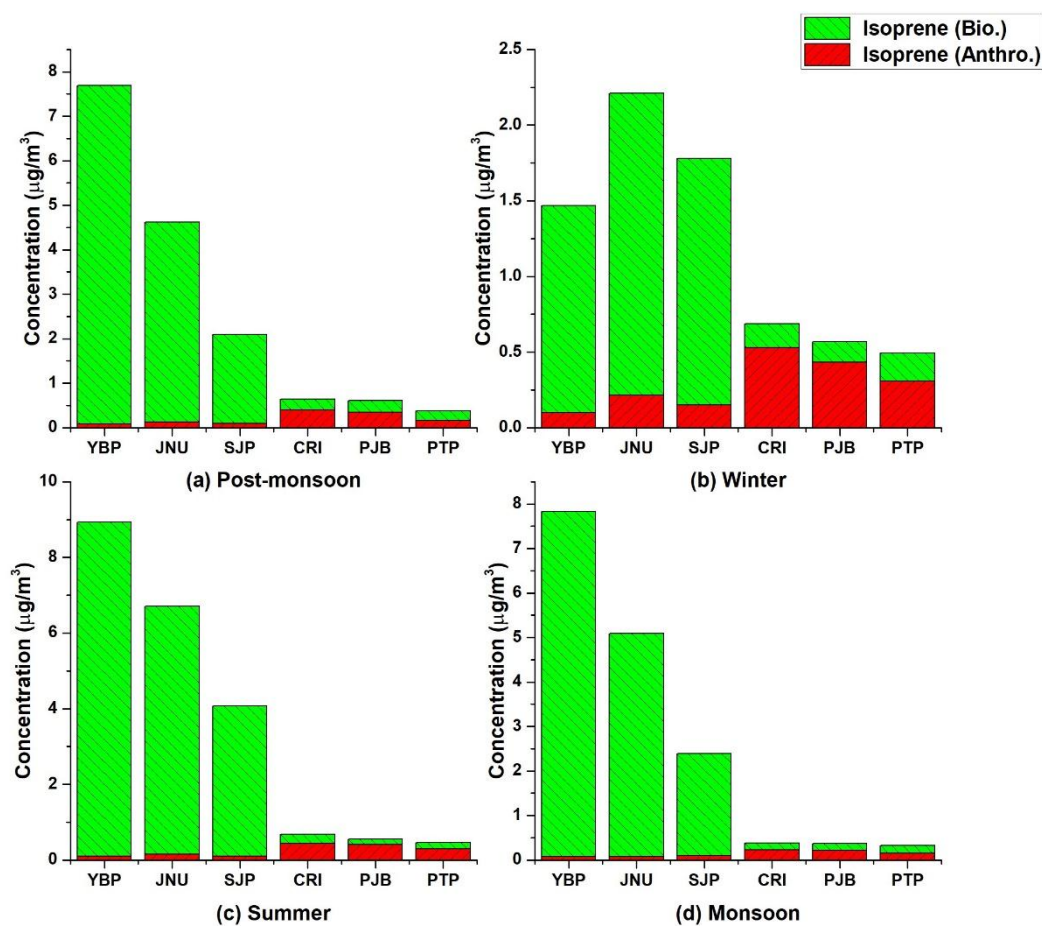
Figure 3.12: Season wise estimation of I_{anthro} and I_{bio} at all the selected sites. The length of the bars represent the total isoprene concentrations at each site.

The anthropogenic sources for isoprene were estimated to be dominant at all the traffic locations in all the seasons. More than 50% isoprene emissions at traffic sites were estimated to be released from anthropogenic sources in summer, post-monsoon and monsoon season. During winters, anthropogenic contribution to ambient isoprene at traffic sites was found to be maximum (66% to 78%) followed by summer (65% to 74%), monsoon (47% to 60%) and post-monsoon (48% to 58%).
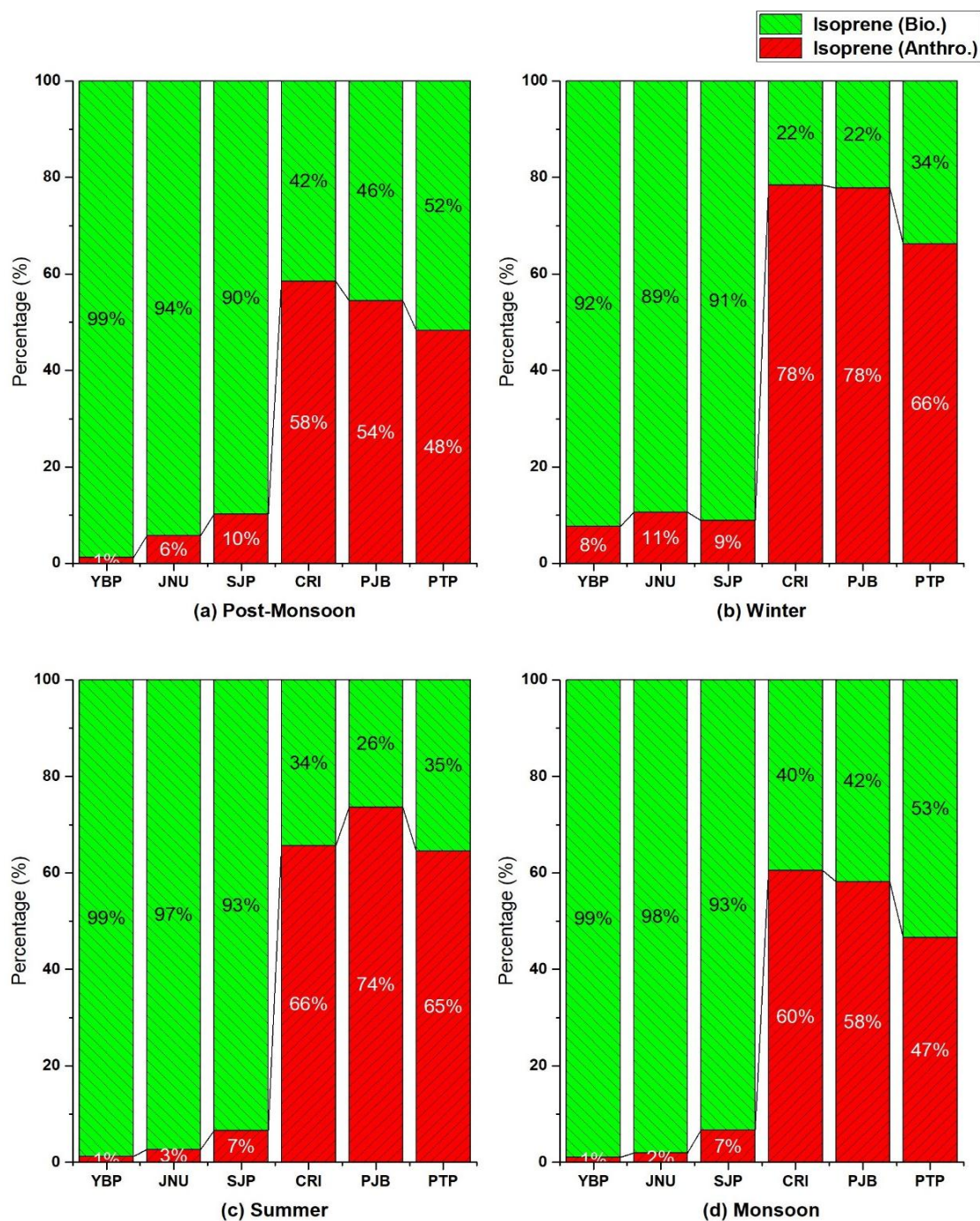
Figure 3.13: The estimated percentage contribution of biogenic and anthropogenic isoprene in all seasons at all the sites.

3.5   Source Identification

3.5.1   Interspecies Ratios

This study also deals with the inter-species ratio of selected compounds. The ratios of these species with one another give an idea about the potential sources of these

compounds under given atmospheric conditions at a particular location. Many studies have used these ratios to identify the emission sources of these pollutants and the age of air mass (Khoder, 2007; Kerbachi et al., 2006; Guo et al., 2007). In this study, we used ratios of toluene/benzene (T/B), m/p-xylene/benzene (mpX/B), and o-xylene/benzene (oX/B) for the identification of potential sources at each site. In the urban atmosphere, the main source of benzene and toluene is the traffic exhaust (Han and Naeher, 2006; Mokhtari et al., 2015). However, in addition to the traffic source, toluene is also emitted from various solvents and household products, which include paints, varnishes, adhesives, and other finishing building materials (ATSDR, 2000). Therefore, the ratio of toluene to benzene (T/B) has been widely accepted as an indicator of traffic emissions. If this value lies in the range of 1.5 to 4.3, it suggests the predominance of traffic sources (Kumar et al., 2017; Liu et al., 2008). However, if T/B ratio is very high or approaching to a value of 10 or more, this implies that strong industrial emissions might exist in the vicinity of the site (Niu et al., 2012). Some studies have also accepted the T/B values lower than 3 as characteristic of traffic emissions (Alghamdi et al., 2014; Brocco et al., 1997; Hoque et al., 2008). In the present study, the mean T/B ratios were found to be 3.66, 3.80, 3.24, 2.64, 2.70 and 3.40 for YBP, SJP, JNU, CRI, PJB, and PTP, respectively during the overall study period (Figure 3.14). These values indicate the presence of traffic as a dominant source around these locations. Even at the vegetative sites, average T/B ratios lie in between 1.5 to 4.5, which suggesting that these species might have been transported from the nearby traffic dominated areas. The T/B ratios observed in this study are comparable to those found in different urban areas across the world viz. Paris, France (2.9-3.4), Jeddah (3.58-4.26), Sydney (4.04), Ankara (4.3), Ahvaz (3.25), Provinces of China (3.85),Windsor (4.3) and Belgium (3.8–4.4) (Alghamdi et al., 2014; Nelson

and Quigley, 1982; Miller et al., 2010; Tong et al., 2013; Yurdakul et al., 2013; Rad et

al., 2014; Buczynska et al., 2009; Vardoulakis et al., 2002).
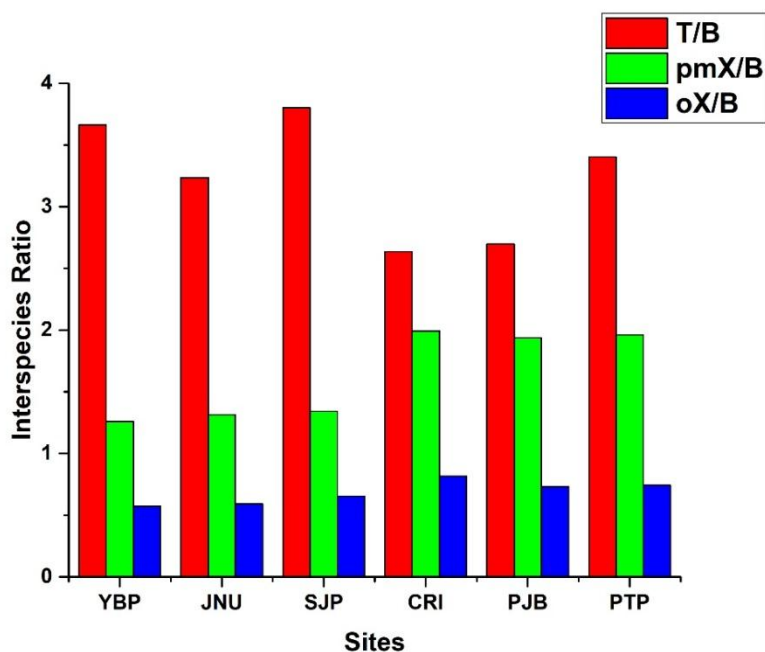
Figure 3.14: Interspecies ratio of selected compounds at distinct sampling locations.

The average m/pX/B, and oX/B ratios at different vegetative sites were found to be in

the range of 1.26-1.34, and 0.57-0.66 respectively. While, at traffic sites, the mean

values of mpX/B, and oX/B ratios lied in the range 1.94-1.99, and 0.73-0.82

respectively. No significant variation of these ratios was observed among similar

types of sites. However, mpX/B, and oX/B ratios at vegetative sites were found to be

lower than those at traffic sites. The lower mpX/B and oX/B ratios indicate the

existence of old air mass as xylene isomers are more reactive species than benzene

(Nelson and Quigley, 1983; Rad et al., 2014; Niu et al., 2012; Gelencsér et al., 1997).

The lifetime of xylene towards OH radical is 7.8 hours which is very less as compared

with benzene having a lifetime of 12 days (Kumar et al., 2017). The old air mass

signifies that the air parcel containing pollutants were transported from some other

location without degradation (Bauri et al., 2016). Moreover, among the vegetative

sites, these ratios are relatively higher at the SJP site as compared to the JNU and

YBP sites. This is possibly due to the traffic sources at the SJP site being comparatively nearer to the park as compared to those near the JNU and YBP sites.

3.5.2   Interspecies Correlation among the Compounds

The Pearson correlation matrices among isoprene and BTEX compounds in both types of sites are given in Tables 3.7 and 3.8 for vegetative sites and traffic sites, respectively. The negative correlation between isoprene and other BTEX compounds at vegetative sites can plausibly be explained on the basis of their major sources at these sites. While isoprene at the vegetative sites, being primarily emitted from vegetation, peaks during the afternoon period, the BTEX species being transported from the nearby traffic dominated locations are lower during non-peak traffic hours in the afternoon. The high correlation of benzene with ethylbenzene and xylene species (r > 0.89) suggests BTEX at vegetative sites could be emitted from nearby traffic dominated locations. Moreover, a very strong correlation (r > 0.98) between m/p-xylene and o-xylene was also observed, which again shows that their sources are the same. The lowest correlation coefficient (r < 0.53) was seen between toluene and other compounds. The possible reason for this result could be the presence of some additional sources of toluene.

Table 3.7: Correlation matrix of the targeted compounds at vegetative sites.

	Isoprene	Benzene	Toluene	Ethyl benzene	m/p-Xylene	o-Xylene
Isoprene	1.00					
Benzene	-0.34*	1.00				
Toluene	-0.19	0.53*	1.00			
Ethylbenzene	-0.41*	0.89*	0.47*	1.00		
m/p-Xylene	-0.41*	0.92*	0.56*	0.85*	1.00	
o-Xylene	-0.42*	0.89*	0.54*	0.83*	0.98*	1.00

*Correlation is significant at 0.01

Table 3.8 reports the correlation coefficient values among the isoprene and BTEX compounds based on the ambient concentrations at the traffic sites. A strong positive correlation between isoprene and BTEX compounds indicates that they have a similar emission source, i.e. traffic. Among the BTEX compounds, high correlation ($r > 0.63$) suggested that the emitted compounds could be mainly attributed to the vehicles at the traffic locations. These results are comparable with those from previous studies which have also reported strong correlation among BTEX compounds (Miri et al., 2016; Rad et al., 2014; Pankow et al., 2003; Miller et al., 2011; Hoque et al., 2008).

Table 3.8: Correlation matrix of the targeted compounds at traffic sites.

	Isoprene	Benzene	Toluene	Ethyl benzene	p/m-Xylene	o-Xylene
Isoprene	1.00					
Benzene	0.81*	1.00				
Toluene	0.65*	0.67*	1.00			
Ethylbenzene	0.73*	0.92*	0.63*	1.00		
p/m-Xylene	0.78*	0.94*	0.66*	0.91*	1.00	
o-Xylene	0.78*	0.94*	0.70*	0.92*	0.94*	1.00

*Correlation is significant at p-value 0.01

3.6   Relationship of Isoprene with Meteorological Variables

Meteorological conditions at a particular location play a significant role in determining the emissions (directly or indirectly), formation, deposition, dispersion, transportation and chemical kinetics of various air pollutants (Kliengchuay et al., 2018). This study investigated the association of isoprene with various meteorological variables like temperature (T), solar radiation (SR), relative humidity (RH), wind speed (WS) and two important gaseous pollutants, i.e. ozone (O_3) and Nitrogen oxides (NOx). Tables 3.9 to 3.12 represent the correlation coefficient of isoprene with ozone, NOx, and meteorological variables in different seasons. It may be observed that

isoprene levels at the vegetative sites generally have a significant positive correlation with ozone, temperature, and solar radiation. This is primarily because ozone formation is a photochemical process which maximizes in the afternoon when temperatures also maximize. This is also the time when isoprene emission from vegetation is the maximum. Such an association of isoprene with temperature and solar radiation has been reported in some of the earlier studies also (Sharkey and Yeh, 2001, Wang et al., 2013). The correlation coefficient between isoprene and ozone at vegetative sites were in the range of 0.77 to 0.87 in post-monsoon, 0.75 to 0.85 in winter, 0.75 to 0.79 in summer and 0.75 to 0.91 in monsoon season. Similarly, the correlation coefficient between isoprene and temperature at vegetative sites were in the range of 0.88 to 0.90 in post-monsoon, 0.86 to 0.94 in winter, 0.84 to 0.87 in summer and 0.87 to 0.90 in monsoon season. On the contrary, a significant negative correlation is found to exist between isoprene and NOx at vegetative sites in all seasons. This is plausible because NOx levels at vegetative sites are primarily because of transport from nearby traffic sites which witness peak NOx levels during morning and evening traffic rush hours and lower NOx levels during the afternoon period (Pancholi et al., 2018). Isoprene at vegetative sites is also found to have a negative correlation coefficient with RH. So far, only a few studies have investigated the role of relative humidity (RH) on isoprene emission rate of plant species. Sakihama et al. (2003) suggest that though relative humidity does not directly affect the isoprene emissions, it rather influences the stomatal opening. Highly humid conditions increase the stomatal opening and thus boost the isoprene emission rate in plants (Tambunan et al., 2007). However, many studies have reported higher isoprene emission rate of plants during the dry season as compared to wet seasons (Serca et al., 2001;

Kesselmeier et al., 2002). Therefore, it is clear that merely the size of the stomatal opening cannot only be responsible for the isoprene emission in plants.

Table 3.9: Correlation coefficient values of various variables with isoprene in the post-monsoon season.

	Sites	Ozone	NOx	Temp	SR	WS	RH
Vegetative site	**YBP**	0.77*	-0.71*	0.90*	0.38	0.44	-0.72*
	JNU	0.81*	-0.76*	0.88*	0.70*	0.40	-0.64
	SJP	0.87*	-0.73*	0.90*	0.66*	0.88*	-0.82*
Traffic site	**CRI**	-0.80*	0.34	-0.66*	-0.75*	-0.48	0.54
	PJB	0.71*	-0.69*	0.52	-0.16	0.41	-0.34
	PTP	-0.64	0.67*	-0.46	-0.46	-0.13	0.29

Table 3.10: Correlation coefficient values of various variables with isoprene in the winter season.

	Sites	Ozone	NOx	Temp	SR	WS	RH
Vegetative site	**YBP**	0.85*	-0.81*	0.94*	0.51	0.63	-0.59
	JNU	0.75*	-0.75*	0.87*	0.56	0.30	-0.10
	SJP	0.81*	-0.73*	0.86*	0.56	0.30	-0.91*
Traffic site	**CRI**	-0.45	0.34	-0.62	-0.80*	-0.13	0.47
	PJB	-0.66*	0.12	-0.51	-0.61	-0.51	0.52
	PTP	-0.94*	0.72*	-0.74*	-0.83*	-0.39	0.82*

Table 3.11: Correlation coefficient values of various variables with isoprene in the summer season.

	Sites	Ozone	NOx	Temp	SR	WS	RH
Vegetative site	**YBP**	0.75*	-0.77*	0.84*	0.91*	-0.04	-0.64
	JNU	0.75*	-0.75*	0.87*	0.56	0.30	-0.10
	SJP	0.79*	-0.73*	0.84*	0.84*	0.42	-0.25
Traffic site	**CRI**	-0.27	-0.58	-0.08	-0.53	-0.31	-0.17
	PJB	-0.66*	0.12	-0.51	-0.61	-0.51	0.52
	PTP	-0.46	0.75	-0.46	-0.64	-0.66*	-0.25

Table 3.12: Correlation coefficient values of various variables with isoprene in monsoon season.

	Sites	Ozone	NOx	Temp	SR	WS	RH
Vegetative site	**YBP**	0.75*	-0.83*	0.90*	0.94*	0.40	-0.53
	JNU	0.80*	-0.78*	0.90*	0.61	-0.03	-0.45
	SJP	0.91*	-0.74*	0.87*	0.86*	0.48	0.25
	CRI	-0.23	-0.19	-0.44	-0.57	-0.07	0.83*
Traffic site	**PJB**	0.12	-0.41	-0.25	-0.37	-0.23	0.21
	PTP	-0.18	0.19	0.33	-0.25	0.28	-0.49

* Correlation is significant at the 0.05

In the present study, the correlation between isoprene and RH at vegetative sites is negative, possibly because RH is generally less during the afternoon period when temperature and isoprene are on the higher side. In general, no significant correlation was observed between isoprene and wind speed at the vegetative sites.

In the case of traffic sites, isoprene is generally seen to have a negative correlation with ozone, temperature, and solar radiation, which is in contrast to the behaviour observed at vegetative sites. This is primarily because isoprene at traffic sites is mainly emitted from vehicular sources. The peak vehicular activity at traffic sites occurs during morning and evening hours and thus isoprene emissions from vehicles at these times are generally on the higher side. But, during the morning and evening hours, ozone, temperature, and solar radiation are on the lower side. In general, isoprene is observed to have no significant correlation with NOx, RH, and WS at traffic sites.

3.7   Ozone Formation Potential and Propylene-Equivalent

For this study, Prop-Equiv was estimated for all the compounds, and Figure 3.15 provides the graphical representation of the average Prop-Equiv concentration of each individual compound. It is inferred from the figure 3.15 that the Prop-Equiv

concentrations were found high at the traffic sites than the vegetative sites. The seasonal trend follows a similar pattern as of ambient concentrations with high Prop-Equiv concentration during winter followed by summer, post-monsoon and monsoon seasons. It is noted that the contribution of isoprene at vegetative sites and m/p-xylene at traffic sites to Prop-Equiv concentrations are significantly higher as compared to the other VOCs. At traffic sites, the m/p-xylene and benzene showed the highest $(28.21 \pm 11.13 \ \mu g/m^3)$ and lowest $(0.96 \pm 0.35 \ \mu g/m^3)$ average values respectively, of the Prop-Equiv concentrations in all the seasons. But at the vegetative sites, instead of xylene, isoprene showed the highest average value $(17.50 \pm 10.21 \ \mu g/m^3)$ for Prop-Equiv concentrations and benzene showed the lowest $(0.36 \pm 0.12 \ \mu g/m^3)$. Among the vegetative sites, the highest Prop-Equiv concentrations were observed at YBP followed by JNU and SJP during summer, post-monsoon and monsoon season. However, during the winter season, a different pattern was observed, with the highest Prop-Equiv concentration at JNU followed by SJP and then YBP. At the traffic sites, the mean values of Prop-Equiv concentrations follow the order; CRI > PJB > PTP in all the seasons.
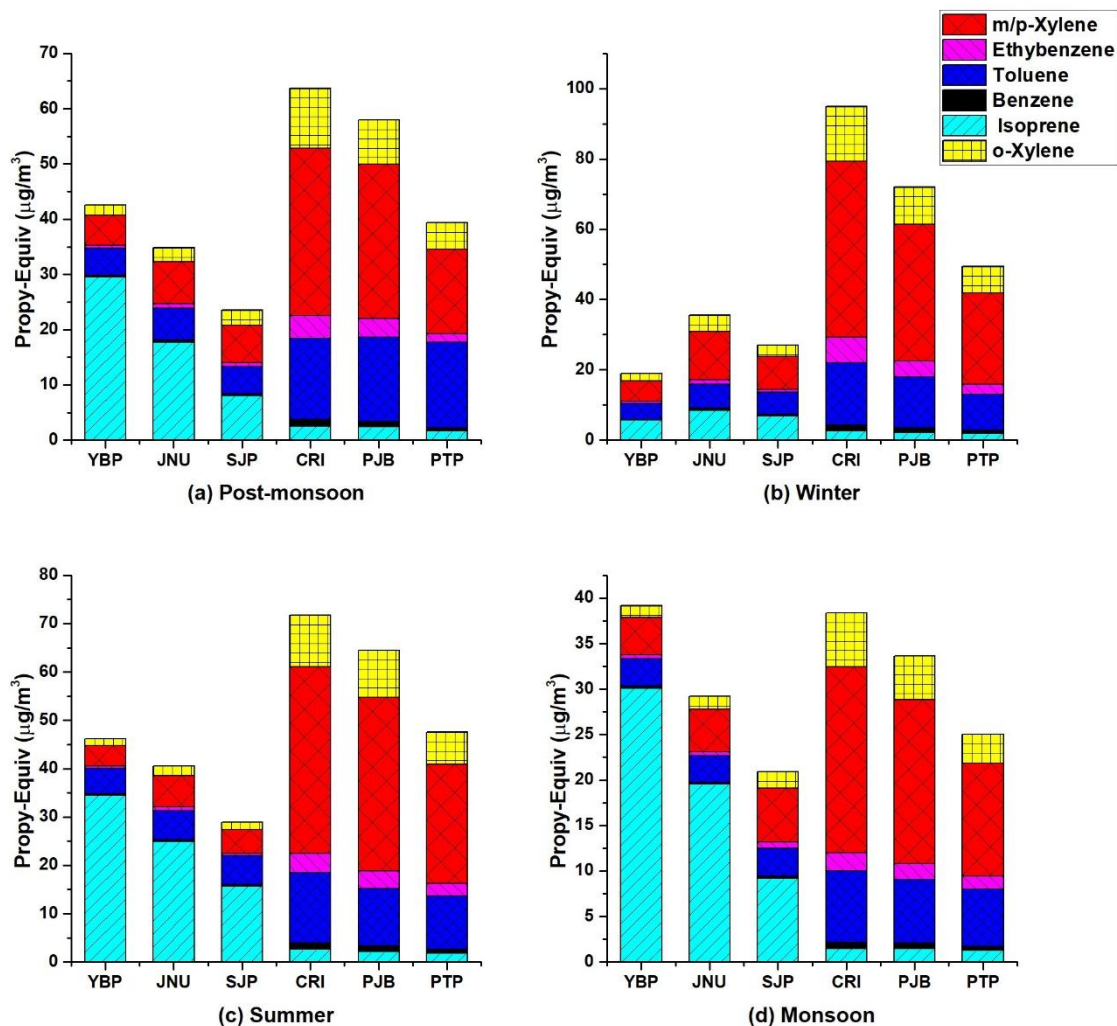
Figure 3.15: Prop-Equiv concentrations (μgm^{-3}) of each compound at each site in the different seasons.

After computing OFP values according to updated MIR coefficients values, more or less similar trends as those of Prop-Equiv concentrations were observed (Figure 3.16). The OFP of selected compounds at the traffic sites were detected more as compared to the OFP of same compounds at vegetative sites. At traffic sites, the order of mean ozone formation potential follows CRI> PJB> PTP in all the seasons. While at vegetative sites, this order varies with the seasons. During post-monsoon and summer, the ozone formation potential of compounds was the highest at JNU, followed by YBP and SJP. However, the trend was different during monsoon with maximum OFP at YBP site followed by JNU and SJP. In the winter season, the order was JNU >

SJP > YBP at the vegetative site. The primary reason for such variation in OFP concentrations in different seasons is the variation in ambient isoprene concentrations. As the MIR value of isoprene is very high (10.61) as compared to the other compounds, a small variation in the ambient concentration may result in higher variation in OFP. However, at traffic sites, the role of isoprene in contributing OFP was negligible as its ambient concentrations at these sites were very less.

Toluene is the key contributor species in OFP at all the sites because of its high MIR coefficient value followed by both xylene species. Among all the compounds, benzene contribution in ozone formation was very less because of its low MIR coefficient value (0.72) followed by ethylbenzene. At vegetative sites, the role of benzene and ethylbenzene in ozone formation was negligible. However, their role is significant in OFP at traffic sites.
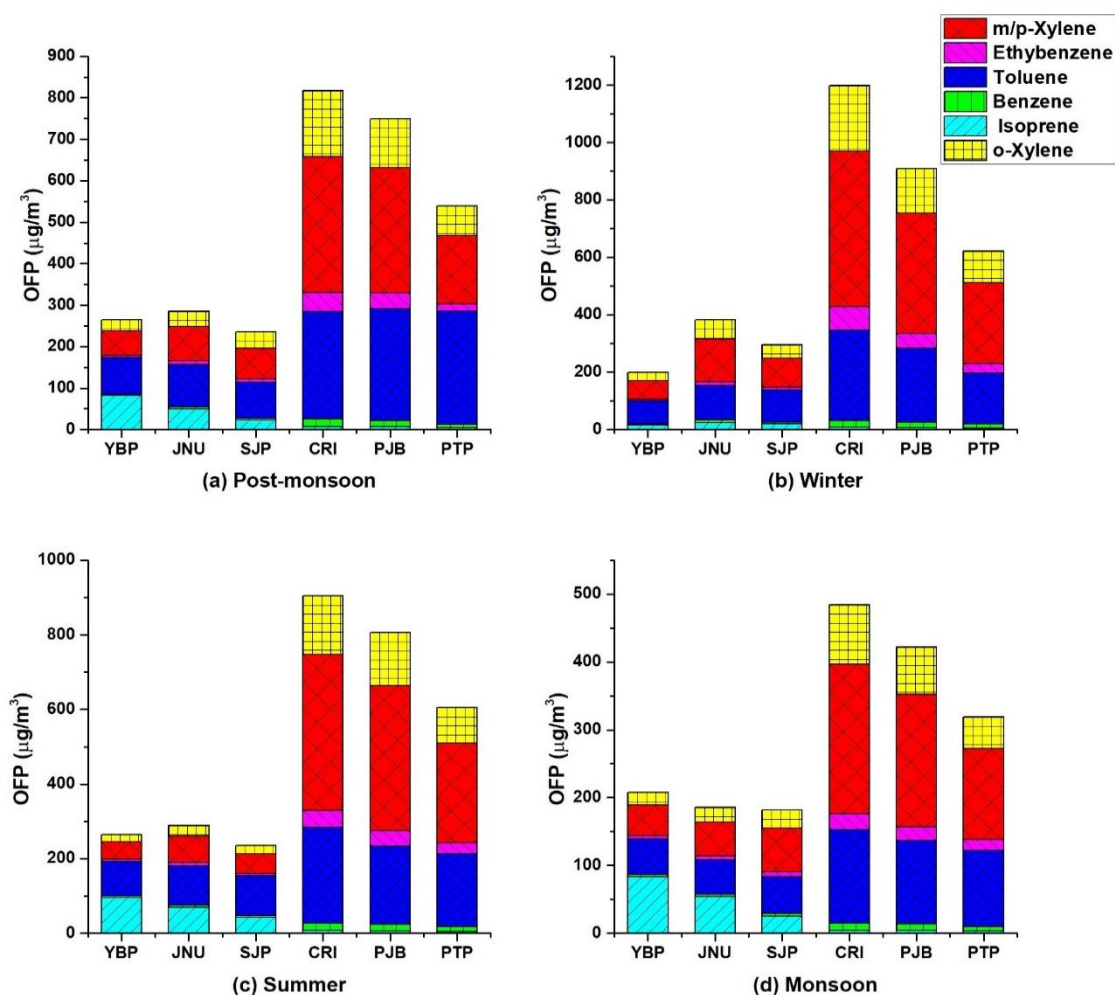
Figure 3.16: Ozone formation potential (OFP) (μgm^{-3}) of each compound at studied sites during four different seasons.

3.8   Health Risk Assessment

In this study, the role of selected VOCs has been studied to evaluate the potential health risks caused by them, as their concentrations in the ambient environment were found quite high. The estimation of cancer risk (CR) associated with benzene and ethylbenzene and non-carcinogenic risks (NCR) in the terms of Hazard Quotient (HQ) for all BTEX compounds were computed based on the United States Environmental Protection Agency (USEPA) guidelines. For the calculations, only the inhalation route of exposure was considered.
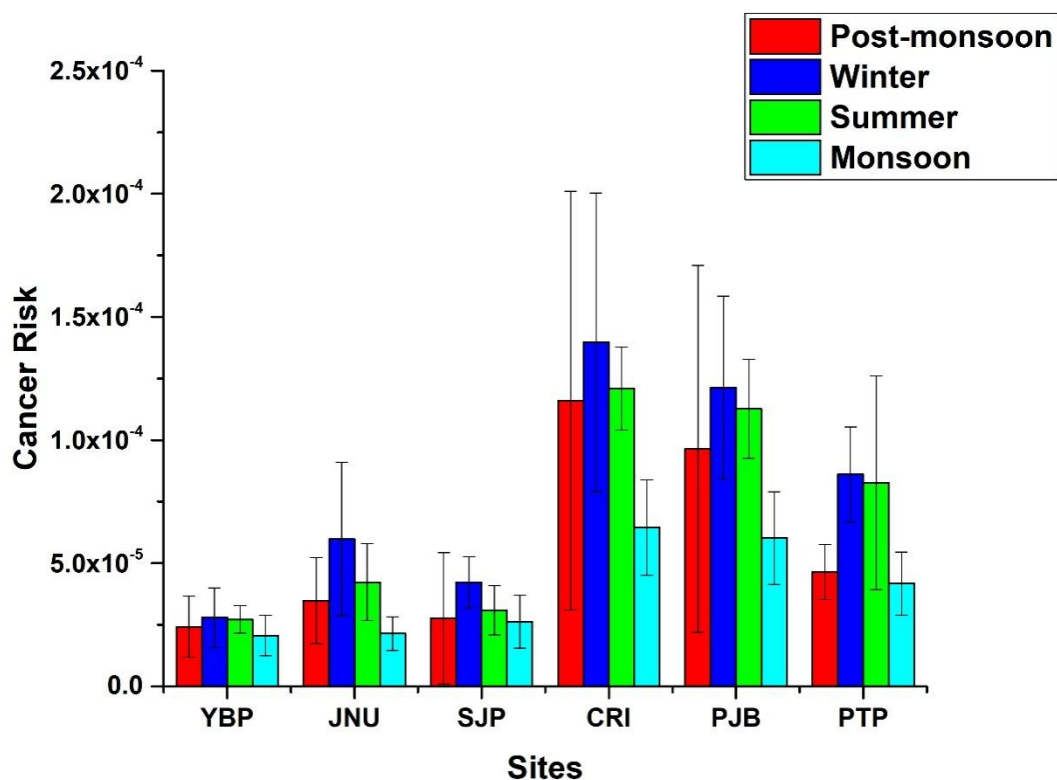
Figure 3.17: Cancer risk (CR) associated with benzene at different sites in different seasons.

The estimated cancer risk associated with benzene in all seasons at different sites is shown in Figure 3.17. It is seen that the average CR values for traffic sites were higher as compared to the vegetative sites in all seasons. Among the traffic sites, cancer risk was found to be high at CRI site followed by PJB and PTP in all seasons. Similarly, higher CR values were observed at JNU, followed by SJP and YBP among vegetative sites. The cancer risk associated with benzene was found to be high during winter season followed by summer, post-monsoon, and monsoon seasons at all sites. It is noteworthy to mention here that the CR values for benzene at all the sites exceeded the values recommended by the World Health Organization (WHO) and USEPA. According to WHO, the acceptable CR values should lie between 1×10^{-5} to 1×10^{-6} while USEPA suggests that the accepted levels should always be under 1×10^{-6} (Miri et al., 2016; Dehghani et al., 2018). Figure 3.18 depicts the average CR

associated with ethylbenzene at all the sites in all the seasons. It may be observed that the seasonal and site-wise trends observed for the cancer risk associated with ethylbenzene were similar to that of benzene. However, the CR values for ethylbenzene were very low as compared to benzene.
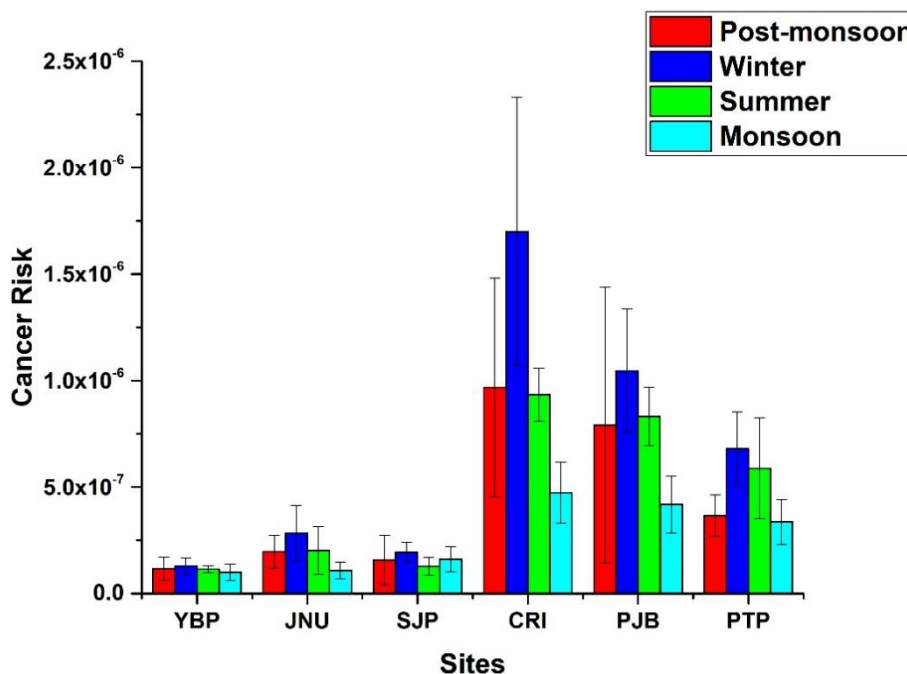
Figure 3.18: Cancer risk (CR) associated with ethylbenzene at different sites in different seasons.

The non-cancer risk in terms of HQ for all BTEX compounds in all the seasons are illustrated in Figure 3.19. The summation of HQ values at different compounds represents the Hazard Index (HI). An examination of the rectangular bars reveals that HQ values for all the compounds were higher at traffic sites as compared to vegetative sites. This is primarily due to high ambient concentrations of all the compounds at traffic sites. HQ and HI values were significantly high during winter followed by summer, post-monsoon and monsoon seasons at all the sites. Among the traffic sites, maximum average HI value was observed at CRI (0.111) followed by PJB (0.095) and PTP (0.063) in all the seasons. For vegetative sites, JNU showed higher HI levels

followed by SJP and YBP during post-monsoon, winter and summer seasons. However, during monsoon season, the maximum HI value was observed for SJP among the vegetative sites. Figure 3.19 also reveals that the HQ of toluene was negligible at vegetative and traffic sites. The maximum contributing species for HQ were benzene, followed by m/p-xylene and o-xylene.

Further, the calculated HI values in different seasons at each site are shown in Table 3.13. All the HI values were found to be lower than one at each site, which suggested that the non-carcinogenic risk associated with BTEX pollutants at these sites is not significant.
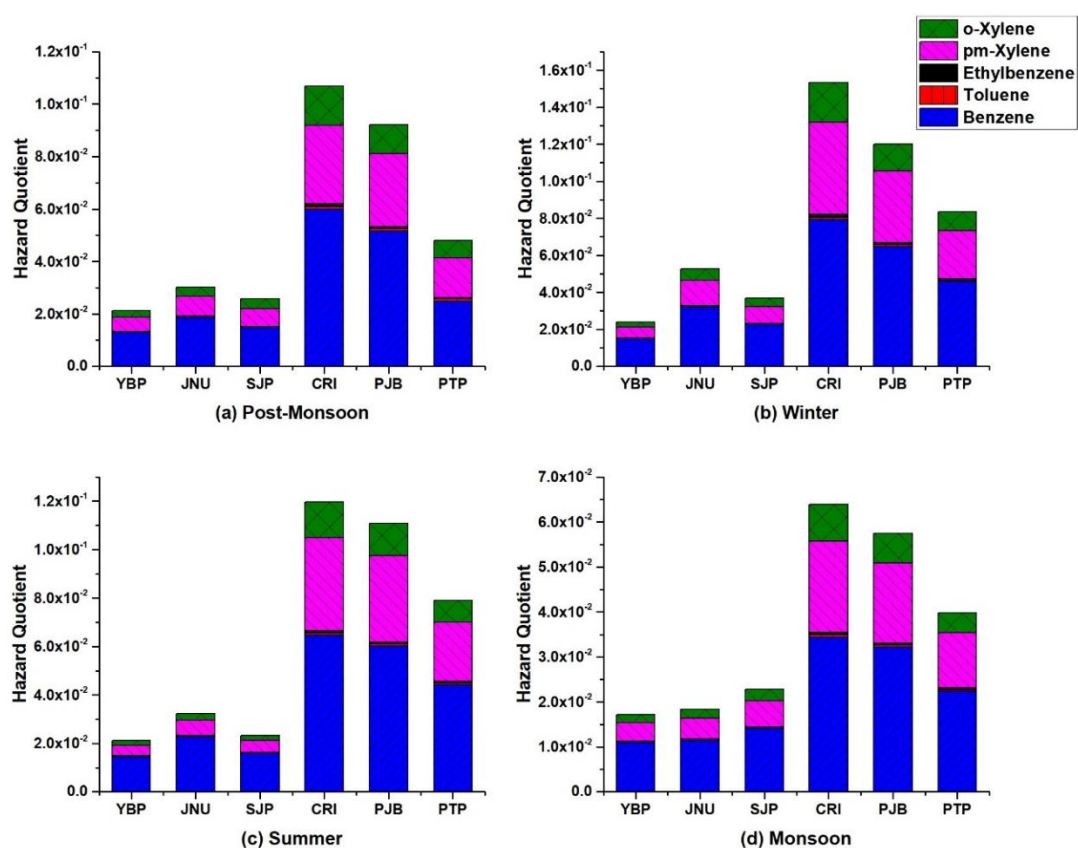
Figure 3.19: Non-cancer risk associated with different BTEX compounds in the form of Hazard Quotient (HQ). The length of each rectangular box represents the Hazard Index (HI).

Table 3.13: Hazard Index at each site during different seasons.

	Post-monsoon	Winter	Summer	Monsoon
YBP	0.0213	0.0241	0.0211	0.0172
JNU	0.0302	0.0527	0.0323	0.0184
SJP	0.0258	0.0368	0.0233	0.0228
CRI	0.1068	0.1532	0.1196	0.0639
PJB	0.0921	0.1200	0.1109	0.0575
PTP	0.0480	0.0835	0.0791	0.0398

CHAPTER 4: CONCLUSIONS

4   CONCLUSIONS

The current research work presents the seasonal and intraday variations of isoprene and BTEX compounds in the ambient atmosphere at vegetative (YBP, JNU, SJP) and traffic (CRI, PJB, PTP) sites of Delhi region. The study also estimates the anthropogenic and biogenic fractions of isoprene at these sites. In addition, the study also examines the association of isoprene with meteorological variables and gaseous pollutants. Ozone forming potential and health risk assessment for selected VOCs were also performed.

The results of the study show that isoprene levels in the ambient atmosphere are significantly higher at the vegetative sites as compared to the traffic sites. Among the vegetative sites, isoprene levels were found to be high at YBP site followed by JNU and SJP. At traffic sites, the isoprene levels were found to be in the order of CRI > PJB > PTP. The seasonal analysis revealed that the isoprene concentrations were maximum during summer followed by the monsoon, post-monsoon, and winter seasons at vegetative sites. In contrast, no significant seasonal variation in isoprene concentrations was observed at traffic sites as isoprene levels remained very low in all the seasons. Intraday variations revealed that isoprene levels at vegetative sites were notably higher in the afternoon as compared to morning and evening, whereas isoprene levels at traffic sites did not show significant intraday variation. Our results indicate that seasonal and intraday variations in solar radiation and temperature play an important role in influencing isoprene levels at vegetation sites.

The levels of BTEX compounds were found to be more at traffic sites as compared to vegetative sites. Toluene was found to be the most abundant BTEX species followed by m/p-xylene, benzene, o-xylene, and ethylbenzene. In general, the seasonal variations of BTEX compounds were in the order of winter > summer > post-

monsoon > monsoon. Higher levels of BTEX compounds were found during peak traffic hours in the morning and evening at all the sites.

With a view to gain insight into the emission of isoprene from vehicular sources, its concentration along with BTEX compounds was evaluated in the vehicular exhaust. Results of this analysis revealed that the isoprene was present only in the exhaust of petrol-driven vehicles while BTEX compounds were found in all types of vehicles (petrol, CNG, and diesel). It was also observed that the petrol-driven vehicles emit VOCs in higher concentration as compared to diesel and CNG operated vehicles.

For the estimation of anthropogenic and biogenic contribution to ambient isoprene, minimum isoprene/benzene ratio in ambient air was used. The analysis showed that ambient isoprene at vegetative sites was mainly because of biogenic contribution. However, the anthropogenic contribution was the dominant source at the traffic sites. More than 60% of anthropogenic isoprene was estimated at traffic sites while at vegetative sites it was merely 2.5%.

For source identification of selected VOCs, interspecies ratios and correlation analysis were carried out. The calculated T/B ratios for all sites ranged from1.5 to 4.3 suggesting the dominance of emissions from traffic sources in these sites. On the other hand, the lower values of mpX/B and oX/B ratios at vegetative sites indicated the existence of old air mass at vegetative sites. Strong and positive correlation among BTEX species at both types of sites suggested a similar origin of these compounds, i.e. traffic. A significant positive correlation between isoprene and BTEX compounds was found at traffic sites, which confirms the vehicles to be the main source of isoprene at these sites.

From the correlation analysis between isoprene and other meteorological variables, it was found that at vegetative sites, isoprene has significant positive correlations with

ozone, temperature, and solar radiation and significant negative correlation with NOx and RH. Contrasting to this, at traffic sites, isoprene was found to be negatively correlated with ozone, temperature, and solar radiation.

Results on Prop-Equiv showed that traffic sites have higher Prop-Equiv concentrations as compared to vegetative sites, with m/p-xylene contributing maximum at traffic sites and isoprene contributing maximum at vegetative sites. Similar results were observed for OFP with higher values at traffic sites. It was found that among the selected compounds, m/p-xylene and toluene are the major contributors to OFP at traffic sites while isoprene and toluene are the main contributors at vegetative sites.

The calculated cancer risk associated with benzene and ethylbenzene were found to be high at traffic sites as compared to vegetative sites. However, cancer risk associated with ethylbenzene were lower as compared to benzene. At all the sites, the benzene associated cancer risk was much more than the values recommended by USEPA and WHO. The non-cancer risk was estimated in terms of HQ and HI (summation of HQ values). All the HI values were found to be lower than one at each site indicating that the non-carcinogenic risk associated with BTEX pollutants was not significant.

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List of Publications

➢ **Prabhat Kashyap**, Amit Kumar, Krishan Kumar. BTEX Concentrations and Associated Health Risks at Urban Vegetative Sites in Delhi, India, *Environmental Claims Journal* (2019), pp. 1-17. DOI: 10.1080/10406026.2019.1640441

➢ **Prabhat Kashyap**, Amit Kumar, Ram Kumar, Krishan Kumar. Biogenic and anthropogenic isoprene emissions in the subtropical urban atmosphere of Delhi, *Atmospheric Pollution Research* (Accepted)

➢ Ram Pravesh Kumar, **Prabhat Kashyap**, Ritesh Kumar, Alok Kumar Pandey, Amit Kumar, Krishan Kumar. Cancer and non-cancer health risk assessment associated with exposure to non-methane hydrocarbons among roadside vendors in Delhi, India, *Human and Ecological Risk Assessment: An International Journal*(2019), pp. 1-15. DOI: 10.1080/10807039.2019.1570077

➢ Ram Pravesh Kumar, Alok Kumar Pandey, Ritesh Kumar, **Prabhat Kashyap**, Krishan Kumar. Assessment of Source Profile of Nonmethane Hydrocarbon in the Ambient Air of Metro City Delhi, India, Current World Environment 12(2017), p. 326. DOI: http://dx.doi.org/10.12944/CWE.12.2.16

List of Conferences

- Prabhat Kashyap, Krishan Kumar "*Study of Isoprene Emissions in Biogenic & Anthropogenic Environment in Urban Atmosphere of Delhi- The Capital City of India*" in 6th International Conference on Environment Pollution and Prevention (ICEPP 2018), The University of Queensland, Brisbane, Australia, December 6-8, 2018.

- Prabhat Kashyap, Krishan Kumar *"Study the Isoprene Emissions in the Urban Ambient Atmosphere of Delhi"* in International Conference on Atmospheric Chemistry and Physics in Highly Polluted Environments, jointly organized by The CIAAS, IIT Delhi and IIT Tirupati 22-24 March 2019, Delhi, India.

- Prabhat Kashyap, Krishan Kumar *"Isoprene emissions from biogenic and anthropogenic sources in the ambient air of Delhi"* in International conference on "Health and Air Pollution: Effects and Management (ICOHAP-EM-2018) organized by International Development Centre Foundation at India International Centre, Auditorium, Main Building, Max Mueller Marg, New Delhi -110003 on 7th & 8th September, 2018.