

## Study of Seasonal and Spatial Variability among Benzene, Toluene, and p-Xylene (BTp-X) in Ambient Air of Delhi, India

Garg, A.<sup>1</sup>, Gupta, N.C.<sup>1,\*</sup> and Tyagi, S.K.<sup>2</sup>

1. University School of Environment Management, Guru Gobind Singh Indraprastha University, Sector - 16 C, Dwarka, New Delhi – 110078, India
2. Central Pollution Control Board, Parivesh Bhawan, East Arjun Nagar, New Delhi - 110032, India

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**ABSTRACT:** This study was carried out to analyze the variations of Benzene, Toluene, and para- Xylene (BTp-X) present in the urban air of Delhi. These pollutants can enter into the human body through various pathways like inhalation, oral and dermal exposure posing adverse effects on human health. Keeping in view of the above facts, six different locations of Delhi were selected for the study during summer and winter seasons (2016-2017). The concentrations of BTp-X on online continuous monitoring system were analyzed by chromatographic separation in the gaseous phase followed by their detection using a Photo Ionization Detector (PID). The concentrations of BTp-X were found maximum at a high traffic intersection area as  $68.35 \pm 48.26 \mu\text{g}/\text{m}^3$  and  $86.84 \pm 32.55 \mu\text{g}/\text{m}^3$  in summer and winter seasons respectively and minimum at a residential area as  $4.34 \pm 2.48 \mu\text{g}/\text{m}^3$  and  $15.42 \pm 9.8 \mu\text{g}/\text{m}^3$  in summer and winter seasons respectively. The average BTp-X concentrations of summer and winter seasons were found as 9.88, 20.68, 28.52, 49.75, 64.04, and 77.59  $\mu\text{g}/\text{m}^3$  at residential, institutional, commercial, low traffic intersection, moderate traffic intersection and high traffic intersection areas respectively. Clearly, it has been found that the concentrations of these compounds were more on the traffic areas indicating that the vehicles are the major emission source. Hence, it may be concluded that the number of vehicles along with the high traffic congestion on the city streets and roads results in more accumulation of aromatic compounds and deteriorate the urban air quality.

**Keywords:** Air Pollution, VOCs, Vehicles, ANOVA, Urban Air.

### INTRODUCTION

Several harmful chemicals are introduced into the urban atmosphere due to rapid urbanization, industrialization, and consumerism during the last few years and resulted in the deterioration of urban air quality (Banerjee and Srivastava, 2011). Delhi, India's capital city and one of the largest city in the world, has experienced alarming levels of air pollution from

various sectors including transport, industry, residential, and other sources which results in the emission of toxic air pollutants in the urban atmosphere. Among various pollutants in the atmosphere, Volatile Organic Compounds (VOCs) have drawn much attention over the last two decades and are reported as toxic compounds because of their participation in various reactions in the troposphere to form secondary air pollutants including ground-level ozone and Peroxy Acyl

\*Corresponding Author Email: [address: ncgupta.ip@gmail.com](mailto:ncgupta.ip@gmail.com)

Nitrates (PAN) ( Atkinson, 2000; Truc and Oanh, 2007). Also among all of the VOCs, special attention has been given to Benzene, Toluene, and Xylene (BTX) and especially to Benzene because of its carcinogenic and mutagenic properties. BTX are listed as Hazardous Air Pollutants (HAPs) in the US Clean Air Act Amendments of 1990. Benzene is regarded as the most hazardous compound among BTX and has been classified as Group 1 and Class A human carcinogen by International Agency for Research Cancer (IARC) and United State Environmental Protection Agency (USEPA) respectively, while, toluene and xylene have been classified under Group 3 category by IARC (USEPA, 1998; ATSDR, 2000; ATSDR, 2005; ATSDR, 2007; WHO, 2010; IARC, 2002).

These compounds may enter into our body through various exposure pathways, including inhalation, oral and dermal which causes various short and long-term effects on human health. The short-term adverse effects of exposure to BTP-X include conjunctive irritation, nose and throat discomfort, sleeplessness, impaired short-term memory, inability to concentrate, tremors, headache, skin problems, nausea, fatigue, and dizziness. While the long-term exposure to benzene can lead to more adverse effects like genotoxicity, haematotoxicity, reproductive effects with various cancer, loss of coordination, anemia, leukemia, and damage to the liver, kidney and central nervous system (Kim et al., 2001; Navasumrit et al., 2005; Kerbachi et al., 2006; Keretese et al., 2008; Badjagbo et al., 2008). Dewangan et al. (2013) observed that benzene has the highest emission factor among BTP-X. Exposure to BTP-X is caused mainly by the emissions of the motor-vehicles and gasoline exhaust systems have been found to be the major cause of BTP-X emission in Delhi (Hoque et al., 2008; Gaur et al.,

2016). Although there are no proper norms and standards for VOCs, Central Pollution Control Board (CPCB) in India has laid down the National Ambient Air Quality Standards (NAAQS) for benzene ( $5 \mu\text{g}/\text{m}^3$ ) on annual average basis (CPCB, 2009). BTP-X monitoring should be considered as the essential part of an air quality management program (AQMP) because of their toxic health effects and their key role in atmospheric chemistry. Therefore, this study has been carried out in order to characterize the seasonal and spatial variations of BTP-X at different locations in Delhi.

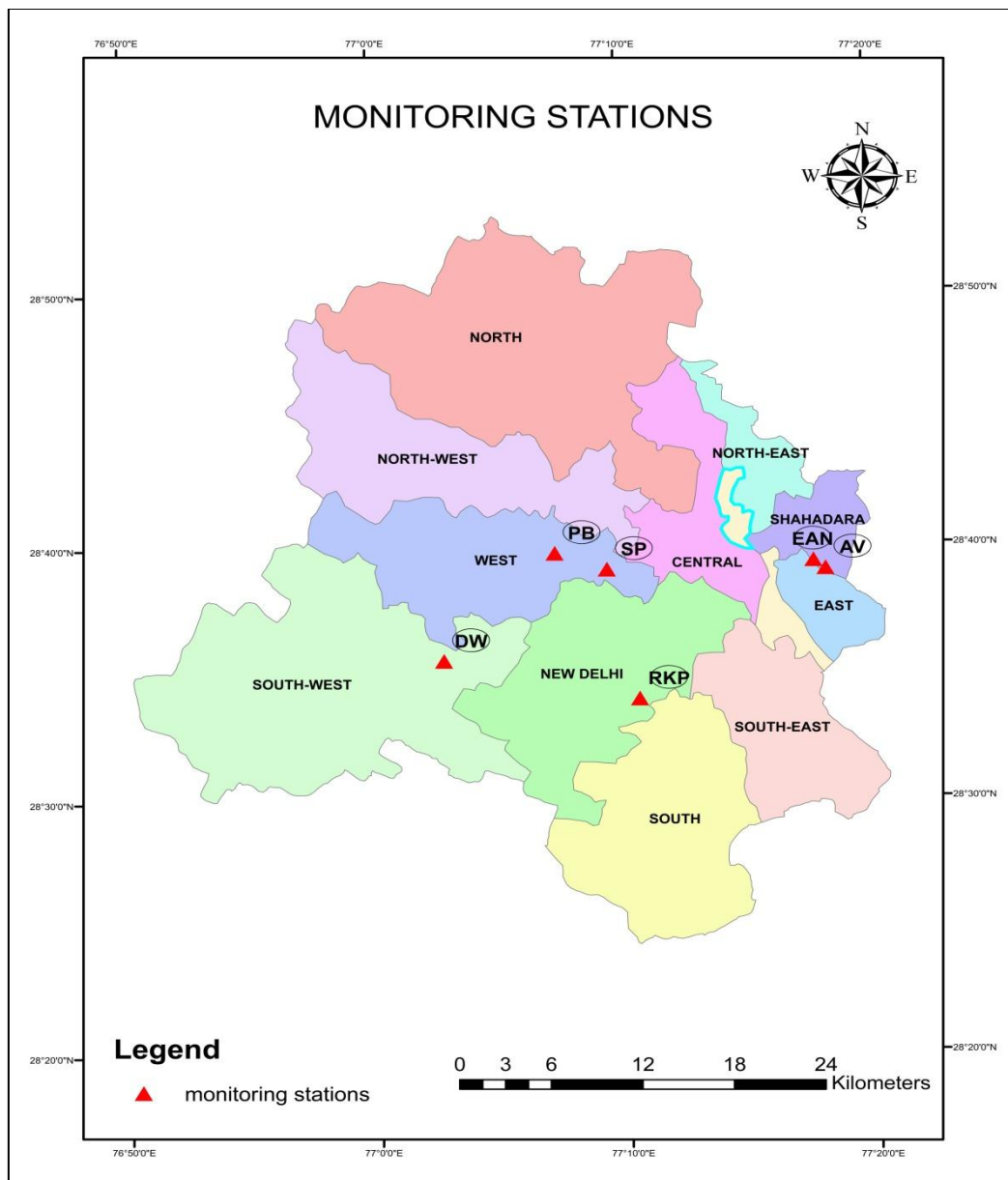
#### MATERIALS AND METHODS

Delhi, the capital city of India has been selected for the study. It is located at  $28.7041^\circ \text{N}$  to  $77.1025^\circ \text{E}$  and spread over an area of  $1483 \text{ km}^2$ . As Delhi is situated at an altitude of nearly 216 m above sea level, it has a sub-tropical climate. The city is consisting of well-defined four seasons, i.e. summer, monsoon, autumn, and winter. The summer season starts from March and ends with June, experienced windy conditions with average temperature as  $32^\circ\text{C}$  and maximum temperature reaches up to  $47^\circ\text{C}$ , whereas winter season starts from November and ends with February, characterized by calm conditions with average temperature as  $12^\circ\text{C}$  and minimum temperature reaches up to  $1\text{-}2^\circ\text{C}$ . Delhi receives most of its rainfall (annual average 714 mm) during July to September from the southwesterly monsoonal winds and some rain during winters from northwesterly cold winds. In present work, six monitoring locations were selected in Delhi and represented in Figure 1. These locations were selected according to the availability of the monitoring stations of CPCB in Delhi region and also on the basis of the vehicular and traffic density of the area. The symbolic representations of these locations according to the vehicular density have been given in Table 1.

**Table 1. Relative Traffic Density of selected locations in Delhi**

S.No.	Location	Symbol	Type of Area	Relative Traffic Density
1	Punjabi Bagh	PB	Residential	o
2	Dwarka	DW	Institutional	+
3	Shadipur	SP	Commercial	++
4	R.K. Puram	RKP	Low Traffic Intersection	+++
5	East Arjun Nagar	EAN	Moderate Traffic Intersection	++++
6	Anand Vihar	AV	High Traffic Intersection	+++++

(+++++ = high traffic density, ++++ = moderate traffic density, +++ = low traffic density, ++ = very low traffic density, + = more low traffic density, o = represents no traffic density)



**Fig. 1. Map of Delhi showing sampling locations**

These locations exhibit significant spatial variations. Location 1, Punjabi Bagh (PB) is a residential area situated in West Delhi. The area is mainly consists of private houses on the bungalow pattern and are so called "Kothis". The area is clean and well managed in infrastructure. Location 2, Shadipur (SH) is a commercial area situated in West Delhi. The area is serviced by Delhi metro railway station. The nearby areas are Mayapuri and Naraina, which are industrial in activities. Location 3, Dwarka (DW) is an institutional area situated in South West Delhi. It is comparatively newly settled area in Delhi. The area is well designed with green infrastructure. Location 4, Rama Krishna Puram (RKP) is a Central Government Employees residential colony situated in South-West Delhi. The area has many educational institutions and schools. The area is characterized by wide colony roads, sprinkling of parks and excellent greenery. Location 5, East Arjun Nagar (EAN) is a moderate traffic area situated in North East Delhi. It is a mixed area with residential and commercial activities. The monitoring location is near to the CPCB. Location 6, Anand Vihar (AV) is a major connectivity hub of East Delhi. It is highly traffic dense area and is connected to metro station, railway terminal and also one of the largest Inter State Bus Terminal (ISBT) of India.

In order to identify the concentrations of Benzene, Toluene, and p-Xylene, an online continuous monitoring system, also known as Continuous Ambient Air Quality Monitoring System (CAAQMS) have been used (CPCB, 2003). The CPCB has laid down the national guidelines for the monitoring and chemical analysis of BTX in ambient air through CAAQMS by using Gas Chromatography (GC) (CPCB, 2012). The concentrations of BTX on online continuous monitoring system were analyzed by chromatographic separation in the gaseous phase followed by their detection using a Photo Ionization Detector (PID). The

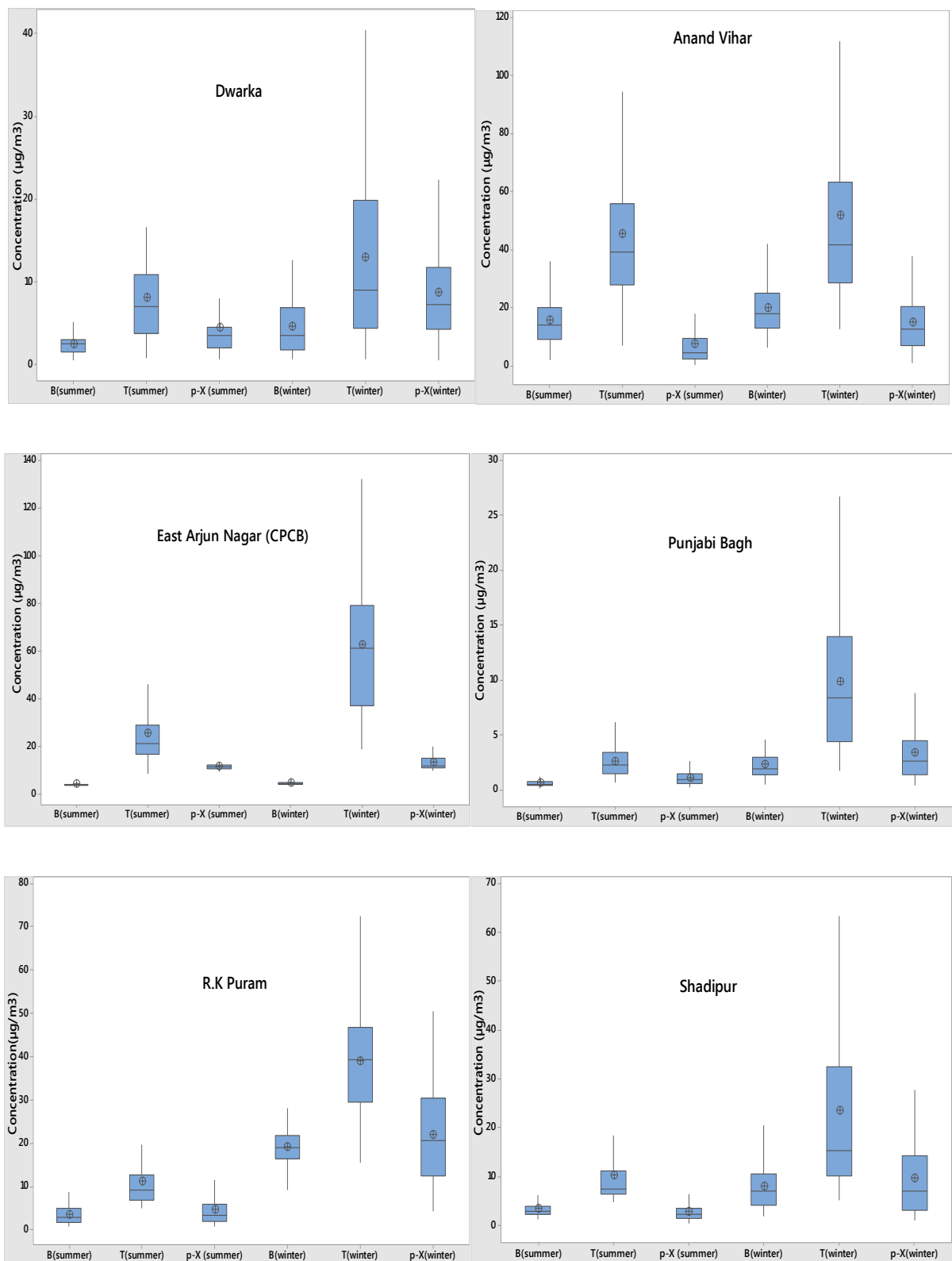
separation method of VOCs at all location is based on GC-PID principle except at EAN location where the separation was based on the Differential Optical Absorption Spectroscopy (DOAS) principle. For the comparative analysis of summer and winter seasons, the data have been analyzed during March-June, 2016 (summer season) and November-February, 2017 (winter season).

For the statistical analysis, the Microsoft Excel and MINITAB software were used to analyze the data. Descriptive statistics have been used to find out the range of concentration, mean concentration, standard deviation and, symmetry among the data. ANOVA hypothesis has been applied to elucidate significant spatial and seasonal variations. The possible sources of BTX emission have been illustrated through Spearman's correlation matrix.

## RESULTS AND DISCUSSION

The minimum, maximum and mean concentrations of Benzene, Toluene, p-Xylene and total BTP-X along with their standard deviation and skewness at different sampling locations in both summer and winter seasons are given in Table 2. The spatial and seasonal variations are represented as box plots in Figure 2. In a box plot, 25<sup>th</sup> percentile and 75<sup>th</sup> percentile have been represented by the lower and the upper boundary respectively. The endpoint of lines above and below the box indicate the maximum and minimum concentrations while the '+' sign represents the mean concentration.

In descriptive statistics, skewness is a measure of the asymmetry of the probability distribution of a real-valued random variable about its mean position. The value of skewness for a symmetrically distributed data, can be positive or negative and generally ranges from (-1.96 to +1.96). Table 2, has shown that BTP-X data at different locations is positively skewed mostly and lies under a symmetrical distribution range.



**Fig. 2. Box plots of B,T and p-X concentrations in summer and winter seasons at six air quality monitoring stations**

**Table 2. Descriptive statistics of BTP-X at various locations**

Locations	Parameters	B		T		p-X		BTP-X	
		Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
Dwarka	Mean	2.53	4.55	8.05	13.01	4.48	8.75	15.06	26.31
	S.D	1.21	3.22	4.84	11.08	7.76	6.03	13.81	20.33
	Min	0.5	0.64	0.74	0.69	0.63	0.56	1.87	1.89
	Max	6.66	12.69	16.62	62.84	75.76	27.97	99.04	103.5
	Skewness	1.22	0.84	0.62	1.44	8.55	1.22	-	-
	N	102	106	102	106	95	105	-	-
AnandVihar	Mean	15.61	20.04	45.41	51.88	7.33	14.92	68.35	86.84
	S.D	9.03	9.72	31.05	12.67	8.18	10.16	48.26	32.55
	Min	2.11	6.15	6.88	192.97	0.34	0.88	9.33	200
	Max	49.95	58.73	244.95	1.73	57.12	56.18	352.02	116.64
	Skewness	1.57	1.25	3.45	3.53	3.2	1.15	-	-
	N	93	115	93	35.23	93	115	-	-
East Arjun Nagar	Mean	4.16	4.55	25.41	62.67	11.68	13.3	41.25	80.52
	S.D	0.83	0.7	16.07	29.59	1.92	3.32	18.82	33.61
	Min	3.47	3.61	8.73	18.72	8.21	9.68	20.41	32.01
	Max	10.35	7.36	151.71	145.91	26.71	29.55	188.77	182.82
	Skewness	5.3	1.22	5.17	0.75	4.97	1.83	-	-
	N	100	115	100	115	100	115	-	-
Punjabi Bagh	Mean	0.6277	2.28	2.61	9.8	1.1	3.34	4.34	15.42
	S.D	0.39	1.29	1.45	6.03	0.64	2.48	2.48	9.8
	Min	0.11	0.54	0.67	1.77	0.22	0.43	1	2.74
	Max	2.35	7.25	7.89	26.72	3.03	11.77	13.27	45.74
	Skewness	1.87	1.22	1.43	0.67	1.23	1.13	-	-
	N	109	116	109	116	109	116	-	-
R.K Puram	Mean	3.59	19.25	11.19	38.95	4.64	21.89	19.42	80.09
	S.D	2.2	4.15	5.85	11.53	3.83	10.49	11.88	26.17
	Min	0.93	9.2	5.02	15.58	0.81	4.44	6.76	29.22
	Max	10.3	31.6	36.1	72.4	18.9	50.44	65.3	154.44
	Skewness	0.86	0.3	1.54	0.39	1.53	0.3	-	-
	N	112	116	112	116	112	116	-	-
Shadipur	Mean	3.37	7.94	10.08	23.51	2.65	9.49	16.1	40.94
	S.D	1.97	4.71	7.49	18.45	1.91	7.79	11.37	30.95
	Min	1.1	1.75	4.65	5.05	0.29	0.87	6.04	7.67
	Max	12.71	20.45	54.19	95.76	11.93	33.06	78.83	149.27
	Skewness	2.53	0.92	3.7	1.46	2.01	1.02	-	-
	N	75	117	75	117	75	117	-	-
Average of 6 locations	Mean	4.98	9.77	17.13	33.30	5.31	11.95	27.42	55.02
	S.D	2.61	3.97	11.13	14.89	4.04	6.71	17.77	25.57
	Min	0.11	0.54	0.67	0.69	0.22	0.43	1.00	1.89
	Max	49.95	58.73	244.95	145.91	75.76	56.18	352.02	182.82

(Mean= Mean concentration in  $\mu\text{g}/\text{m}^3$ , S.D. = Standard Deviation in  $\mu\text{g}/\text{m}^3$ , Min= Minimum concentration in  $\mu\text{g}/\text{m}^3$ , Max= Maximum Concentration in  $\mu\text{g}/\text{m}^3$  and N= Number of sampling days)

The mean concentration of Benzene, Toluene, p-Xylene and total BTP-X at all six sampling locations of Delhi were  $4.98 \pm 2.61$ ,  $17.13 \pm 11.13$ ,  $5.31 \pm 4.04$  and  $27.42 \pm 17.77 \mu\text{g}/\text{m}^3$  respectively for the summer season and  $9.77 \pm 3.97$ ,  $33.30 \pm 14.89$ ,  $11.95 \pm 6.71$  and  $55.02 \pm 25.57 \mu\text{g}/\text{m}^3$  respectively for the winter season. The maximum average concentration of total BTP-X was found at AV ( $68.35 \pm 48.26 \mu\text{g}/\text{m}^3$  in summer and  $86.84 \pm 32.55 \mu\text{g}/\text{m}^3$  in winter), while minimum at PB ( $4.34 \pm 2.48$

$\mu\text{g}/\text{m}^3$  in summer and  $15.42 \pm 9.8 \mu\text{g}/\text{m}^3$  in winter). High levels of total BTP-X at AV might be attributed to very high traffic density of automobile and slow movement of the traffic.

The total BTP-X concentration at all six study locations has been represented in increasing order: PB (residential area) < DW (institutional area) < SP (commercial area) < RKP (low traffic intersection area) < EAN (moderate traffic intersection area) < AV (high traffic intersection area).

Average concentration of total BTP-X has been estimated as 9.88, 20.68, 28.52, 49.75, 64.04, and 77.59  $\mu\text{g}/\text{m}^3$  at residential, institutional, commercial, low traffic intersection, moderate traffic intersection, and high traffic intersection area respectively. AV, the high traffic intersection area (31%) had the highest BTP-X contribution followed by EAN, moderate traffic intersection area (26%), RKP, low traffic intersection area (20%), SP, commercial area (11%), DW, institutional area (8%) and PB, residential area (4%) (Figure 3).

In this study, it has been observed that Toluene was found as the most abundant species among BTP-X. Toluene concentration varies from 50–66 % of the total BTP-X concentration at different locations. The average concentration of Toluene ( $20.04 \pm 9.72 \mu\text{g}/\text{m}^3$  in summer and  $45.41 \pm 31.05 \mu\text{g}/\text{m}^3$  in winter) was recorded maximum at location AV. A study of Delhi by Gaur et al. (2016) also reported that toluene has the highest concentration among BTP-X.

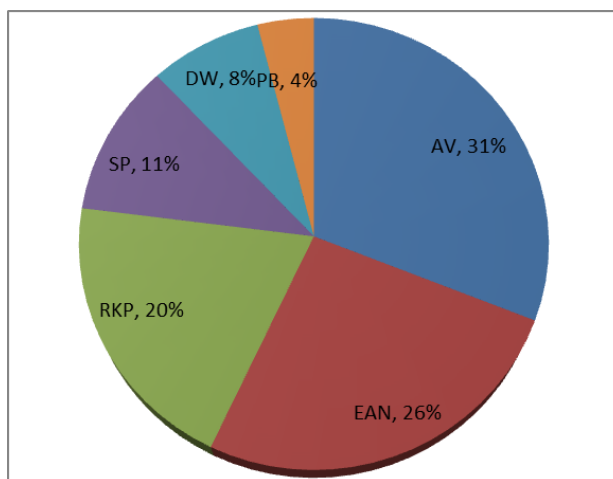


Fig. 3. Percentage contribution of total BTP-X at different locations

In summer season, the concentration of benzene was found under NAAQS standards at all locations except AV ( $15.61 \mu\text{g}/\text{m}^3$ ) where the concentrations were found three times higher than the annual average standard value of benzene prescribed by CPCB (i.e.  $5 \mu\text{g}/\text{m}^3$ ), while in winter season, AV ( $20.04 \mu\text{g}/\text{m}^3$ ), RKP ( $19.25 \mu\text{g}/\text{m}^3$ ) and SP ( $7.94 \mu\text{g}/\text{m}^3$ ) have exceeded NAAQS standards limit. This significant increase in benzene concentration indicates that dispersion of benzene is not that much easy in the urban atmosphere of Delhi and therefore, requires serious thought for reduction. Singh et al. (2016) have also observed high levels of VOCs in Asian countries, which is a major problem in a megacity like Delhi. The

reason for such high concentration was an increase in vehicular population in Delhi from 5 million vehicles in 2007 to 7 million in 2013 and 8.8 million in March 2015 (DSH, 2015).

The seasonal and spatial variations of BTP-X were analyzed through a non-parametric two-way ANOVA test. Table 3 shows the results obtained by this test for different parameters. The test was applied at 0.05 level of significance ( $\alpha$ ). Results obtained in Table 3 show p-value due to variation in seasons to be 0.017 which is less than  $\alpha$ -value and also, F-value computed for seasons is 12.28 which are greater than the F-critical value (6.61) for two seasons. Hence, we can interpret that the two seasons exhibit significant seasonal

variations and these variations could be attributed to the meteorology of Delhi, as in summer temperature rises to 48°C and in winter it decreases to 3°C. In winter, temperature inversion, low mixing height, and more stable atmospheric condition slow down the dilution process of these pollutants and results in more accumulation of these compounds. Whereas, in summer, atmospheric conditions are stable, which increases dilution and dispersion process and results in the reduction of the pollutant concentration (Rad et al., 2014; Hoque et al., 2008).

Similarly, the p-value obtained due to variation in different monitoring locations was 0.024 and also, F-value computed for different monitoring locations is 7.20 which is greater than the F-critical value (5.05). Hence, by applying this test, we can easily conclude that there is a significant variation in BTP-X level among different monitoring locations also.

The Correlation analysis has been done to explain the possible sources for BTP-X emissions (Wang et al., 2002). A strong value of correlation among the species indicated that they might be mainly originated from the same source. As shown in Table 4, the moderate-strong positive correlation was observed among Benzene, Toluene, p-Xylene and BTP-X. A moderate correlation between Benzene and Toluene

(0.69) and a strong correlation between Toluene and p-Xylene (0.8) may indicate their emission through the common sources, possibly vehicular emissions. A high correlation value of Benzene, Toluene, and p-Xylene with BTP-X was observed. A strong correlation between Toluene and BTP-X (0.98) during summer season indicates that toluene has predominately high concentration than other VOCs. A moderate correlation between Benzene and p-Xylene (0.63) indicated that p-Xylene has sources other than vehicular emission.

Toluene/Benzene (T/B) ratio helps in the estimation of the dominant source among both. T/B ratio in this study has ranged from 2 to 4.3 at all sampling locations except EAN, where it ranges from 6.1 to 13.8. The reason behind such a higher T/B ratio at EAN, the presence of nearby industries results in the higher emission of toluene. Also, an average value of T/B ratio is 4. Hence, we may conclude that toluene is the dominating source of BTP-X emission and its concentration is generally two to four times higher than that of benzene. Spatial and Seasonal variations among T/B ratio have been represented in Figure 4.

The levels of BTP-X measured at all the locations were quite similar to those reported by various studies in other areas of India (Table 5).

**Table 3. Two way ANOVA test for BTP-X based on locations and seasons**

Source of Variation	Sum of square	Degree of freedom	Mean squares	F-value	p-value	F- critical value
Locations	6696.14	5	1339.23	7.19	0.024	5.05
Seasons	2285.23	1	2285.23	12.28	0.017	6.61
Error	930.36	5	186.07			
Total	9911.73	11				

**Table 4. Spearman's correlation coefficients between B, T, p-X and BTP-X**

Pollutants	Benzene	Toluene	p-Xylene	Total BTP-X
Benzene	1			
Toluene	0.69	1		
p-Xylene	0.63	0.80	1	
Total BTP-X	0.81	0.98	0.86	1



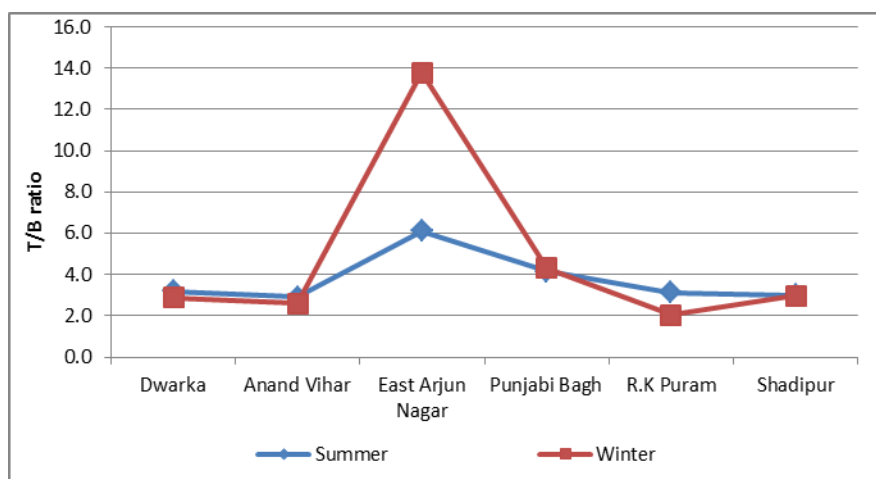


Fig. 4. Spatial and Seasonal variation in T/B ratio

Table 5. Comparison of our study with other studies

Study	Location	Place	Pollutants	Levels ( $\mu\text{g}/\text{m}^3$ )
Baimatova et al., 2016	Almaty, Kazakhstan	Ambient air	BTEX(o-xylene)	53, 57, 11, 14
Rad et al., 2014	Ahwaz, Iran	Ambient air	BTEX	1.78, 5.19, 0.51, 1.13
Woo et al., 2015	Yeosu, Korea	Industrial area	BTEX	1.52, 0.73, 0.22, 0.52
Hazrati et al., 2016	Ardabil, Iran	Ambient air	BTEX	8.65, 40.56, 4.92, 7.44
Chen et al., 2011	Changsha, China	Buses	BTEX	68.7, 179.7, 62.5, 151.8
Mukherjee et al., 2003	Kolkata	Buses	BTX(o,p xylene)	527.3, 472.8, 1265.5, 402.8
Majumdar et al., 2008	Kolkata	Petrol pumps	BTEX(m,p,o xylene)	137.5, 643.6, 118.0, 209.7, 68.2
Majumdar et al., 2011	Kolkata	Ambient air	BTEX(m,p,o-xylene)	29.2, 45.4, 13.1, 32.9, 11.9
Srivastava et al., 2006	Mumbai	Ambient air	Total VOCs	630 -728
Singla et al., 2012	Agra	Road-side Petrol pump	BTX(o,m,p) BTX(o,m,p)	8.55, 4.65, 1.45, 3.15 23.2, 7, 2.05, 6.3
Singh et al., 2013	Nagpur	Petroleum refinery	Total BTEX	3.69-56.67
Hoque et al., 2008	Delhi	Ambient Air	BTEX (o,m,p) JNU CP Okhla AIIMS	48 ,85, 7 ,30, 15 97, 180, 21, 83, 40 89, 204, 16, 61, 41 110, 191, 24, 90, 41
Srivastava, 2005	Delhi	Ambient air	BTEX	300, 34, 34, 27
Singh et al., 2012	Delhi	Roadside	BTX	9.38, 29.08, 8.97
Gaur et al., 2016	Delhi	Roadside	BTEX	60.22, 162.68, 49.42, 25.25
This study	Delhi	Ambient air	Total BTp-X	9.88-77.59

**CONCLUSIONS**

The study (March 2016 to February 2017) in urban ambient air of Delhi at six

different locations has mean concentrations for Benzene, Toluene, p-Xylene and total BTp-X as 4.98, 17.13, 5.31 and 27.42

$\mu\text{g}/\text{m}^3$  for the summer season and 9.77, 33.30, 11.95 and 55.02  $\mu\text{g}/\text{m}^3$  for the winter season respectively. The total BTP-X concentrations showed significant spatial and seasonal variations, as analyzed by a two way ANOVA hypothesis. The concentration of BTP-X was found almost twice during winter season comparing to the summer season. The higher concentrations during the winter season was recorded due to the poor meteorological conditions of Delhi like inversion of temperature, low mixing height, and more stable atmospheric conditions. These conditions slow down the dilution process of these pollutants and results in more accumulation of these compounds in the urban air. Such higher concentrations of these compounds during the winter season may have the high impact on the health of Delhi's population. The number of vehicles and also the traffic congestion on roads are the significant contributors for the emissions of VOCs. As, in this study, the high traffic intersection area (31%) has the highest BTP-X contribution followed by moderate traffic intersection area (26%), low traffic intersection area (20%), commercial area (11%), institutional area (8%) and residential area (4%) suggested that vehicular pattern type and infrastructure of an area plays a significant role in the distribution of such pollutants. A high correlation between Benzene, Toluene and p-Xylene and their daily measurements at different locations again showed that the heavy traffic congestion along with more vehicular emissions on the roads is the main source of aromatic compounds. In this study, Toluene was found as the most abundant species varying from 50–66 % of the total BTP-X at different locations. At many locations, the levels of benzene were found higher than the NAAQS standards prescribed by CPCB. This indicates that in the urban atmosphere BTP-X does not dissipate easily in the environment and

therefore, needs serious thought for reduction. Improved management technologies like- improved fuel quality, better urban traffic management strategies, policy planning, strategies such as odd-even, and an increase in green spaces in the urban area may result in the reduction of such pollutants.

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