



BTEX in Ambient Air of India: a Scoping Review of their Concentrations, Sources, and impact

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Abstract Toxic gaseous organic air pollutants such as benzene, toluene, ethylbenzene, and xylene isomers (m, p, and o-x) (BTEX) are considered hazardous due to its adverse impacts on human health and on climate change. This review identifies the major research questions addressed so far and the research gap in research articles, published between 2001 and 2022, focusing on the ambient BTEX concentrations in different locations in India along with its sources, ozone formation potential (OFP), and associated health risks. The ambient levels of BTEX were also compared with those of other Asian countries. A comparison of ambient BTEX levels with different microenvironments in India is also presented. BTEX concentrations were found in the range of 30.95 to 317.18 $\mu\text{g m}^{-3}$ and multi-fold higher in urban environments than those measured in the rural air. In most

reported studies, the order of occurrence of BTEX compounds was toluene > benzene > xylene isomers > ethylbenzene and winter had higher concentrations than in other seasons, including summer. As far as BTEX levels in classified areas of urban environments are concerned, traffic locations have shown the highest BTEX concentrations, followed by residential, commercial, and industrial locations. OFP indicated that xylene isomers and toluene contributed to ozone formation. The major gaps in reported studies on BTEX measurement are (1) source apportionment; (2) impact on lower tropospheric chemistry, human health, and climate change; and (3) removal techniques from air.

Keywords BTEX · Ozone formation potential (OFP) · Volatile organic compound (VOCs)

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1 Introduction

Volatile organic compounds (VOCs) are classified by the World Health Organization (WHO) as organic compounds with boiling points of 50–260°C and saturated vapor pressure > 133.32 Pascal at 20°C (WHO, 2000). Major aromatic VOCs such as benzene (B), toluene (T), ethylbenzene (EB), and xylene isomers (m-, o-, and p-xylene) are jointly known as BTEX and form a vital group found in urban regions (Han & Naehar, 2006; Lee et al., 2002). VOCs are hundreds of species that are directly emitted into the atmosphere from biogenic and anthropogenic sources (Guo et al., 2012).

Ambient VOCs influence the lower tropospheric chemistry by secondary organic aerosol formation and its ozone formation potential with NO_x. In the presence of high NO_x concentrations in the environment, the OH-initiated mechanism is preferred for SOA formation, in which radical forms of RO₂ (peroxy) and RO (oxy) react with nitric oxide (NO) to form nitrogen dioxide (NO₂) and in the presence of sunlight; these NO₂ molecules react with VOCs to form ozone, a known secondary air pollutant. Due to their chemical reactivity and ability to create tropospheric ozone and other photochemical oxidants, VOCs influence climate change (Caselli et al., 2010; Duan et al., 2008; Hoque et al., 2008; Lin et al., 2016; Majumdar et al., 2011; Zhou et al., 2011).

Many VOCs have been reported to affect human health upon chronic exposure, even at low levels. Among BTEX, benzene has been categorized as a human carcinogen type A, whereas ethylbenzene has been documented as a possible human carcinogen, all of which pose non-carcinogenic health hazards. The short- and long-term health effects of BTEX in various human target organs such as the kidney, liver, central nervous system, respiratory system, and reproductive system have also been systematically investigated and documented (Chen et al., 2018; IARC, 2012; McKenzie et al., 2012; Lupo et al., 2011; Kim et al., 2009; Buczynska et al., 2009; Topp et al., 2004).

Various identified significant anthropogenic sources of BTEX include petrochemical industries, paint factories, vehicular emissions, gasoline evaporation, combustion of fuels, solvents, and solid waste decomposition (Cai et al., 2010; Kansal, 2009; Rad et al., 2014; Srivastava et al., 2004). Incomplete combustion of biomass and biofuel is one of the major

sources of BTEX (Sahu & Saxena, 2015; Sahu & Lal, 2006). Globally, VOC emissions from biogenic as well as anthropogenic sources are estimated to be 1200 to 1600 TgC year⁻¹ (Guenther, 1995). In India, the first estimate of total annual VOC emissions from anthropogenic sources was 21 million metric tons (mt) (Varshney & Padhy, 1998), whereas Sharma et al. (2015) estimated anthropogenic NMVOCs in 2010 at 9.81 Tg. According to recent studies, biomass and municipal solid waste (MSW) combustion emitted an estimated 13 (5–47) Tg of NMVOCs in India in 2011 (Stewart et al., 2021a).

Densely populated Southeast Asia has become a global hotspot of air pollution, especially during the winter months of the past few years. This has become not only a local or regional but also a global concern owing to its long-range transport and climate change implications apart from being a threat to millions of inhabitants. As one of the major stakeholders in this region, India is investing hard in mitigating air pollution to achieve clean air through national-level efforts such as the National Clean Air Program. It is essential to generate understanding through research and studies regarding sources and the impact of air pollutants to provide policymakers with adequate rationale for formulating strategies for air pollution mitigation. The sources and contribution of VOCs and their contribution to ozone formation are currently the subject of grave concern and scientific research worldwide (Seco et al., 2013; Tan et al., 2012; So & Wang, 2004). Despite these adverse effects, studies on BTEX measurements are minimal in India. Most Indian studies involving air pollution have focused on addressing aerosol particulates, and their characterization (e.g., organic matter, ionic, and elemental species). India has implemented policies and strategies to control particulate emissions from various sectors. Some of these policies and strategies targeted towards sources such as the transport sector, domestic combustion, and waste burning may also help to reduce VOC emissions. However, specific policies for controlling of VOCs in India are still scarce. VOCs contribute considerably to the ambient particulate pollution load as a precursor through secondary aerosol formation; hence, more policies should focus on the emission of VOCs, especially BTEX from combustion and non-combustion sources to air pollution mitigation.

This review aims to compile the present state of knowledge and findings on ambient BTEX in

different locations in India, the associated impact on lower atmospheric chemistry, and their health risk assessments. It also aims to identify the data gap and the areas where more studies are required involving BTEX for air pollution mitigation.

2 Methodology

The review has been prepared by summarizing the findings of more than 110 research papers (publication year: 2001–2022) reporting studies conducted within the Asian region, which were published in national and international journals. The data reported in this review were obtained through a literature search from the Web of Science, Science Direct, Research Gate, and Google Scholar, and the keywords employed in the literature search were volatile organic compounds, BTEX, Chemical precursors, hazardous VOCs, Source identification, health risk, carcinogen, scientific reports, and review papers. This review was restricted to studies conducted in ambient air. Studies on BTEX reported in specific microenvironments (e.g., petrol pump, dumpsites, industry) were included to compare the ambient levels with microenvironments. A few Asian studies were also incorporated in this review to compare ambient BTEX levels in India with those in other Asian countries. Limited studies on VOCs have been conducted in India to investigate the enrichment of hazardous materials emitted from different biogenic and anthropogenic activities. Based on different objectives, the outcomes of the reported studies have been reviewed to understand the following major aspects: (a) the status of BTEX in different locations in India, their spatio-temporal variation and contributing sources; (b) comparison of ambient BTEX levels in ambient environments vis-à-vis other microenvironments; (c) comparison of ambient Indian BTEX levels with other Asian cities; and (d) the impact of BTEX on health and lower tropospheric chemistry (i.e., ozone formation and SOA formation).

3 Ambient Levels of BTEX in India

3.1 Status of BTEX in India

Approximately 28 research papers were available to address the scenario of VOCs in India from 2001

to 2020, out of which only three studies have been conducted in rural areas (Kumar et al., 2017, 2018; Masih et al., 2018) whereas other studies have been conducted in urban areas that are focused only on the concentration levels of VOCs and their impact on climate change. The reported studies on BTEX level during 2001–2020 in different locations in India are summarized in Table 1. Previous studies on VOCs in India have been conducted in metro cities such as Delhi (Garg & Gupta, 2019; Kumar et al., 2017, 2018; Singh et al., 2016; Singh & Tomer Neetu, 2012; Hoque et al., 2008; Srivastava et al., 2004), Kolkata (Dutta et al., 2009), and Mumbai (Pandit et al., 2011), along with many other cities such as Ahmedabad (Sahu et al., 2016), Agra (Singla et al., 2012), Darjeeling (Sarkar et al., 2014), Gorakhpur (Masih et al., 2016, 2018), Chennai (Mohan & Ethirajan, 2012), and Dehradun (Bauri et al., 2016). Supplementary table S1 shows details of reported BTEX mean concentration in different locations in India. From 2001 to April 2020, the average mass concentrations of benzene ranged from 6.6 to 348.8 $\mu\text{g m}^{-3}$, with a mean of $46.07 \pm 46.70 \mu\text{g m}^{-3}$, which is multi-fold higher than the prescribed limit (5 $\mu\text{g m}^{-3}$) (NAAQS, 2009). Similarly, the concentration of toluene varied between 8.10 and 303.42 $\mu\text{g m}^{-3}$ with a mean concentration of $71.29 \pm 55.65 \mu\text{g m}^{-3}$. As a limiting value for the protection of human health from toluene, WHO recommends a maximum of 260 $\mu\text{g m}^{-3}$ averaged over a week (Mohan & Ethirajan, 2012; Parra et al., 2009). The total concentration of ethylbenzene and xylene (-o, -p) varied from 1.50 to 36.60 $\mu\text{g m}^{-3}$ (mean value: $14.41 \pm 10.60 \mu\text{g m}^{-3}$) and 1.12 to 52.18 $\mu\text{g m}^{-3}$ (mean value: $20.37 \pm 16.36 \mu\text{g m}^{-3}$) respectively. The average concentration of BTEX decreased in the following order: toluene > benzene > xylene isomers > ethyl-benzene. Sarkar et al. (2014) studied in Darjeeling in the year 2012 BTEX attributed most (72%), followed by non-BTEX substituted aromatics (22%) and halocarbons (6%). In India, mean concentration of benzene was observed for Mumbai (ranged: 45.31–348.4 $\mu\text{g m}^{-3}$), Delhi (48–110 $\mu\text{g m}^{-3}$), Kolkata (33.56–77.18 $\mu\text{g m}^{-3}$), Chennai (38 $\mu\text{g m}^{-3}$), Dehradun (29.76 $\mu\text{g m}^{-3}$), Gorakhpur (7.1–29.2 $\mu\text{g m}^{-3}$), and Agra (9.5–14.7 $\mu\text{g m}^{-3}$) found to be 36, 17.2, 11.6, 7.6, 5.8, 2.7, and 2.4 times higher than the prescribed limit of NAAQS respectively. The reported BTEX concentration levels in different locations of other Asian countries are summarized in Table 2.

Table 1 Reported BTEX concentration levels in different locations of India during 2001–2020 with sampling and analysis method involved

Study period	Location	Site/area	Adsorbent/absorbent used for sampling	Instrumental technique used for chemical analysis	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl benzene ($\mu\text{g}/\text{m}^3$)	Xylenes ($\mu\text{g}/\text{m}^3$)	References
2001–2002	Mumbai	R	ACT	GC-MS	45.31	29.16	0.2	1.12	Shrivastava et al. (2006)
		C			127.2	128.7	0.29	0.4	
		I			201.5	79.64	0.27	0.21	
2001–2002	Delhi	T			348.4	303.42	2.01	0.92	Hoque et al. (2008)
		R	ACT	GC-FID	48	85	7	45	
		C			97	180	21	123	
2003–2004	Kolkata	I			89	204	16	102	Dutta et al. (2009)
		T			110	191	24	90	
		R	ACT	GC-FID	33.56	41.41	10.96	28.18	
2003–2005	Kolkata	C			77.18	86.22	16.41	52.18	Majumdar et al. (2011)
		T			63.65	73.24	36.25	45.42	
		R	ACT	GC-FID	50.2	62.6	18.4	18.4	
2005–2006	Mumbai	Urban average	Grab sampling (Tedlar Bag)	GC-FID	46.93	15.44	19.09	17.79	Pandit et al. (2011)
2006	Mumbai	Open dump site (Deonar & Malad)	Flux box and multibed adsorbent tube	GC-MS	286.1	70.5	0.5	0.3	Majumdar and Srivastava (2012)
2006–2007	Raipur	I	Tedlar Bag	GC-FID	144.5	87.14	0.2	0.2	Sharma et al. (2015)
2008–2010	Delhi	Urban	ACT	GC-FID	16.52	55.98	–	14.83	Singh and Tomer-Neetu (2012)
2008–2009	Chennai	R	Tenax and Carbo-pack B tubes	GC-MS	38.23	156.14	27.37	49.74	Mohan and Ethirajan (2012)
2010–2011	Agra	Roadside	ACT	GC-FID	14.7	8.1	–	7.2	Singla et al. (2012)
		PP			19.5	12.9	–	3.6	
2012–2013	Dehradun	Urban average	ACT	GC-FID	29.76	83.54	9.93	42.87	Bauri et al. (2016)
2013–2014	Delhi	Rural	Charcoal Tube	GC-FID	6.06	25.93	3.55	6.27	Kumar et al. (2017)
2013–2014	Delhi	R	ACT	GC-FID	8.8	31.4	5.5	39.3	Kumar et al. (2018)
		C			11.8	39.1	6.6	47.4	
		Rural			6.1	25.4	3.6	9	
2014–2015	Gorakhpur	R	ACT (coconut shell)	GC-FID	7.1	19.5	BDL	1.2	Masih et al. (2016)
		C			11.4	21.7	1.5	1.3	
2014–2015	Gorakhpur	I			29.2	33	3.4	3	Masih et al. (2018)
		T			15	38.6	5.2	5.9	
		Urban	ACT (coconut shell)	GC-FID	12.1	22.1	–	1.3	
	Rural			7.4	17.9	–	1.1		

R residential, C commercial, I industrial, T traffic, PP petrol pump, ACT activated charcoal tube

3.2 Spatio-temporal Variations of BTEX

Very few studies on temporal VOCs (BTEX) measurements have been reported for the Indian sub-continent (Table 1). In most cases, VOCs showed higher concentrations in the morning, followed by a fall in the midday and an increase in rush hours of the evening (Garzón et al., 2015). Mohan and Ethirajan (2012) observed that VOC levels were higher in the morning than at other times of the day, and that the concentration difference between the morning and evening samples did not indicate a fixed trend of VOCs. Srivastava et al. (2005a) studied different locations in Mumbai and observed concentrations of VOCs were lowest in residential site as compared to commercial, industrial, and traffic intersection and petrol pumps during winter season due to less anthropogenic activities. Singla et al. (2012) revealed that toluene was the second most abundant species in BTEX. The levels of benzene and toluene were higher at night, while other VOCs (ethylbenzene, m, p-xylene, and o-xylene) showed higher levels at a day. The seasonal variation in BTEX varied from region to region. Moreover, BTEX concentrations varied between different sample locations in the same region. The seasonal variation of BTEX concentration varied among the different sites and higher concentrations were reported in winter than in spring or summer. India is a tropical country, receives a high amount of sunlight during the summer season, and, thus, photochemical degradation becomes dominant during summer as compared to primary emissions and secondary formation. However, a low mixing height during the night may result in higher concentrations during winter (Lyu et al., 2016; Tan et al., 2012; Tang et al., 2008; Zhang et al., 2012). Bauri et al. (2016) also studied the seasonal variation of BTEX and observed that toluene was the most abundant species, followed by benzene, ethylbenzene, and xylene isomers in the ambient air of Dehradun. Majumdar and Srivastava (2012) revealed that the targeted VOCs (BTEX) showed higher average levels in winter than in summer which might be due to the lower mixing height and less dispersal in winter. Masih et al. (2016) observed that the context of seasonal variability of VOCs levels was highest in winter followed by autumn and summer for rural and urban areas, which could be possible due to the strength of emission sources and their distribution as well as changes in hydroxyl (OH[•]) radical levels and

prevailing meteorological conditions. Garg and Gupta (2019) reported a comparative study during rush and non-rush hours at Delhi and revealed that the total concentrations of BTEX were 1.2–1.8 times greater than non-rush hours; it might be heavy vehicular density in rush hours. The results showed that the mean concentration of BTEX in the ambient air was significantly higher at urban sites than in rural areas, where toluene had been shown highest concentration among the selected VOCs (benzene, ethylbenzene, xylene isomers) in both regions. Figure 1 describes the level of BTEX at urban and rural sites of India. The urban site was mainly influenced by vehicular emissions, while at the rural site, due to traffic and vehicular emissions, more than 60% of VOCs are emitted; therefore, it appears as an essential source of ambient VOCs in urban areas. In this review, urban areas are divided into industrial, commercial, residential, and traffic sites. Figure 2 shows the variation in the average BTEX concentration at different sites among different regions of India. In urban sites, BTEX has been found to be 8%, 11%, 16%, and 21% for residential sites; 33%, 26%, 15%, and 19% for industrial sites; 18%, 25%, 29%, and 29% for commercial sites; and 41%, 38%, 40%, and 31% for traffic sites respectively.

3.3 Sources of BTEX

BTEX emissions are generally exhausted by diesel vehicles, paint, and other anthropogenic sources (such as industrial processes, solvent usage such as toluene). The source apportionment technique has been widely used for the identification and quantification of the source contributions of VOCs including BTEX. This method employs models known as receptor models (such as positive matrix factorization (PMF), chemical mass balance (CMB)). These models are based on the mass balance principle and certain pre-set assumptions, and several mathematical and statistical tools that can effectively quantify sources (Badol et al., 2008; Ling & Guo, 2014; Qin et al., 2022). Principal component analysis/absolute principal component scores (PCA/APCS), were used to identify the variance in VOC sources (Stewart et al., 2021b). In India, only a few source apportionment and emission estimation studies have been carried out so far. Srivastava (2004) studied VOC (BTEX) sources in different areas of Mumbai; results observed that evaporative emissions (petrol, vehicle

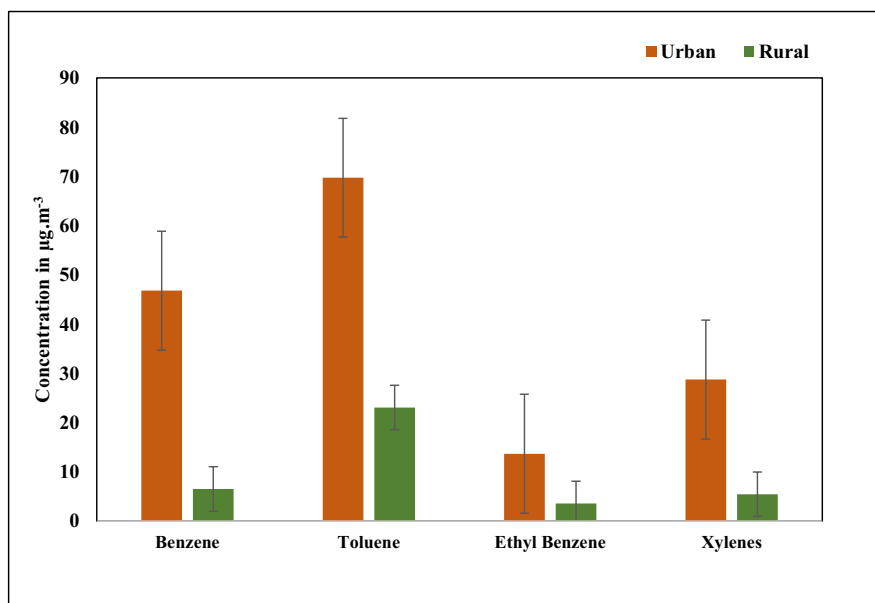
Table 2 Reported BTEX concentration levels in different locations of other Asian countries during 2001–2020 with sampling and analysis method involved

Year	City/region, country	Site/area	Sampling technique and adsorbent used	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl benzene ($\mu\text{g}/\text{m}^3$)	Xylenes ($\mu\text{g}/\text{m}^3$)	References
2001	Seoul/Korea	Urban	Canister sampling	3.2	24.5	3	6.7	Na and Kim (2001)
2002	Guangzhou/China	Roadside	Tekmar stainless steel multi sorbent tubes	26.7	77.2	3.1	12.1	Chan et al. (2003)
2002	Guangzhou, Macau Nianhai/China	Urban	Multi bed adsorbent tubes	51.5 34.9 20.0	77.3 85.9 39.1	17.8 24.1 3.0	81.6 95.6 14.2	Wang et al. (2002)
2002	Karachi/Pakistan	Traffic	Canister sampling	16.6	26.8	8.2	–	Barletta et al. (2002)
2003	Tsui/Hong Kong	Urban	Summa stainless steel canister	30.5	200.8	5.1	45.6	Ho et al. (2004)
2004	China	Urban	Tekmar stainless steel multi sorbent tubes	44.7	79.4	–	–	Zhao et al. (2004)
2005	Guangzhou/China	Shopping Mall	Adsorbent tubes	28.8	51.8	9.4	24.8	Tang et al. (2005)
2006	China	Urban	Stainless steel canister	463	252	476	250	Lü et al. (2006)
2007	Hanoi/Vietnam	TC street	SKC charcoal tubes	72.6	62.3	16	31.6	Truc and Oanh (2007)
2008	Beijing/China	Ambient air	Stainless steel canister	8.37	11.41	5.14	13.35	Duan et al. (2008)
2009	Daegu/Korea	Industrial	Canister sampling	8.8	88.03	19.43	20.22	Choi et al. (2009)
2009	Kacaeli/Turkey	Landfill	Stainless steel tubes filled with carbo-graph	140.3	1271.7	239.9	343	Durmusoglu et al., (2010)
2010	Yokohama/Japan	Industrial	10-L Flex polyester bags	25.2	27.8	31.45	31.81	Tiwari et al. (2010)
2012	Seoul/Korea	Ambient air	Carbonsieve adsorption traps	0.47	92	0.42	0.68	Kim et al. (2012)
2013	Vietnam	Ambient air	Activated charcoal tubes	56	121	21	87	Lan and Minh (2013)
2014	Bangkok/Thailand	Petrol station	Charcoal tubes	589.91	1694	96.74	533.75	Rattanaojittrakorn and Prueksasit (2014)
2014	Beijing/China	Ambient air	Canister sampling	1.72	5.41	1.19	2.62	Li et al. (2014)
2014	Ahvaz/Iran	Ambient air	Activated coconut shell charcoal tube	1.78	5.19	0.51	9.74	Rad et al. (2014)
2015	Turkey	Industrial	Chromosorb stainless steel tube	4.7	3.9	0.99	2.76	Civan et al. (2015)
		Residential		0.68	1.6	0.25	0.47	
		Roadside		0.53	1.1	0.39	2.06	
		Rural		1.9	3.9	0.66	0.97	
2016	Ardabil/Iran	Outdoor	Charcoal tubes	8.65	40.56	4.92	7.44	Hazrati et al. (2016)

Table 2 (continued)

Year	City/region, country	Site/area	Sampling technique and adsorbent used	Benzene ($\mu\text{g}/\text{m}^3$)	Toluene ($\mu\text{g}/\text{m}^3$)	Ethyl benzene ($\mu\text{g}/\text{m}^3$)	Xylenes ($\mu\text{g}/\text{m}^3$)	References
2017	Yalova/Turkey	Main road Side road Residential Industrial Rural	Stainless steel tube	1.98 1.53 1.33 1.88 1.1	6.19 4.36 4.14 37.03 2.2	1.3 1.13 1.03 2.97 0.82	3.26 3.53 3.19 11.33 1.75	Teccer et al. (2017)
2018	Hefei/China	Industrial Traffic Residential Development Zone	Summa Canister	7.37 8.46 8 7.57	10.58 13.29 11.01 9.84	3.24 5.14 3.65 3.72	3.73 8.71 5.29 4.65	Hu et al. (2018)
2019	Guilin/China	Urban	Stainless steel canister	8.88 2.92	9.96 4.2	3.15 2.85	3.05 2.07	Zhang et al. (2019)
2020	Tehran/Iran	warm season cold season	Activated charcoal tubes	3.97 5.32	15.57 30.53	2.79 11.6	5.71 6.54	Maleki et al. (2020)
2020	Hanoi/Vietnam	Urban	Stainless steel carbon tube	40.86	103.19	20.83	47.29	Ly et al. (2020)

Fig. 1 Variation in the reported concentrations of benzene, toluene, ethylbenzene, and combined isomers of xylenes between urban and rural sites of India for the period of 2001–2020

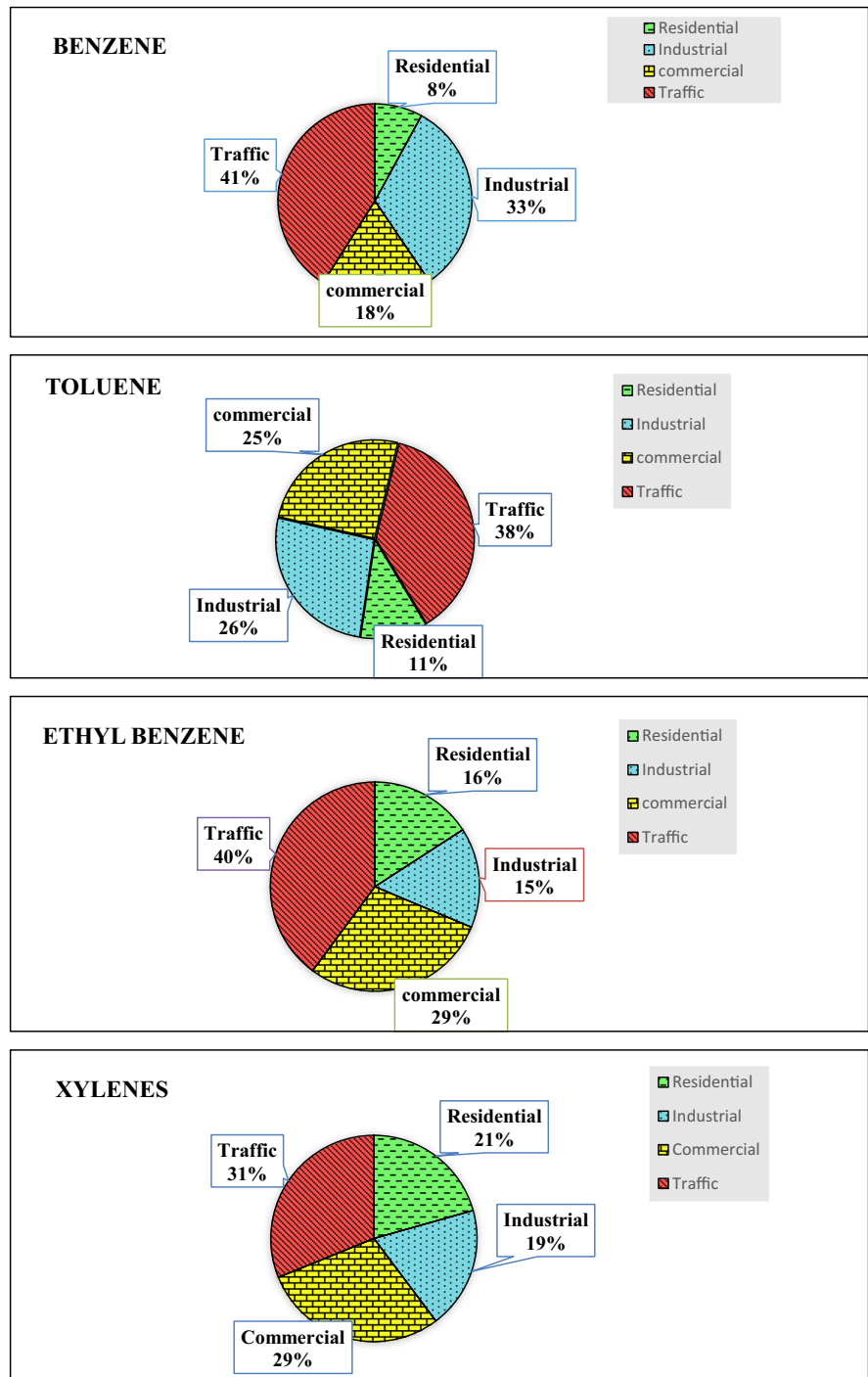


exhaust, and diesel internal combustion emissions) and oceanic emissions were the dominant sources of VOCs in industrial areas and petrol pumps also. In Delhi, a similar pattern of results was observed (Srivastava et al., 2005b). Pandit et al. (2011) studied results that revealed that vehicle emissions and refinery operations explained 54% of total VOC emissions, with the order of sources being petrochemical industries (15%) > paint solvent (15%). Darjeeling, a high-altitude city in the Himalayan range, revealed that gasoline- and diesel-vehicle emissions are the main sources of VOC, which accounted for more than 60%, followed by solvent evaporation (18%) and other sources (Sarkar et al., 2014).

Diagnostic ratios are another tool used to understand and differentiate between BTEX emission sources (Singh et al., 2016; Tiwari et al., 2010; Guo et al., 2012). If toluene-to-benzene ratio (T/B) showed a range between 1.5 and 4.3, it might indicate vehicular emissions, while if the ratio exceeds >4.3, it reflects the contribution of other nearby sources (Kumar et al., 2017; Niu et al., 2012). In vehicular exhaust, benzene and toluene are the major emitted constituents in the environment (Tunsaringkarn et al., 2010; Lee et al., 2002). The ratios of toluene to ethyl-benzene (T/E), benzene to ethyl-benzene (B/E), and xylene to ethyl-benzene (X/E) are very useful to understanding the photochemical age of VOCs (Zhang

et al., 2012). Kumar et al. (2017) found the average value of T/B ratios of 5.23 and revealed that vehicular exhaust was the dominant source, whereas the low ratio of xylene to benzene explained the aging of air mass. Similarly, Kumar et al. (2018) found T/B ratios 3.8–4.3 for urban sites and 5.3 for rural sites. X/B ratios 4.9 and 4.5 for urban sites in Delhi suggested the fresh air mass/local sources, and rural sites at 1.4 showed the old air mass from diffusion/dispersion of the pollutants. Bauri et al. (2016) studied at Dehradun and observed that T/B ratios were higher in traffic areas (>3) while relatively lower in commercial and residential areas, which were indicated as vehicular emissions while lower T/B ratios (<3) suggested the use of solvents and cleaning shops in a nearby area. Mohan and Ethirajan (2012) observed in his study that the greater T/B ratio reveals that in the location under study, there are several sources of VOCs, whereas vehicles are one of its contributors to pollution; for a comparatively shorter life, xylene (m-xylene) will not remain in the atmosphere longer (Liu et al. 2008). Singla et al. (2012) reported lower X/B ratio of 0.26, which indicated higher concentrations of benzene and exposure of more reactive species to photochemical degradation. The lower X/B ratio also indicates the aging of air mass. In Vietnam, the lower value of toluene:benzene (1.6) observed could be caused by the poor quality of the petrol (Hajizadeh et al., 2018). T/B

Fig. 2 Averaged percentage of reported relative source contribution estimates of atmospheric BTEX in urban environments of India (documented during 2001 to 2020)



ratios also vary with vehicle type, the composition of the fuel, and different industrial activities

(Tunsaringkarn et al., 2014). Table 3 presents the diagnostic ratios at different locations in India.

Table 3 Reported source diagnostic ratios of VOCs in ambient air of different locations of India

References	Site	T/B	m-p X/B	o-X/B	EB/B	m, p-X/EB
Hoque et al. (2008)	Residential	1.97	0.64	0.34	0.15	–
	Commercial	1.94	0.87	0.41	0.21	–
	Industrial	2.54	0.74	0.47	0.17	–
	Traffic	1.8	0.79	0.37	0.21	–
Singla et al. (2012)	Urban area	0.74	–	0.26	–	–
Masih et al. (2016)	Urban area	1.8	–	0.2	0.2	0.7
Bauri et al. (2016)	ISBT (traffic)	3.88	1.04	0.58	0.53	–
	Ghantaghar (commercial)	3.26	0.73	0.67	0.38	–
	Panditwari (residential)	3.29	1.09	0.79	0.46	–
	Doon University (institutional)	2.02	0.57	0.5	0.46	–
	Malsi (petrol pump)	2.9	0.9	0.54	0.26	–
Mehta et al. (2020)	Site 1 (traffic area)	0.78	0.22	0.14	0.14	1.53
	Site 2 (traffic area)	0.74	0.19	0.12	0.12	1.51
	Site 3 (traffic area)	0.83	0.2	0.13	0.11	1.77

T/B toluene/benzene, m-p X/B meta-para xylene/benzene, o-X/B ortho-xylene/benzene, EB/B ethyl benzene/benzene, m-p X/EB meta-para xylene/ethyl benzene

4 BTEX in Specific Microenvironments

A microenvironment can be defined as a distinctive part of a larger environment. A microenvironment such as petrol pumps and dumpsites may have a specific source associated with it which causes the level of BTEX to differ from the immediate ambient environment. BTEX levels of the microenvironment compared to the ambient environment are also shown in Table 1. Several toxic VOCs are emitted as landfill gas (LFG) because of their low solubility and high volatility and degradation processes. Majumdar and Srivastava (2012) studied in Deonar and Malad dumpsites of Mumbai and reported mean concentrations of BTEX of 286.1, 70.5, 0.5, and 0.2 and 144.5, 87.14, 0.2, and 0.2 $\mu\text{g m}^{-3}$, respectively. The observed levels were much lower than the mean BTEX levels reported by Durmusoglu et al. (2010) as 140.3, 1271.7, 239.9, and 341.3 $\mu\text{g m}^{-3}$, respectively, in a solid waste landfill site in Turkey. Due to differences in climate, topography, waste deposit characteristics, degradation stage, operational conditions, and other factors, each landfill may have different emission patterns (He et al., 2012). VOCs emitted in open dumpsites identified in LFG only 1%, but their negative impact on the environment cannot be overlooked. Singla et al. (2012) studied in Agra the mean concentrations of benzene, toluene, o-xylene, m-xylene, and p-xylene

which were $19.5\pm 3.7 \mu\text{g m}^{-3}$, $12.9\pm 1.1 \mu\text{g m}^{-3}$, $3.6\pm 0.5 \mu\text{g m}^{-3}$, and $11.1\pm 1.5 \mu\text{g m}^{-3}$, respectively.

5 Comparison of BTEX Level in India with Other Asian Countries

Among the Asian countries, India is the second-largest contributor to the emissions of non-methane VOCs (Kurokawa et al., 2013). The BTEX levels of India is 1.5 times lower than those in China and two- to threefold higher than those in other Asian countries like Japan (Hu et al., 2018; Tang et al., 2005), Iran (Kermani et al., 2021; Maleki et al., 2020; Hazrati et al., 2016; Rad et al., 2014), Hong Kong (Ho et al., 2004), South Korea (Na & Kim, 2001), and Pakistan (Barletta et al., 2002). It might be the use of low-grade fuel in developing areas and road maintenance (Li et al., 2017). Kim et al. (2012) studied at urban areas of Korea; it revealed that among the VOCs, aromatic VOCs had shown a significant contribution with 74% followed by other VOCs like halogenated paraffin, halogenated olefin, and halogenated aromatic VOCs. Choi et al. (2009) revealed that the area-specific trends of VOC concentration were to be industrial > commercial > residential, in these areas; toluene and xylene have been shown to be remarkably high from measured VOCs (BTEX). Hajizadeh et al. (2018) studied at

Yazd (Iran) between 2015 and 2016; the average BTEX concentration was found to be $114 \pm 119 \mu\text{g m}^{-3}$; among them, toluene ($38 \pm 42 \mu\text{g m}^{-3}$) and xylene ($41 \pm 45 \mu\text{g m}^{-3}$) have shown the highest concentrations; it might have been originated from industrial activities. Rad et al. (2014) measured in an urban area of Ahvaz (Iran) year 2013 mean concentrations of benzene, toluene, ethylbenzene, and xylenes, which were 1.78, 5.19, 0.51, and $1.13 \mu\text{g m}^{-3}$, respectively. Ji et al. (2020) described that the average mass concentration of BTEX for urban areas is often higher in southern regions of China, ranging from 0.71 to $132.09 \mu\text{g m}^{-3}$ with a mean value of $33.42 \pm 28.68 \mu\text{g m}^{-3}$. Hu et al. (2018) found 64.84, 58.92, and $57.31 \mu\text{g m}^{-3}$ for industrial, development, and resident area, respectively, which are approximately equal from the background area ($54.94 \mu\text{g m}^{-3}$) and traffic zone ($85.94 \mu\text{g m}^{-3}$) that showed relatively higher than other sites in eastern China. High VOC concentration in north China is largely caused by people burning coal for heating during cold season (Liu et al., 2021). Bretón et al. (2022) revealed that toluene may have originated from non-vehicular sources, according to the statistical study.

6 Impact of Ambient BTEX

6.1 Impact on Lower Tropospheric Chemistry

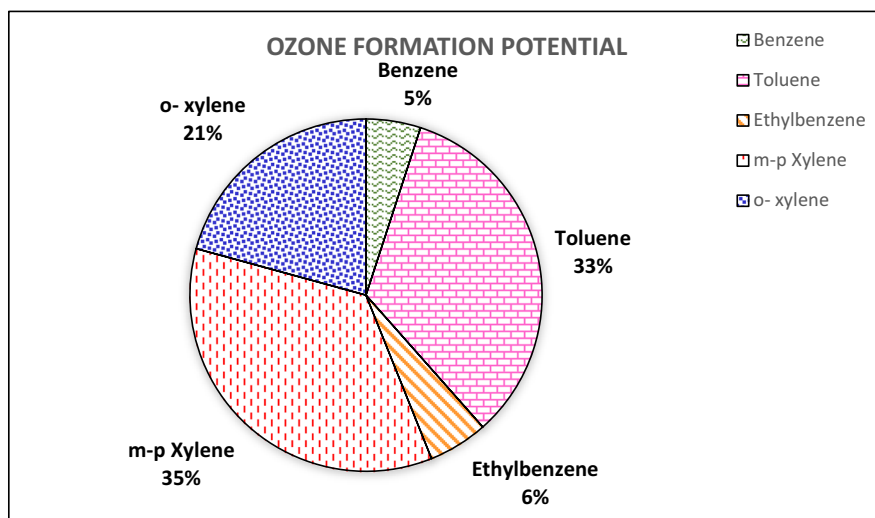
In different regions, ground-level ozone formation is a major concern in air pollution. Photo-chemically

active atmospheric VOCs and oxides of nitrogen (NO_x) are considered primary precursors for forming atmospheric ozone in the presence of sunlight (Alghamdi & Rahim, 2014; Hajizadeh et al., 2018; Prabhu et al., 2022; Tan et al., 2012). Peroxy radicals (RO₂), RCHO, and hydroperoxy (HO₂) are produced by the degradation of VOCs. When NO to NO₂ is converted, these radicals compete with O₃ (Xue et al., 2014). Benzene, toluene, and ethylbenzene are relatively stable and do not separate immediately after release, with an atmospheric lifetime of 9.4, 1.9, and 1.6 days respectively. However, the atmospheric lifetime of xylene is only 15.6 h and does not usually stay in the atmosphere for long (An et al., 2014; Liu et al., 2008). For VOCs, the ozone formation potential (OFP) can be evaluated by the maximum incremental reactivity (MIR) scale (Carter, 1994). In earlier published literature (Kumar et al., 2018; Garg & Gupta, 2019; Bauri et al., 2016), individual BTEX contribution towards OFP had been evaluated by the use of the following equation, which was adopted from Carter (2009):

$$\text{OFP} = \text{concentration of VOCs} \times \text{MIR} \quad (1)$$

The OFP is calculated by the multiplication of the individual VOC concentrations and the MIR coefficient (dimensionless) (Fanizza et al., 2011; Som et al., 2007; Sorahan et al., 2005). MIR coefficients are intended as an effective tool for ozone control programs used in relatively high conditions of NO_x. Supplementary table S2 shows details of reported

Fig. 3 Reported averaged contribution (in percentage) of benzene, toluene, ethylbenzene, m-p xylene, o-xylene in the ozone formation potential



mean concentration of OFP in India. Figure 3 illustrates the average percentage contribution of benzene, toluene, ethylbenzene, m-p-xylene, and o-xylene in the OFP which were found to be 5%, 33%, 6%, 35%, and 21% respectively. Na et al. (2005) evaluated ozone formation potential based on the MIR scale and concluded that xylene (m-p-xylene and o-xylene) was the major contributor and toluene was the second largest contributor in ozone formation. Masih et al. (2016) observed that the highest contribution to ozone formation was toluene (OFP=437.7) followed by xylene (OFP=85.4), benzene (OFP=43.9), and ethyl-benzene (OFP=29.6), at Gorakhpur. Kumar et al. (2018) conducted a study at both urban and rural sites of Delhi which revealed major contributors for ozone formation were m/p-xylene with values of 188.60 and 232.90 $\mu\text{g m}^{-3}$, respectively, for urban sites, and toluene (78.60 $\mu\text{g m}^{-3}$) was the major contributor in the rural site. In previously reported studies for ozone formation, toluene and xylene isomers were major contributors among BTEX (Tan et al., 2012; Cai et al., 2010; Zhang et al., 2012; So & Wang, 2004). In general, based on MIR scale, OFP decreased in the following order: xylenes (m, p-xylene and o-xylene) > toluene > ethylbenzene > benzene (Garg & Gupta, 2019; Hoque et al., 2008; Duan et al., 2008); in contrast, Yokohama suggested decreased order as follows: m, p-xylene > toluene > ethylbenzene > o-xylene > benzene (Tiwari et al., 2010). In this context of OFP, propylene equivalent concentration and MIR were used to evaluate the photochemical reactivity of VOCs with OH radicals and estimation of the contribution of individual organic compounds in ozone formation (Cai et al., 2010; Chameides et al., 1992; Li et al., 2017; Zhang et al., 2012). Hoque et al. (2008) found that OH radical reaction with BTEX leads to higher oxide formation followed the pattern –ethylbenzene < benzene < o-xylene < toluene < -m,-p xylene.

6.2 Impact on Human Health

International Agency for Research on Cancer (IARC) classified benzene as a group 1 (proven) carcinogen, which has a lifetime risk of leukemia for chronic exposure of 1 $\mu\text{g}/\text{m}^3$ which is $4.4\text{--}7.6 \times 10^{-6}$ (WHO, 2000). Ethylbenzene is classified as a group 2B (possibly) carcinogen. Excess lifetime cancer risk of below 10^{-6} (i.e., risk of cancer for less than one

person in one million population) may be acceptable (IARC, 2012; USEPA, 1989). The estimated cancer risk for target species exceeded one in a million population's threshold value which indicates significant cancer risk. The cancer risk was due more to benzene exposure for its high unit risk and a higher concentration than ethylbenzene. For the ambient air of Kolkata, human exposure to xylene mixture and toluene is maximum due to their higher observed concentration (Majumdar et al., 2011). However, in Darjeeling, maximum exposure is from toluene, followed by benzene and others (Sarkar et al., 2014). The occupational exposure of petrol pump refueling attendants is much higher than that of municipal solid waste (MSW) dumpsite workers. Refueling attendants are maximally exposed to toluene, followed by xylenes, benzene, and ethylbenzene. For dumpsite workers, the exposure is maximum from benzene than the other species (Majumdar et al., 2015).

In the risk of lifetime exposures to cancer risk (ILCR), benzene and toluene were highest due to their concentration, followed by non-cancer (HQ) ethylbenzene and xylene. Limited numbers of studies carried out in the Indian context research have shown that ambient VOCs are harmful to human health (Dehghani et al., 2018; Masih et al., 2016; Miri et al., 2016; Som et al., 2007; Massolo et al., 2010; Hoque et al., 2008; Majumdar (né Som) et al., 2008). Probabilistic cancer risk was reported high (715 in a million) in Darjeeling, followed by south Kolkata (497 in a million), Central Kolkata (329 in a million), and North Kolkata (154 in a million). Mehta et al. (2020) observed that benzene and xylene isomers had been discovered to have greater HQs than ethylbenzene and toluene in keeping non-cancer risks of BTEX, and the average ILCRs of benzene and ethylbenzene were 3.58×10^{-5} and 1.47×10^{-5} , respectively, which were found in the suggested range 10^{-6} to 10^{-4} . Masih et al. (2016) revealed that benzene levels had been found to exceed the acceptable risk of 1×10^{-6} at all sites and ethylbenzene in the roadside areas at Gorakhpur, although the non-cancer risk of HQ for all areas was equal to or below 1 and showed no adverse effect on health; this study was similar to that observed by Garg and Gupta (2019) at Delhi. Dutta et al. (2009) studied the HQ of BTEX in the range of 8.21×10^{-3} – 7.76×10^{-1} in the ambient air of Kolkata. The dumpsite emissions are especially hazardous to the health of those who

work there, posing both carcinogenic and non-carcinogenic risks (Majumdar & Srivastava, 2012). Gao et al. (2018) studied in Beijing revealed the carcinogenic risk of benzene (7.50×10^{-6}) was 7.5 times higher than the value advised by the US EPA.

7 Discussion

In India, from 2001 to 2020, the mean BTEX concentrations were found in the range 30.95 to 317.18 $\mu\text{g m}^{-3}$ and multi-fold higher in urban environments than those measured in rural environments. The ambient concentration in the reported urban areas of India is alarmingly high than most Asian cities and many fold higher than NAAQS, India. The BTEX levels of India are 1.5 times lower of China and two- to threefold higher than those of the other Asian countries like Japan, Iran, Pakistan, and South Korea. The seasonal pattern of BTEX concentration is higher in winter than in spring or summer. OFP obtained results have shown the highest potential of xylene (m-, p-, and o-xylene) and toluene than benzene and ethylbenzene due to its high reactivity. BTEX levels had the highest exposure contribution on traffic areas. Vehicular and industrial emissions are the primary anthropogenic source of BTEX in ambient air. The health risk assessment based on the observed dataset suggested that cancer and non-cancer risks exceeded the prescribed threshold values established by US EPA and WHO.

Most of the reported studies in India on VOC measurements are confined to monitor BTEX and many of them exhibit diurnal variation, with greater concentrations in the morning, decreased concentration throughout the middle of the day, and increased concentration during the evening rush hours. The major sources of BTEX emissions are observed to be emissions from vehicular and industrial emissions, biomass burning, and coal combustion. Very few studies on source apportionment of ambient VOCs or ambient BTEX are reported using US EPA regulatory air quality receptor models viz. EV-CMB, PMF, and UNMIX 6.0, and most of the BTEX source identification studies are based on reported source diagnostic ratios. As far as two major issues related to atmospheric VOCs, (1) formation of secondary products in atmosphere viz ozone and PAN and (2) adverse health effects/health risk calculations, very

limited studies are reported in India and all of them confined to address the calculations of ozone formation potential and health risks using measured BTEX concentrations.

8 Conclusion

A total of 188 species of VOCs have been listed as hazardous air pollutants by US EPA. BTEX was found to be the most reported VOC composition. BTEX and ozone not only affect human health but also impact the chemistry of the atmosphere via numerous photochemical reactions.

This review helps to understand the nature, source, and impact of BTEX in urban ambient air of India which will help to control and mitigate their adverse effects. Control of BTEX will augment India's effort to minimize impact on human health and combat climate change to achieve the United Nations Sustainable Development Goals towards healthy human life and minimizing climate change impact in sustainable cities of the near future (Huang et al., 2021; Varotsos & Cracknell, 2020; Shikwambana & Kganyago, 2020).

The scoping review also helps to identify the study gaps in detailed understanding of these group of air pollutants. Limited studies in urban India have reported on hazardous VOCs other than BTEX, such as halogenated and oxygenated VOCs. Meanwhile, a detailed study is required to address VOCs (aromatic, halogenated, and oxygenated) and their impact on lower tropospheric chemistry. Especially studies on secondary organic aerosol formation of BTEX and their contribution in high level of particulate pollution in urban atmosphere of India in recent times need to be studied in detail. In the last two decades, there is a lack of studies on VOCs in rural India; out of that, only 3 studies have been done in rural areas, while other studies have been done for urban areas, which are only focused on the concentration level of VOCs and its impact on climate change. Local governments in India adopted various control strategies for BTEX. In general, to more effectively reduce BTEX air pollution and support ongoing improvements to India's ambient air quality, it is important to expedite the formulation of guidelines for harmful VOCs. A better understanding and effective control of air pollution are necessary via several statistical and modeling techniques.

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Data Availability All datasets generated or analyzed during this study are included in this article (and its supplementary information files).

Declarations

Conflict of Interest The authors declare no competing interests.

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