

Volatile Organic Compounds in India: Concentration and Sources

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Abstract

This article highlights the key observation of various studies conducted in Indian scenario. In India, the major sources of volatile organic compounds (VOCs) are vehicle exhaust. Other sources include emissions from diesel internal combustion engines, oceanic emission and evaporative emissions. Various aspects of VOCs are studied in detail by various authors in the Indian context. VOC sampling methods vary from each other depending on the techniques, the type of adsorbent used, and the method of extraction, analysis and identification techniques. In India, the most widely used method for VOCs sampling are pre-concentration on sorbent tubes or whole air (grab sampling) sample taken in canisters or tedlar bags. From the studies, it can be concluded that ambient VOCs show a clear seasonal pattern and found to be higher during winter months due to temperature inversion in Delhi and Kolkata. For better understanding; accurate characterisation of vehicular emission contribution is required for the country like India.

Keywords: BTEX; India; NMVOC; Sampling methods; VOCs

Introduction

Rapid urbanization and industrialization has brought about serious air pollution problems and has impacted human health in major Asian developing countries. Air pollutants like particulate matter (PM), oxides of nitrogen (NO_x), carbon monoxide (CO), sulphur dioxide (SO₂) and volatile organic compounds (VOCs) pose a serious health hazard and serious concern for agriculture and global climate as well [1-3]. Among the gaseous air pollutants, VOCs are the key components both in polluted and remote regions of the troposphere. In tropospheric photochemistry, VOCs play a key role due to the high abundance of water vapor and intense solar radiation flux [4]. According to US Environmental Protection Agency (USEPA, 2001) 21 out of 33 hazardous air pollutants are associated with motor vehicles, which are the largest source of VOCs and the fine particulates in urban areas. VOCs refer to a group of organic species which have high vapor pressure in the earth's atmosphere [5] and can be defined based on parameters such as boiling point (in EU), chemical composition and reaction chemistry (in USA and Canada). Since 1980s, photochemical mechanisms of hundreds of VOC species have been intensively studied and a review of literature is provided in Atkinson and Arey [6]. Even after so many decades, interest in the VOCs role in the atmosphere of urban areas is increasing due to their adverse impacts on the environment and human well-being.

Sources and sinks

Naturally occurring VOCs, often referred to as are the biogenic volatile organic compounds (BVOCs) which are emitted into the atmosphere from vegetation [7]. Globally, the largest sources of VOCs are tropical and extra-tropical forests, which emit VOCs (like isoprene, a- and b-pinene and methanol) in large quantities [8,9]. Annual global VOC flux from plants has been estimated to be 1150 tg-C, consisting of 44% isoprene, 11% monoterpenes, 22.5% other reactive hydrocarbons and 22.5% other non-reactive hydrocarbons [10]. Key anthropogenic sources in urban areas include vehicle emission- exhaust and fuel evaporation, solvent usage, industrial processes, oil refining and biodecomposition of wastes [11,12]. Others sources include coal fired power plants, landfill site, petrochemical industries, solvent industries dry-cleaning activities, degreasing, commercial and domestic painting. In addition, production, storage, and use of fossil fuels can lead to the emission of VOCs such as alkanes, alkenes and aromatics, although it is a much smaller source on a global scale, but can dominate on regional levels [9]. Vehicular emissions are one of the major sources of VOCs in urban areas [13]. VOCs emitted into the atmosphere includes major

class of chemicals like alkanes, alkenes, oxygenated VOCs (2-methyl-3-buten-2-ol, acetone, etc.), aliphatic and aromatic hydrocarbons, which can alter the atmospheric chemistry [6,14]. Once emitted, VOCs undergo four main processes: dispersion, transformation, chemical reactions and deposition. Dispersion provides transportation and dilution by distributing the VOCs over different air parcels of the atmospheric boundary layer. Physical transformation includes condensation of gaseous VOCs into organic particles, adsorption on their surface or solution in water droplets. Chemical reactions convert VOCs into organic or inorganic molecules, which in turn undergoes dispersion and transformation processes. Deposition includes wet and dry deposition of VOCs into the water and soil reservoirs by sedimentation or scavenging processes [15].

Atmospheric chemistry

The chemistry includes: VOCs as a precursor of ozone (O₃) formation, photochemical smog and acid deposition; VOCs role in climate change; VOCs in secondary organic aerosol (SOA) formations. Ozone is a secondary air pollutant formed by the photochemical reaction of the precursor pollutants and primary oxidant to other highly reactive trace gases [16,17]. The production of O₃ at ground level is of particular concern, since it is known to have adverse effects on vegetation, materials and human health (respiratory problems, skin irritation) [18]. Formation of O₃ in the atmosphere is mainly due to a photochemical reaction of NO_x, VOCs and CO in the presence of solar radiation [19-21]. Jenkin and Clemitshaw [18] has described the detail of the ozone chemistry. Formation of SOA involves oxidation of VOCs in the atmosphere to form low or semi-volatile products, which can then condense onto existing particles or nucleate to form new particles. SOA has an effect on climate change, health and visibility reduction [22]. The VOCs contributes to climate change in two ways [23]: a) primary contribution arising from the direct effect if the VOC is a halocarbon,

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due to the atmospheric lifetime and infra-red absorption properties of the VOC and reflected by its direct global warming potential (GWP) values, or the indirect effect if the VOC is a hydrocarbon, due to its chemical effect on the atmosphere, b) secondary contribution from the CO₂ eventually arising from the atmospheric degradation of the VOC or by its incineration aided by the combustion of a fossil fuel.

Health impacts of VOCs

VOCs and its public health impacts are drawing increasing concern from the environmental health research community, environmental regulatory agencies, industries, as well as for the public. Adverse health effects of VOCs include headache, nausea, eye/throat/nose irritation, damage to liver, kidney and central nervous system. Benzene, toluene, ethylbenzene, o-, m- and p-xylene (BTEX) form an important group of aromatic VOCs. Among these, Benzene is classified by the International Agency for Research on Cancer as Group 1 human carcinogen. Toluene, ethylbenzene, o-, m-, and p- xylenes have been found to develop adverse health impacts on respiratory and neurological effects [24]. Majumdar, Mukherjee and Sen [25] observed the estimated cancer risk exceeding the threshold value of 1×10^{-6} indicating significant cancer risk to the people living in the Kolkata city. Human (specifically children) who live near heavily traveled streets or highways may be at an elevated risk of developing cancer, including leukemia [26,27]. Considering the global scenario not even EPA proposed any standard for ambient VOCs. Occupational Safety and Health Administration (OSHA) and World Health Organization (WHO) have some guidelines, but these are recommendations and not mandatory to adopt [14,28].

Many authors [4,6,10,14,28-30] have reviewed about the VOC in terms of analytical methodologies, ambient air concentration, indoor concentration, health impact, biogenic VOC, non-methane volatile organic compounds, etc. Sahu [4] discussed VOCs and their measurement in the troposphere. Usually, gas chromatography-based methods have been used for the detection of VOCs, but now fast and sensitive techniques like proton-transfer reaction mass spectrometer has come into the picture. Gas-phase tropospheric chemistry of biogenic volatile organic compounds was reviewed by Atkinson and Arey [7]. Han and Naeher [28] reviewed the traffic related air pollution exposure assessment studies in the developing world and discussed the advantages and disadvantages of various monitoring methods for these pollutants. Seco, Penuelas and Filella [29] in their review observed the emission and uptake by plants and atmospheric sources, sinks, and concentration of short-chain oxygenated VOCs (formaldehyde, acetaldehyde, methanol, and ethanol etc.). Kansal [10] reviewed the sources and reactivity of non-methane hydrocarbons (NMHCS) and VOC in the atmosphere. He reported that global natural emission of non-methane hydrocarbons and VOC is always higher than the emission for the anthropogenic sources. Among the anthropogenic sources, transportation and biomass burning are the major ones. Talapatra and Srivasatava [14] talked about measuring technologies, variability studies, source apportionment, and newer technologies to remove VOCs etc. Also, they have discussed about sustainable development in terms of industrial, infrastructural as well as the overall growth of the country. Saxena and Ghosh [30] analyse the different monitoring sites and BTEX concentration in Delhi. They found that the concentration of BTEX was higher in commercial sectors because of the increased traffic volume due to large office complexes and big shopping malls. Hasan, Said and Leman [31] reviewed the health effect from VOC and useful tools for future prevention. They have discussed the VOC exposure and health effect to the workers and how it can be prevented with the help of Computerized Fluid Dynamic (CFD) technique. Suvarapu, Seo and Baek [32] reviewed the VOC and

polycyclic aromatic hydrocarbons (PAH) in an Indian atmosphere reported during 2000-2012. This review also predicts the lack of research data about the concentrations of VOC and PAH in some other metropolitan cities such as Chennai, Hyderabad and Bangalore.

Olumayede and Okuo [33] reported the variation characteristics and concentration of ambient VOCs in the urban atmosphere of southwestern Nigeria. Juskiewicz and Kijak [34] measured the quantitative contribution of the traffic to the air pollution with VOCs in Kraków (Poland) between 1997- 1999. They found toluene (48.4 µg/m³) as most abundant VOC followed by acetylene, benzene, xylenes and alkylbenzene. Buczynska et al. [35] determined the influence of the modernization and renovation of a traffic artery in the region of Mortsel (Antwerp, Belgium) on the concentration of volatile organic compounds such as: benzene, toluene, ethylbenzene and m-, p-, o-xylenes (BTEX). The average concentrations of BTEX before these works in 2003 were: 1.6, 7.0, 0.9, 2.3, and 0.9 µg/m³, for benzene, toluene, ethylbenzene, m-, p- xylenes, and o-xylene, respectively. However, after the completion of the works, in 2005, they were slightly higher: 2.5, 9.5, 1.6, 3.4, and 1.3 µg/m³, respectively. They concluded that all the compounds originated from the road traffic. Muezzinoglu, Odabasi and Onat [36] determined the diurnal pattern of VOCs levels in the urban center of Izmir (Turkey) and found that toluene to be the most abundant VOC followed by xylenes, benzene and alkylbenzenes. Wang and Zhao [37] revealed the positive correlation between the VOC levels and traffic density and they highlighted a potential exposure of the high concentrations to pedestrians, commuters, and traffic-exposed workers.

This review paper provides a comprehensive review of literature focused on VOCs in India. It is based on the review of the most recent publications in this area of research. The aim of this review is to address the significant gaps by analyzing the different studies. A total of 20 studies were found from India. Only 25% of the studies have done source apportionment. More than 50% of the work has been done only on BTEX while other includes VOC. The literature search was performed using Web of Knowledge, NISCAIR, Science Direct, Springer and Google Scholar using various combinations of keywords such as vehicle exhaust, traffic emissions, VOC, BTEX and source apportionment.

VOC Concentrations in India

India has been a leading giant among developing nations and has a lots of pressure from different domestic and international forums to formulate principles and regulations towards VOC control along with many other footsteps [14]. A rapid increase in the growth of number of registered motor vehicles underlines the importance of a detailed understanding of the VOC emission contribution from traffic.

Analytical methods

VOCs measurement in ambient air is often difficult, because of the different types of VOCs and their potential concern, variety of techniques for sampling and analysis, and the lack of standardized and documented methods [38]. VOCs sampling methods vary from each other according to the techniques, type of sorbent used, extraction method, analysis and identification technique. In India, the most widely used method for VOCs sampling are pre-concentration on sorbent tubes or whole air (grab sampling) sample taken in canisters or tedlar bags shown in Table 1.

VOCs characterization

Characterization of VOCs (BTEX) in India is defined by selecting

References	Sampling Technique	Average Sampling Time	Advantages	Disadvantages
Padhy and Varshney [39]; Srivastava et al.[40]; Pandit et al.[41]	Whole Air Sampling (cnisters, tedlarbags, hydermic-disposable syringe)	10-20 min	Representative of a snapshot in time, quick, No degradation problem of trapping material, duplicate analysis	Complex sampling apparatus, pressure should be as high as possible, difficult to clean, loss of target compounds may occur
Padhy and Varshney [42]; Srivastava et al. [43]; Khillare et al.[44]; Hoque et al. [45]; Sehgal et al. [46]; Singh et al. [47]; Mohan and Ethirajan [48]; Srivastava et al. [43, 49, 50]; Kumar and Tyagi, [51]; Som et al.[52]; Majumdar et al. [53, 25]; Singla et al.[54]	Pre-Concentration on Sorbent Tubes (activated charcoal tubes, Tenax TA, GC etc.)	Active (2-4 h) Passive (1-4 weeks)	More than one sorbent can be used in series, cost effective, few errors, easier to handle	Breakthrough, labour intensive, loss of sample during extraction
Singh et al. [55]	Real Time Monitors	Real Time data	Real time data, flexible	High cost

Table 1: The widely used sampling technique for monitoring VOCs in India.

various sites of different sectors i.e., Residential sector, industrial sector, commercial sector, traffic or busy road site, petrol pump (refueling stations), petrochemical complex or refinery. Summarization of some of the studies on VOCs is shown in Table 2. Padhy and Varshney [39] estimated the total NMVOC at 13 sites in the urban environment of Delhi during November 1994 to June 1995. Grab samples of ambient air were collected with the help of a 30 ml air tight hypodermic disposable syringe and analyzed by GC-FID. The levels of TNMVOC in the ambient environment of Delhi varied between 1.3 and 32.5 ppmv during the monitoring period. The maximum and the minimum value of 32.5 and 1.3 ppmv were recorded at sites South Extension and JNU, respectively. According to author relatively high (13-26 ppmv) level of TNMVOC at Paharganj, Minto Bridge, AIIMS, South Extension, Ashram and Darya Ganj. The highest concentration at these sites was due to heavy traffic, frequent idling and deceleration of vehicles, motor vehicle exhaust. Also the author has found that NMVOC levels (7-20 ppmv) are high at the sites DLTA, Chankyapuri, WWF, Vijay chawk, KA Marg and Safdarjung Flyover, where traffic volume is low and free from traffic congestion. A similar study was conducted by Varshney and Padhy [40], the concentration of TVOCs in Delhi varied between 3-42 ppmv. Srivastava et al. [41] monitored VOCs (n-hexane, benzene, heptane, toluene, p- and o-xylene, ethyl benzene and n-decane) in different type of indoor environment in Mumbai. The author concluded that higher toluene (21.6 ppbv) and xylene (11.2 ppbv) concentration levels were found in the recently renovated rooms while benzene concentration was found to be higher in the kitchen (32.3 ppbv) and smokers room (15.1 ppbv). In Delhi, Hoque et al. [42] monitored at four different categories; institutional cum residential area (JNU), commercial area (Connaught Place), industrial area (Okhla) and traffic intersection area (AIIMS). Activated charcoal method was used for sample collection followed by the analysis of compounds in the GC-FID. Their study reported the highest concentration of BTEX at AIIMS due to high traffic density, slow movement of the traffic and more frequent idling of the vehicles, followed by CP than Okhla and the lowest concentration was found at JNU. The mean concentration of toluene ($204 \pm 70 \mu\text{g}/\text{m}^3$) and benzene ($110 \pm 53 \mu\text{g}/\text{m}^3$) was the highest at the Okhla site which is surrounded by industries (most of paints and varnishes), motor vehicle serving stations and electric motor winding and AIIMS due to high traffic density. A similar study by Khillare et al. [43] reveals that there is an approximately a 60% rise in benzene concentration in the post-CNG period. This may be due to a sharp rise in vehicle population. Among BTEX, highest abundance of toluene observed in the present study is in agreement with the study of Kumar and Tyagi [44] and Srivastava et al. [45] while Srivastava [46] has reported

benzene as the most abundant species. Similar sites were monitored by Singh et al. [47] in the urban environment of Delhi. The sampling sites were selected based on land use pattern, i.e., gasoline filling station (Preetvihar), residential (Pritampura), commercial (Old JNU), industrial areas (Shahdra) and traffic intersection (ITO, DhaulaKuan). Total average (2008-2010) B/T/X concentrations varied between 8.52 ± 1.90 to $25.02 \pm 2.10 \mu\text{g}/\text{m}^3$ / 21.86 ± 2.32 to $84.01 \pm 8.15 \mu\text{g}/\text{m}^3$ / 9.95 ± 1.88 to $22.32 \pm 1.76 \mu\text{g}/\text{m}^3$ respectively. Lowest values were observed at JNU whereas the highest at PV location. This study concludes that the highest concentrations of B/T/X were observed in the vicinity of petrol pump at Preet vihar location. In the present study significant decrease in BTX levels have been observed in national capital Delhi as compared to the previous studies. Singh et al. [48] have found that concentration under no failing condition was 0.1 ppm - 0.5 ppm, but it changes drastically under filing condition 1 ppm-20 ppm at the petrol pump. These levels were considered to be sufficiently high to represent the degree of risk to the population living close to these busy sites. Som et al. [49] identifies the difference in the concentration of benzene from 5% to < 3% reduction of benzene in gasoline and with the introduction of catalytic convertor. This study includes two phase monitoring (Phase I: 2001-2002 and Phase II: 2003-2004) made inside and outside of a passenger car fitted with and without catalytic convertor. In phase I period, benzene content in gasoline was 5% and the ambient air and in-vehicle (without catalytic convertor) concentration of benzene was found to be as $214.8 \mu\text{g}/\text{m}^3$ and $721.2 \mu\text{g}/\text{m}^3$ respectively. In a phase II study, benzene content was reduced to 3% and with modified engine type, the ambient air and in-vehicle concentration of benzene was found to be as $30.8 \mu\text{g}/\text{m}^3$ and $112.4 \mu\text{g}/\text{m}^3$, respectively. Toluene level was not significantly different in the two phases. Therefore, it can be concluded, commuters in Kolkata travelling in cars are exposed to higher concentrations of BTEX than the other urban cities because of inadequate emission control, insufficient road space and slow driving speed. Srivastava et al. [50] conducted a similar study on different micro environmental regions in Mumbai i.e., petrol pump, arterial road, highway, parking areas, traffic junction, slums etc. Maximum concentration was observed at traffic junctions ($305 \text{mg}/\text{m}^3$) which is attributed to vehicular Emissions and minimum concentrations were observed in residential areas ($1.88 \text{mg}/\text{m}^3$). Higher concentration was found at traffic junctions, parking areas, repair garages and petrol pump due to startup emissions of engines and the use of solvents for cleaning the parts.

Unlike Kolkata, no declining trend was observed in benzene concentration in Mumbai, which can be due to the industrial releases,

City	References	Methodology	Site	Concentrations
Delhi	Varshney and Padhy [56]	Grab Sampling (30 ml air tight hypodermic disposable syringe)	13 sites based on traffic volume & vehicle speed	TVOCs varied between 3 and 42 ppmv
	Padhy and Varshney [39]	Grab Sampling (30 ml air tight hypodermic disposable syringe)	13 sites based on traffic volume & vehicle speed	TNMVOC varied between 1.3 - 32.5 ppmv
	Srivastava et al. [57]	TO-17, CMB	Residential/commercial/industrial/traffic/petrol pumps	Major contributor were: diesel engine exhaust (~50%), vehicle exhaust (~23%), evaporative exhaust, degreasing, others
	Hoque et al. [45]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	Traffic/Commercial/Industrial/Institutional	BTEX: 456 ± 224 µg/m ³ (Traffic), 421 ± 222 µg/m ³ (Commercial), 411 ± 152 µg/m ³ (Industrial), 186 ± 107 µg/m ³ (Institutional)
	Khillare et al. [44]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	Academic cum residential/Commercial/Traffic site	Academic cum residential (Pre/Post CNG): 66 ± 17/59 ± 21 µg/m ³ Commercial: 118 ± 40/217 ± 52 µg/m ³ Traffic :152 ± 48/287 ± 64 µg/m ³
	Singh et al. [55]	Real time monitor	Petrol Pump/Residential/Traffic Site	Benzene: 8.9 ppm (Petrol Pump), 1.37ppm (Residential), 1.69 ppm (Traffic)
	Sehgal et al. [46]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	40 Petrol Filling Stations	Max. BTX(µg/m ³): 6406, 5890, 9512 (dry); 3372, 3905 and 12832(rainy)
	Singh et al. [47]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	Petrol Pump/Traffic/Commercial/Industrial/Residential	BTX (µg/m ³): 4.95-35.31/17.33-120.28/4.70 -29.13 petrol pump > traffic intersection > industrial > residential > commercial
Mumbai	Srivastava et al. [59]	Thermal desorption, GCMS	<ul style="list-style-type: none"> 35 outdoor locations (petrol pumps, slums, highways, parking areas etc) 10 indoor locations (air conditioned and non-air-conditioned offices, bedrooms, shops etc.) 	<ul style="list-style-type: none"> Outdoor VOCs: carbonyl compounds viz. aldehydes and ketones, polynuclear aromatic hydrocarbons, oxygenated hydrocarbons, amine & halogenated compounds Indoors VOCs: aliphatic, halogenated and aromatic hydrocarbons, alcohols, ketones & aldehydes; 13/80 OVOCS & 7/17 IVOCS are hazardous air pollutant
	Srivastava et al. [60]	Thermal desorption, GCMS	Residential/industrial/commercial/traffic intersections/petrol refueling stations.	Benzene conc. was higher in all the location
	Pandit et al. [41]	Grab Sampling (Tedlar Bags) n= 254, Factor Analysis (FA)	Residential/industrial/traffic junctions/commercial/petrol pumps/remote area	Contribution (%): Vehicular exhaust (33), Refinery (21), Petrochemical (15), Solvent (11), Polymer Industry (8), Unidentified Source (12)
Kolkata	Som et al. [53]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	In-vehicle/out vehicle in passenger car, traffic congested route	Road side mean Benzene conc(µg/m ³): 214.8 (phase1); 30.8 (phase2); Invehicle Conc: 721.2 (phase1); 112.4 (phase2)
	Majumdar et al. [54]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID, CALINE 4, CMB	3 busy traffic sites	<ul style="list-style-type: none"> 38.8–44.8% VehicleExhaust, Up to 37.9% Coal Combustion, other source (pesticides, wood combustion, printing)
	Majumdar et al. [25]	152 samples, Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	Combination of residential, commercial, small industries	Seasonal Mean Conc (µg/m ³): 13.8 - 72.0 (benzene); 21.0 - 83.2 (toluene); 7.6 - 21.6 (ethyl benzene); 22.1 - 57.3 (m-and p-xylene); 7.8 - 21.2 (o-xylene)
Agra	Singla et al. [55]	Activated Charcoal Tube, Desorption with CS ₂ , GC-FID	Road Side/Petrol Pump	BT, o-mX, p-X (µg/m ³): 14.7 ± 2.4, 8.1 ± 1.2, 2.1 ± 0.8, 5.1 ± 1.2 (Road side); 19.5 ± 3.7, 12.9 ± 1.1, 3.6 ± 0.5, 11.1 ± 1.5 (Petrol Pump)
Chennai	Mohan & Ethirajan [48]	TO- 17, n= 50, Thermal desorption, GCMS	Petrochemical complex	Mean Conc. :~17 µg/m ³ BTEX ratio: 1:2.6:0.3:0.2 to 1:9.5:2.1:1.4

Table 2: Summarization of VOCs studies in different cities of India.

a significant contributor in Mumbai, does not show any evidence of coming. Mixing ratios of carbonyls and BTEX in ambient air Kolkata during March to June 2006 were measured by Dutta et al. [51] The BTEX concentration in their study was lower than those observed in Delhi. Singh et al. [47] monitored BTX with activated charcoal tube using a portable constant low flow volume sampler (20-25 ml/min) for 150-180 minutes. They monitored at residential, commercial, industrial, traffic-intersection and near a gasoline filling station in Delhi during November 2010 – February 2011. This study indicates that the mean BTX concentrations at all sites were found higher than the limiting value prescribed by central pollution control board (i.e., 5 µg/m³, annual average for benzene). Two representative sites, a roadside and a petrol pump in Agra were chosen by Singla et al. [52] for the collection of BTX samples during April 2010-March 2011. The mean concentrations of benzene, toluene, o-, m-xylene, and p-xylene

were 4.9 ± 0.4 µg/m³, 2.7 ± 0.8 µg/m³, 0.69 ± 0.2 µg/m³ and 1.7 ± 0.2 µg/m³ respectively at roadside. Higher BTX concentrations at petrol pump were found to be statistically significant at 95% significance level and are presumably due to contribution from both moving vehicular traffic and petrol pump activities. Moreover, there is no legislation for VOC in ambient air in India. As per the National Ambient Air Quality Standard (NAAQS) of India, benzene is the only VOC whose standard has been prescribed as 5 µg/m³ since November 2009. Benzene concentration exceeds this limit in almost all the Indian studies [45,53]. These studies have given us a much better idea of the BTEX concentration and seasonal concentration in different metro cities of India (Delhi, Kolkata, and Mumbai). However, these studies represent only about the concentration of VOCs (BTEX) in different areas of the monitoring regimes.

City	References	Source Type	Observations
Delhi	Srivastava et al. [57]	Diesel engine exhaust (26-58%), vehicle exhaust (14-23%), evaporative exhaust (10-18%), auto repair (4-16%), degreasing (2-4%), natural gas (2-12%), others (2-6%)	<ul style="list-style-type: none"> • Dominated Source: Diesel internal combustion engine, need for developing • Source profile for Indian situations in order to have a more realistic source apportionment
Mumbai	Srivastava et al. [45]; Pandit et al. [41]	Evaporative emissions (60-70%), vehicle exhaust composite (11-33%), degreasing (2-20%), diesel internal combustion (4%), refinery (21%), others (4-7%),	<ul style="list-style-type: none"> • Refueling losses contribute to TVOCs • Need of vapor recovery system
Kolkata	Majumdar et al. [65]	Vehicle Exhaust (38.8-44.8%), Coal Combustion (up to 37.9%), other source (pesticides, wood combustion, printing)	<ul style="list-style-type: none"> • High emission factor values was due to higher avg. age of the vehicular fleet along with poor maintenance, old technology, bad road condition, and slow average vehicular speed

Table 3: Major sources identified across Indian studies.

Source Apportionment of VOCs

Receptor modeling is often used to estimate source contribution of VOCs. The most commonly used models include chemical mass balance (CMB), principal component analysis (PCA) /absolute principal component scores (APCS) and positive matrix factorization (PMF). While the multivariate receptor models (PCA/APCS and PMF) analyze a series of observations simultaneously in order to determine the number of sources, their chemical composition and their contributions to each observation, the CMB receptor model uses the ambient concentrations of the chemical species and source profile of different sources to estimate the contribution of each source to the pollutant [54-56]. In India, source apportionment studies have been performed in Delhi, Mumbai and Kolkata as shown in Table 3.

In Delhi, diesel internal combustion engines have been reported as a key source of with their contribution ranging between 26% to 58% of the total observed VOC concentration [57]. On the other hand, in Mumbai, evaporative emissions were found to be the dominating source ranging between 50% to 70% and vehicle exhaust contribute in the range between 11% to 20%. Pandit et al. [58] reported that vehicle exhaust emissions contribute approx. 33% to TVOCs using PCA. Similar results were noticed in the study conducted by Majumdar et al. [59] in Kolkata. This work concluded that the dominant source was vehicular exhaust emissions, which contributed 38.8% to 44.8% toward the TVOCs level. The emission factor of benzene for heavy, medium, and light vehicles was found to be 13.4, 21.0, and 31.2 mg vehicle⁻¹ km⁻¹ respectively. Majumdar et al. [56] studied the vehicular emission factors of BTEX in three different sites of Kolkata during December 2003 to February 2005, using CMB model to identify the sources and estimate their percentage contribution. The dominant source was vehicular exhaust emissions, which contributed 38.8% to 44.8% toward the TVOCs level. The emission factor of benzene for heavy, medium, and light vehicles was found to be 13.4, 21.0, and 31.2 mg vehicle⁻¹ km⁻¹ respectively. Srivastava and Majumdar [60] identified the major sources of VOCs in four metro cities of India - Delhi, Mumbai, Chennai, and Kolkata and reported highest evaporative emissions in Delhi followed by Chennai, Mumbai, and Kolkata. They concluded that vehicular emissions are the major contributors followed by other activities like paints, newspaper printing, computer printers, graphic art applications and consumer products. In India, more of the source apportionment studies must be carried out, which can be helpful in figuring out the major source and bringing down the VOCs concentration.

Conclusion

From the above studies it can be concluded that ambient VOCs show a clear seasonal pattern and found to be higher during winter months due to temperature inversion in Delhi and Kolkata. CMB receptor modeling which have been used in many studies estimated that the contribution to VOCs is not only from the road traffic but also

from other sources. Among the anthropogenic sources, transportation and biomass burning are the major sources [61-63]. Despite taking measures to control benzene content in gasoline, which is a known human carcinogen, the levels are rising again in Indian cities. Some of this data may not be very relevant as vehicle technology improves [64,65]. Therefore, we need better assessment of VOCs. Significant gaps noted during this review were as follows:

- Apart from BTEX, other harmful VOCs like 1,4-dichlorobenzene (1,4-DCB), and 1,1,1-trichloroethane (1,1,1-TCE) etc have not been given due importance.
- Despite the increasing attention devoted in the last years to characterize pollutant emissions, a comprehensive characterization of the VOC is still lacking in India.
- Lack of availability of VOC source profiles, and detailed emission inventories for VOCs.

There is a need for clear strategies for controlling evaporative emissions from refueling stations, storage tanks, underground tanks, etc. Further research is needed to emphasize on source specific exposure assessment studies [66], since this serves directly as the basis for exposure regulations and public health measures. For better understanding, accurate characterization of vehicular emission contribution is required.

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