RECENT TRENDS OF VOLATILE ORGANIC COMPOUNDS IN AMBIENT AIR & ITS HEALTH IMPACTS: A REVIEW

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Abstract: The global atmospheric pollutants present in the atmosphere are one of the representatives of volatile organic compounds (VOCs), which have their origin from both natural and anthropogenic sources but mobile sources particularly vehicles are recognized as a predominant source of emission. These compounds have both direct as well as indirect effects they make an essential involvement in the formation of photochemical smog & tropospheric ozone similarly they are known to be carcinogen BTEX are potentially toxic air pollutants among all VOCs. The exposure to high levels of these compounds may cause neuro-toxic symptoms mild exposure may cause irregular heartbeat, headache, dizziness, nausea etc. benzene is known as human carcinogen WHO estimates four in one million risk of leukemia on exposure to a concentration of 1 mg l /m3. About 50% of inhaled BTEX in air is absorbed in the body. Thus air toxics can pose special threats in urban areas because of the large number of people residing nearby roads facing heavy traffic especially in developing countries like India. Therefore, in this review we are summarizing various sources, sinks, national and international monitoring comparisons of these volatiles and their health impacts reported till date.
Keywords: Benzene, toluene, ethylbenzene, xylene, sources, carcinogen, VOCs, health impacts

1. INTRODUCTION

Volatile Organic Compounds (VOC's) are universal atmospheric species of both natural and anthropogenic sources including motor vehicle and other combustion processes consuming fossil fuels, petrol storage and distribution, solvent usage and other industrial processes [1]. The mono- aromatic volatile organic compounds like benzene, toluene, ethyl benzene, xylenes (BTEX), released to the ambient air, frequently take part in splitting and spreading between the environmental compartments like water, soil, vegetation etc. or it may involve partitioning between phases within an environmental compartment. VOC's present in air can affect in two ways direct & indirect. These are known for their carcinogenic nature and likely they play a role for secondary pollutant like O3 in troposphere. After VOCs are discharged into the atmosphere, they cause not only pollution problem on local scale but also play an important role on regional scale like acid rain, photochemical ozone formation introduced by the reaction with OH radicals in the troposphere in the presence of nitrogen oxides and sunlight and increased risk of cancer [2]. Moreover their environmental effects, VOCs also have many harmful effects to human health even at lower concentrations affecting different target organs e.g. central nervous system, respiratory system, liver, kidney reproductive system etc. [3,4]. VOCs in general have a positive correlation with severe symptoms of asthma among children [5]. Risk assessment for the toxic pollutants are broadly used in different countries as a monitoring decision making processes to which a population is or may be exposed to a certain chemical is determined, and the degree of exposure is measured in relation to the kind and degree of hazard posed by the chemical, thereby allowing an assessment of the probable health risk due to that chemical for the population involved. The human health risk assessment process includes exposure assessment that determines the amount and extent of the exposures and risk estimation [6, 7]. The major sources of air pollution include mobile sources, stationary sources and open burning sources. The former refers to traffic- related sources, including ground traffic (bus, private cars, taxi, motorcycle, etc.), underground traffic (metro or subway) and air traffic, and the latter is mainly industrial, commercial and personal emissions. The traffic related air pollution is the main source of air pollution, contributing to at least 70-75% of the total air pollution. Whereas emission from stationary sources generally have contributed to 20-25 % of the air pollution, while open burning and forest fires have contributed approximately 3-5% according to department of environment (DOE, 1996) [8].There is mounting evidence that air pollution has both acute and chronic health effects. In the short- term high levels of air pollution lead to an acute condition. While possible long-term health effects of exposure to air pollution are unknown and difficult to detect. The United Nations estimated that over 600 million people in urban areas worldwide were exposed to dangerous levels of traffic- generated air pollutants [9]. Air pollution and its public health impacts are represent increasing concern from the environmental regulatory agencies, industries, as well as the public. The outdoors air pollution is closely related to disorder and mortality from respiratory and cardiovascular diseases, asthma, influenza eczema, bronchitis, dry night- time cough, ear/nose/ throat infections and skin rash. Present data available in the literature shows that it is crossing the limiting value. Therefore there is need to do more systematic work in similar direction. In India it become more important because this country is in developing phase & in urban area there is very close proximity of residence and busy road is quite often. People residing in an urban area especially in India spend more time while commuting for their work and residence. Therefore it becomes more important to get the actual air quality parameters for Indian cities. In this present review we are briefly summarizing all work related to VOCs concentration and its health impacts.

2. SOURCES OF VOCS

Volatile organic compounds (VOCs) are existent in fundamentally all natural and synthetic materials, from gasoline to flowers, from water to wine. The uses of these multipurpose compounds are immeasurable, but include fuels, solvents fragrances, biocides and flavor constituents. VOCs frequently exist as vapors or liquid at room temperature but could also be in the form of solids (naphthalene and para-dichlorobenzene), used as mothballs and bathroom deodorants. A total of 17.9 million tons per year of man-made VOCs (excluding methane, which is relatively un reactive) were released by the OCED European countries in 1980. The value was comparatively close to that assessed for the USA in the same year (approximately 20 million tons) [10]. There are two varieties of all sources of VOC's i.e anthropogenic & Natural. Anthropogenic sources include man made sources like mobile transportation & stationary sources (industries) there details are as follows.

A. Anthropogenic source

These are further subdivided into following classes.

B. Mobile sources

The major source of VOCs emission by Mobile sources (such as motor vehicle) it includes road traffic (by the type of vehicle) like passenger cars light-duty trucks, heavy- duty trucks, motorcycles & also (by the type of fuel) such as gasoline diesel & other fuels (LPG, etc) it is reported that in the conjunction prone area produce more VOCs in the atmosphere and will affect the health of the people living in the multistory building near traffic road intersection area. Further there are several other mobile sources contain shipping (including harbors railways), railways, air traffic, off-highways (tractors etc.) [11]. In complete combustion of fossil fuel is known for the byproducts formation of benzene in the atmosphere. Therefore, traffic congestion always gives high value of benzene in the atmosphere & may affect climate & people living commuting through these places.

C. Stationary sources

The Stationary sources of VOCs like Non-industrial combustion sources include residential, commercial heating, district heating, and internal combustion engines. Other than this waste treatment and disposal includes incineration, storage, landfill, waste and waste water treatment etc. VOCs emission are also from some agriculture and food industry sources such as fermentation process, vegetable oil extraction, and agriculture open burning sources , fertilizers, animal farming (manure) additionally there are certain industrials combustion sources of VOCs production includes iron and steel industry , Non- ferrous metal, pulp and paper industry, Residential and commercial heating, district heating , internal combustion engines, storage and handling etc. they discharge VOCs during combustion process.

D. Natural sources

Natural sources of VOCs include volcanoes, vegetation and bacteria. But vegetation is the most abundant natural source of VOCs and increasing efforts are devoted to improving its determination. Release to the atmosphere occurs because VOCs present in the oil cells of plants are exuded as vapor into surrounding epithelial cells or intercellular spaces and reach the leaf surface through mesophyll and epidermal cells or through cuticles [12]. The types of hydrocarbon emitted by vegetation depend on the composition within the oil cell and may differ according to the plant family. The emission rate of each component is determined by the product of its concentration in the oil cell and the saturated vapor pressure. Since saturated vapor pressures follow a log-linear relationship with temperature, strong diurnal and seasonal variations in the flux of VOCs in the atmosphere are observed. Isoprene, terpenes, alcohols, carbonyl compounds and esters are the major components released by plant emission. Some of these can actively participate in photochemical smog pollution, being extremely reactive with OH radicals and ozone [13, 14, 15].

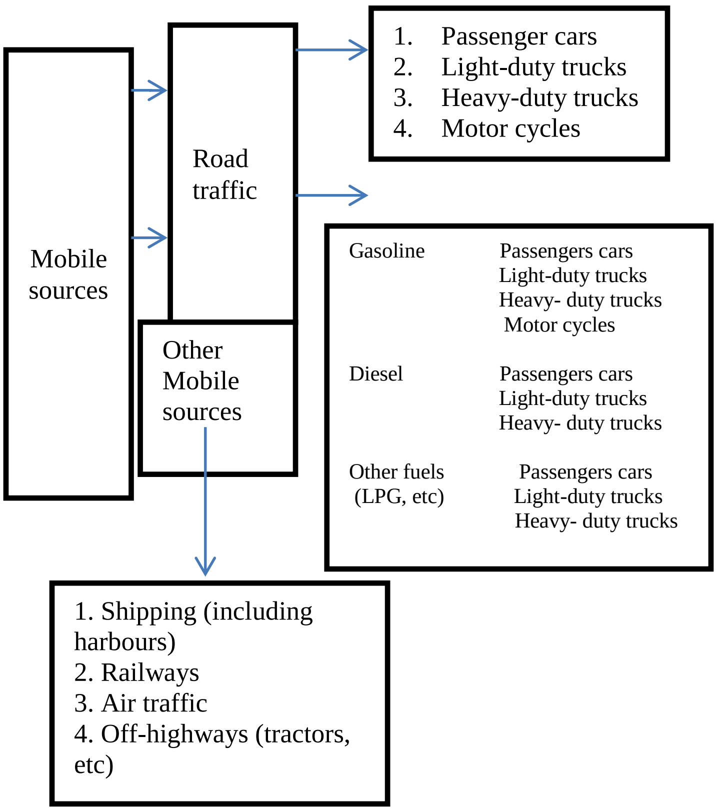

Fig. 1: Sources and sources categories used in the VOCs emission inventory prepared by the OCED for Western Europe after OCED (1990) [11].

3. SINKS OF VOCS

For most VOCs air is the main route of exposure. In some special cases, drinking water is an important route (e.g. chloroform from chlorinated water) for some natural VOCs, food and beverages are important routes (e.g. limonene, a natural component of citrus fruits but also a synthetic addition to soft drinks , teas, etc). Travel through soil has been hypothesized to be important in the case of homes or schools built on contaminated landfill.

4. NATIONAL AMBIENT AIR QUALITY STANDARDS FOR VOC'S

The National Ambient Air quality standards set by Central pollution control board (CPCB) , since 2009 these were summarized in Table-1 ,The 8-h and 1-Time weighted Average limits for ozone were (100,180), And annual Time weighted Average limits for benzene, Benzo (a) pyrene , were (05µg/m^3), (01 ng/m^3), respectively. It has to be noted that an exposure level lesser than the suggested or guiding standard does not mean that a life- long exposure at such level is nontoxic. Certain standards are 8-h based whereas others are 1-h based, still others are annual and 24- h based. In addition most of the standards were not well-known based on NOELs (No observed adverse effect levels) or LOAELs (lowest observed adverse effect levels).

Instead several aspects including economic feasibility and technical feasibility, have been considered in establishing these standards. So many of the standards particularly those regulatory ones, are much greater than their respective NOELS or LOELS. In addition, for many pollutants, due to inadequate pool of evidences, the standards may need to be improved based on new findings or new economic and technical feasibilities. For certain carcinogens, such as benzene, there seems no NOAELs or LOAELs for its carcinogenicity. The criteria for these carcinogens are generally established by considering feasibility and acceptability to the public. Attention has to be paid even when the exposure level of an air pollutant is lesser than NOAELS, LOAELS.

For one thing, human exposure to a pollutant has numerous sources other than via air, like water and food. In addition, commonly in ambient or occupational environment there are many corresponding air pollutants, some of which may have additive or even synergistic effects. For examples, both benzene and toluene can affect the central nervous system and they generally coincide with each other in the air due to numerous shared resources. Thus, it will be better if we consider this simultaneity while setting criteria for these pollutants [16].

TABLE-I. NATIONAL AMBIENT AIR QUALITY STANDARDS BY CENTRAL POLLUTION CONTROL BOARD (CPCB) 2009 [17].

Sno	**Pollutants**	**Time weighted Average**	**Concentration in Ambient Air**		
			Industrial, Residential, Rural and other Area	***Ecologically sensitive area***	***Methods of measurement***
1	Ozone µg/m^3	8- hour 1-Hour	100 180	100 180	UV photometric, Chemiluminescence, chemical method
2	Benzene µg/m^3	Annual	05	05	Gas chromatography (GC) based continuous analyzer Adsorption desorption followed by GC analysis
3	Benzo (a) pyrene	Annual	01	01	Solvent extraction followed by HPLC/ GC analyses

5. INTERNATIONAL AMBIENT AIR QUALITY STANDARDS FOR VOC'S

The US Environment protection agency (USEPA) has not recommended any standards for BTEX and other ambient VOCs. But the US Occupational Safety and Health Administration (OSHA,2004) established 1 ppm (3.19 mg/m^3) and 200 ppm (753.6 mg/m^3) 100 ppm (434 mg/m^3), 100 ppm (434 mg/m^3) as a 8-h work day or 40-h work week weighted average regulation limits for Benzene, Toluene, Ethyl benzene , Xylene respectively. These were summarized in Table-2.

TABLE-II. REGULATORY VALUES SET BY OSHA [18].

Pollutants	**Duration**	**Values**
Benzene	8-h work day or 40-h work week	1ppm (3.19mg/m3)
Toluene	8-h work day or 40-h work week	200ppm (753.6mg/m3)
Ethyl benzene	8-h work day or 40-h work week	100ppm (434 mg/m3)
Xylene	8-h work day or 40-h work week	100ppm (434 mg/m3)

TABLE-III. LIMITS OF AIR CONTAMINANTS OSHA STANDARDS: - [19].

Substance	8-hour time weighted average	Acceptable ceiling concentration	Acceptable maximum peak above the acceptable ceiling concentration for an 8-hr shift	
			Concentration	*Max Duration*
Benzene[(a)] (Z37.40-1969)	10 ppm	25 ppm	50 ppm	10 min
Toluene (Z37.12-1967)	200 ppm	300 ppm	50 ppm	10 min

The World health organization (WHO, 2001) Table -4 also has guidelines for BTEX but they are not a threshold value for benzene in terms of its carcinogenicity, only unit risk was provided. For PAHs, BaP can serve as an indicator and the risk slope for it was set at 8.7×10^{-2} $[\mu g/m^3]^{-1}$

Pollutants	Average Time	Guidelines
Benzene	NA	(4.4-7.5) $\times10^{-6}$ $[\mu g/m^3]^{-1}$
Toluene	1 week	260 mg/m^3
Ethyl benzene	1 year	22000 mg/m^3
Xylene	24 h	4800 mg/m^3
PAH (BaP)		8.7×10-2 [µg/m3]-1

6. MONITORING AND MEASUREMENTS OF BTEX

Air quality monitoring involves finding in a very minute concentration (ppb range) for numerous classifications of VOCs. This requires adequate sensitivity to trap the compounds of interest for successive analysis using suitable chromatographic technique [21]. Commonly two basic principles are existence monitored e.g., active sampling that contains pumping of controlled air flow into the sampler for a definite sampling period and subsequently air drawn-in is delivered through the adsorbent for adsorption of pollutant being monitored; however passive sampling is dependent on diffusion of pollutant from bulk air to the adsorbent directly. Thus the model adsorbents likely to have characteristics like large available pore volume, no catalytic activity, hydrophobicity, high thermal and hydrothermal stability and easy restoration properties. In general the research papers have mentioned activated charcoal as the adsorbing media, whereas there have been substantial studies towards cost effective alternative new materials like surface modified zeolites, product synthesized from fly-ash [21-22]. Target VOCs identified in USEPA a compendium method TO-14 or TO-7 were usually monitored using adsorption, thermal desorption and following analysis on GC-MS or GC-FID [22-23].So for the sake of simplicity we are further classifying the status of BTEX monitoring in the following two parts.

A. National status of BTEX

VOCs exposure study in India which presented very high level of BTX the values obtained in the range of 527.3/472.8/1265.5/402.8 [24]. A BTEX exposure assessment in ambient air of metropolitan city, Kolkata revealed that the consequences of BTEX emission were much higher than the acceptable value and range between 3.0×10^5 and 8.9×10^6 for benzene and ethyl benzene respectively and shows significant high level of BTEX. The prevailing Benzene & ethyl benzene level is estimated to pose a significant cancer risk to general city population. After air compartment, BTEX was found to be residing in soil followed by water with the total environmental load of BTEX as high as 9.7×10^4 kg [25]. Majumdar et al. [26], studied the exposure level of petrol pumps workers in Kolkata & found that the exposure of benzene & toluene were 3.9, 5.5 fold higher than that of ambient air. Recently,AK. Singh et al. [27] did the monitoring assessment and status of BTEX in urban area of Delhi; they revealed that the lowest values of BTX were observed at JNU whereas highest at Preet vihar location near vicinity of petrol pump. G Chattopadhyay et al.[28],determined BTX exposure assessment During three years in 1992, 1993, 1994 the BTX level in ambient air of Kolkata display values in the range of 1004,7082,491respectively these study revealed that primary source of high concentration of benzene are automobile exhaust and large number of coal burning stoves in Kolkata. Barletta et al. [29], revealed that Traffic-related VOC pollution has regularly been established to be a more serious problem in the developing countries than in the United States and Europe, as shown by the VOC data obtained in Karachi, Pakistan the values for BTX in the range of 16.6, 26.8, 8.2 respectively. Anjali Srivastava et al.[30],demonstrated the Concentration of total VOCs near traffic road intersection area the values in the range of 630,678,728 they found that values obtained for benzene at all location were much higher than the prescribed guidelines by World Health Organization (WHO) for ambient air quality. However all other VOCs level found to be below the WHO guidelines Assessment of BTX at Road side & petrol pump in Agra revealed that among BTX benzene has highest concentration [31]. Raza Rafiqul et al. [32], studied the Assessment of BTEX in urban atmosphere of Delhi in this study sampling locations were JNU, CP, AIIMS, Okhla out of these locations maximum average concentration of BTEX was found at site AIIMS while minimum at site JNU. These were summarized in Table-5.

TABLE –V. NATIONAL STATUS OF BTEX

Study	Year	Location	Sampling	Analysis	Subject or place	Pollutants	Level μg/m^3
D.Majumadar et al.	2011	Kolkata	Sorbent tubes containing activated charcoal (60-80 mesh)	GC-FID	Ambient air	BTEX (m,p,o-xylene)	29.2/45.4/13.1/32.9/11.9
Anjali Srivastava et al.	2006	Mumbai	Battery –operated air sampler (model-index PST 3000A)	GC-MS	Traffic intersection Worli naka Sion CST	Total VOCs	630 678 728
Mukherjee et al.	2003	Kolkata, India	Charcoal adsorbent tubes	GC-FID	Bus driver	BTX (o,p xylene)	527.3/472.8/1265.5/402.8
D Majumdar et al.	2008	Kolkata	Sorbent tubes containing activated charcoal	GC-FID	Petrol pumps	BTEX (m,p,o xylene)	137.5,643.6,118.0,209.7,68.2
Singh A.K et al.	2012	Delhi	Activated charcoal tubes	GC-FID	Roadside	BTX	9.385/29.085/8.9775
G Chattopadhyay et al.	1996	Calcutta	Coconut shell activated carbon traps	GC	Ambient air	BTX	1004/ 7082,/491
Barletta et al.	2002	Karanchi Pakistan	Canister sampling	GC-FID	Traffic street	BTX	16.6/26.8/8.2
Vyoma Singla et al.	2011	Agra	SKC-activated charcoal, SKC-personal sampler	GC-FID	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
Raza Rafiqul et al.	2008	Delhi	Activated Charcoal tubes	GC-FID	Ambient Air	BTEX JNU CP Okhla AIIMS	48 ,85, 7 ,30, 15 97, 180, 21, 83, 40 89, 204, 16, 61, 41 110, 191, 24, 90, 41

B. International status of BTEX

Volatile organic compounds are a class of air pollutants sharing the similar characteristic of high volatility in the ambient environment. Presently there are more than 300 different types of VOCs that can be identified by chromatography. The concentration of VOCs in the air is determined by such methods as emissions, evaporation, deposition, and photochemical reactions under the sunlight. Among traffic- related VOCs, aromatic compounds, including benzene, toluene, ethyl benzene, and isomers of xylene (BTEX), namely m-, o-, and p-xylene, have public health significance. In urban regions, these aromatic VOCs are largely released from traffic vehicles. Presently, traffic is a prime source of ambient VOCs in various urban areas in industrialized countries. Furthermore the dispersion of outdoor VOCs, indoor VOCs may also come from indoor tobacco smoking, household cleaning or degreasing, air freshening, domestic heating and cooking, painting, disinfecting, and varnishing, etc. Among the BTEX compounds, benzene has been extensively predictable as a human carcinogen (IARC, 2002) and the others also possess high toxicity, particularly to central nervous system in humans. So, this group of VOCs has received much consideration in exposure assessment studies. Control plans have been established to lower their levels in ambient air. Just like particulate matter, personal exposure of VOCs cannot be exactly estimated based on several micro environmental exposure levels and exposure time durations [33]. Batterman et al.[34], revealed the Exposure assessment from stationary monitoring sites cannot give the real exposure profile in urban areas, then the level of traffic VOCs reductions extremely as the distance from the main roads traffic increases, causing high spatial variations in the spreading of VOCs Indeed, the impact of industrial sources on VOC levels beside traffic road appeared insignificant .Representing that air VOCs were so much restricted to the small area around the source that even curbside levels were regularly establish to have lower concentration of VOCs than the middle lanes of the main roads. Certainly, in some studies comparing VOC exposures in several commuting modes, roughly the similar inference was reached: private cars or taxis were exposed to higher levels of VOCs than buses or trains [35, 36]. Such factors as traffic density, wind, temperature, and city buildings create the spatial variation even greater [37]. Due to the difficulties in directly evaluating these small-scale spatial variations, it is a favorable job to examine whether it is possible to find some traffic indicators as substitutes for traffic-related VOCs and NO2 exposures. Certain good results have been produced but their potential for generalization necessities to be validated in further studies [38]. In one study, traffic volume and the percentage of traffic jam were able to account for 0.76–0.80 of the variability in concentration changes of benzene, toluene, and ethyl- benzene. In addition, ambient VOC levels have clear seasonal variation and are higher in the winter season, as was observed in an exposure study in Greece [39, 40,41]. Wang et al. [42], revealed BTEX levels in ambient air of three cities in Southern China. Bravo et al. [43], studied the benzene & toluene level in Mexico City gave altered levels of benzene at different monitoring sites, some of which were slightly high the values in the range of 82.4,319.8 .Ten-year fixed site monitoring data of VOCs in Mexico City [44]. A study conducted in the US on traffic-related exposures between highway patrol troopers establish low levels of VOC exposures [45]. Gloria et al. [46], studied VOCs exposure assessment performed at a roadside urban station in Hong Kong shows significant high level of BTEX the values in the range of 4.85,28.8,3.113.98,2.85 respectively. Vo Thi Quynh Truc et al. [47], pointed out that most of these monitoring data are from fixed-site monitoring, whereas traffic-related exposure in traffic environment may be higher and pose a more serious danger to travelers and traffic-exposed employees. A Roadside BTEX exposure emission in Thailand shows a very high level of BTEX at two sites namely (DBP Street, NT Street) than TC Street. L.Y. Chan et al. [48], revealed VOCs exposure study performed at roadside microenvironments of metropolitan, Hong Kong shows a quite low level of BTEX & the values in the range of 26.7,77.2,3.1,12.1 respectively. Aykan Karademir et al. [49], studied Health risk assessment of BTEX emission in the landfill environment reveal that landfill BTEX emission do not pose a health threat to workers at the landfill site Vasu Tiwari et al. [50], shown Ambient levels of VOCs in the vicinity of petrochemical industrial area of Yokohama, Japan it was observed that aliphatic fraction was dominant at industrial site. Anna Jolanta Buczynska et al. [51].,studied the average BTEX (m,p,o- xylene) concentration before reconstruction works in 2003 were: 1.6,7.0,0.9,2.3,1.3 $\mu g/m^3$ respectively however after completion of work in 2005 they were slightly higher: 2.5,9.5,1.6,3.4,and 1.3 $\mu g/m^3$. A.A. Olajire et al. [52], indicated that, exposures to VOCs were very high for some occupations (petrol pump attendant and shoe stall salesperson). VOC concentrations measured at the studied locations are influenced by traffic and industrial activities .Mariusz Marc et al. [53], identified the BTEX concentration in ambient air by using diffusive passive air sampler the values obtained in the range of 0.87,2.91,1.3,5.9 respectively. Bae et al. [54], reported that shoe stall workers near traffic road intersection area were exposed by both proximity to roadways (outdoor sources of pollution) as well as by the materials they use for their trait (solvents, polish and adhesives as indoor sources) A study evaluated the exposure assessment of Public bus driver and Taxi-cab driver revealed that the Taxi-cab driver exposed to significantly high level of VOCs then the public bus driver [55]. Workers from five different occupations like traffic police officer, parking garage attendant, service station attendant, roadside storekeeper and underground storekeeper are exposed to highly-elevated aromatic VOC levels during work [56]. JE Colmam Lerner et al. [57], detected VOCs in occupational environment revealed that highest concentration of VOCs emitted from electrochemical repair & car painting Centre followed by chemical analysis laboratories & sewing work room .Ki-Hyun Kim et al. [58], identified BTEX levels by using GC-FID-TD between the four urban sites indicated that their distributions are tightly affected by local source processes in each area. Recently Lei Li et al. [59], indicated that the air pollution of BTEX in the urban area in China was more serious than the cities in other countries. Daniel Sanjuan et al. [60] revealed BTEX emission from wineries was 52 ng m^{-3} in the working ambient air. Gulcin Demirel et al. [61], demonstrated that exposure of BTEX was found to be higher for the students living at the urban traffic site. Recently Wei Wei et al. [62], revealed that Benzene & Toluene emitted from petroleum refinery in Beijing shows value in the range of 7.8%, 5.9% respectively. Rabah Ketbachi et al. [63], Compared to US & European cities Algiers show serious problems of air pollution particularly in high traffic areas where the benzene regulatory limit value of 10 $\mu g/m^{-3}$ is largely exceeded. Tran Thi Ngoc Lan et al. [64], identified that Motorcycles are the biggest contributor to BTEX pollution in HoChiMinh These were summarized in Table-6.

TABLE-VI INTERNATIONAL STATUS OF BTEX

Study	Year	Location	Sampling	Analysis	Subject or place	Pollutants	Level $\mu g/m^3$
L.Y. Chan et al.	2002	Hong Kong	Tekmar stainless-steel multi-sorbent tubes	GC/MSD	Roadside	BTEX	26.7/77.2/3.1/12.1
Aykan Karademir et al.	2009	Turkey	Stainless –steel tubes filled with carbograph TTD.	TO-17	Landfill	BTEX	140.3/1271.7/239.9/341.3
AnnaJolanta Buczynska et al.	2009	Antwerp, Belgium	Radiello diffusion tubes	GC-MS	Street traffic	BTEX Before construction After construction	 1.6,7.0,0.9,2.3,1.3 2.5,9.5,1.6,3.4,1.3
Vo Thi Quynh	2007	Thailand	SKC charcoal tubes	GC-FID	TC Street	BTEX (m,p,o-	65/62/15/43/22

Truc et al.					DBP Street NT Street	xylene)	123/87/24/56/30 123/87/24/56/30
Lirong Zhao et al.	2004	China	Tekmar stainless-steel multi-sorbent tubes packed with tenax and carbonsieve S-3	GC/MSD	Urban street	BT	44.7 / 79.7
Vasu Tiwari et al.	2010	Japan	10-L Flek polyester bags	GC-FID	Industrial area	BTEX	25.52/27.80/31.45/ 31.81
Huixiong Lu et al.	2006	China	Stainless steel canister	GC/MSD	Hospital of Guangzhou	BTEX	463 /252 /476 /250
Wang et al.	2002	China	Multi bed adsorbent tubes	GC/MSD	Guangzhou Macau Nanhai	BTEX BTEX BTEX	51.5/77.3/17.8/81.6 34.9/85.9/24.1/95.6 20.0/39.1/3.0/14.2
Bae et al.	2004	Seoul,Korea	Activated Charcoal Tubes	GC/MS	Shoestall sales person	BTX	732/6777/5382
Jo and Yu	2001	Taegu, Korea	Tenax traps	GC	ETS bus driver Non- ETS bus driver ETS taxi driver ETS taxi driver	BTEX BTEX BTEX BTEX	28.1/88.7/8.1/30.2 14.5/49.5/7.0/21.4 44/141/10.2/37.3 24.8/80.8/8.8/23.6
Jo and Song	2001	Taegu, Korea	Tenax traps	GC/FID	**Traffic policemen** Smoker Non- smoker **Gas station attendant** Smoker Non- smoker	BTEX BTEX BTEX BTEX	35.3/114/7.8/22.1 24.2/125/7.7/27.2 84.4/141/12.9/55.1 72.1/126/12.1/50.7
Bravo et al.	2002	Mexico	Canister sampler	GC/FID	Gas station	BT	82.4/319.8
Lau and Chan	2003	Hong Kong, China	Tekmar stainless-steel adsorbent tubes packed with tenax and carbonsieve S-3	GC/MSD	Non-A/C bus A/C bus Taxi	BTEX BTEX BTEX	4.8/54.3/3.1/6.2 6.1/72.9/6.9/15.5 5.9/43.5/4.4/7.8
Gomez- Perales et al.	2004	Mexico	Canister sampler	GC-FID	Mini bus Bus Metro	Benzene Benzene Benzene	22 19 13
Bono et al.	2003	Biella and Torino, Italy	Charcoal adsorbent tubes	GC-FID	Gas pump attendant Policemen Policemen	Summer BTX Winter BTX Summer BTX Winter BTX	503/712/379 161/568/285 31/215/73 21/144/150
Gonzalez-Flesca et al.	2000	Rouen , France	Personal Sampler	Passive Sampling	Non- smoker	Benzene	10.3
Batterman et al.,	2002	Detroit, USA	Stainless-steel adsorbent tubes packed with Tenax and Carbonsieve S -3	GC-MS	Bus Patrol trooper	BTEX BTEX	4.5/10.2/9/2.1 4/10.4/0.9/4.5
Gloria M.Y. Chiu et al.	2002	Hong Kong, Chiu	Canister Sampler	GC/MSD	Roadside	BTEX (m,p,o xylylene)	4.85/28.81/3.11/3.98/2.8 5
A.A. Olajire et al.	2013	Nigeria	sorbent tubes containing activated charcoal	GC-FID	Roadside (Hong Kong) Thailand China	BTEX (m,p,o) BTEX (m,p,o) BT	3.0/26.2/3.2/4.0 12.7/72.8/6.0/25.7/13.6 44.7/79.7
Mariusz Marć et al.	2013	Tczew, Poland	Diffusive passive sampler Radiello	TD-GC-FID	Ambient air	BTEX	0.87/2.9/1.3/5.9
JE Colmam lerner et al.	2012	Argentina	Passive diffusion monitor (3M-3500)	GC-FID	Occupational Environment	BTX (p,o) E+M	0.18,1.11,0.38,0.49,0.50
Ki-Hyun Kim et al.	2012	Korea	Carbonsieve adsorption traps	GC-FID-TD	Ambient air	BTEX(m,p,o)	0.47,92,0.42,0.51.0.17
Lei Li et al.	2014	China	Canister sampling	GC-MS/FID	Ambient air	BTEX(m,p,o)	1.72,5.41,1.19,2.09,0.53
Daniel Sanjuan –Herraez et al.	2014	Spain	VERAM Passive sampler	GC-MS	Wineries	BTEX (m,p,o ng)	29,15,9,5,14
Gulcin Demirel et al.	2014	Turkey	Passive sampler	GC-MSD	Ambient air	BTEX Personal Indoor	1.68,26.23,0.70,11.2,0.8 2.29,26.55,0.73,1.13,0.82

						Outdoor	1.23,6.11,0.26,0.47,0.38
Wei Wei et al.	2014	China	Summa Canister	GC-MS	Petroleum refinery	BT	7.8 %, 5.9%
Rabah Kerbachi et al.	2006	Algeria	Tenax solid-adsorbent	GC-MS	Ambient air	BTEX (m,p,o) Roadside Urban Semi-rural	 27.1, 39.2, 6.3, 19.2, 7.6 9.6, 15.2, 0.9, 3.2 6.5, 13.7, 0.8, 4.4
Tran Thi Ngoc Lan et al.	2013	Vietnam	Activated charcoal tubes	GC-FID	Ambient air	BTEX (m,p,o)	56, 121, 21, 64 , 23

7. NATIONAL LEVEL HEALTH IMPACT STUDIES OF BTEX

Benzene and ethyl-benzene are well known carcinogens Benzene can also affect hematopoietic system, the central nervous system and the reproductive system. Toluene can affect the reproductive and the central nervous systems too. Ethylbenzene and xylene can have respiratory and neurological effects Among the BTEX compounds benzene has been established as a human carcinogen both by International Agency on Research on cancer (IARC) and American conference of Governmental Industrial Hygienist (ACGIH) [65].various VOCs are included in the list of 188 hazardous air pollutants (HAPs) recognized by USEPA. (HAPs) are the pollutants identified or suspected to cause cancer or other severe health effects or adverse environmental effects. HAPs have a likely to partition into different components of environment, and certain of them have significantly long lifetime in one environmental component or other making them persistent in ecosystem. Persistence is an essential characteristic for determining complete human health and ecological impact of a chemical released to the environment. Persistent pollutants pose a greater possible concern per unit release since they cannot be rapidly removed from the environment. An appropriate quantity of persistence is the characteristic time a chemical remains in the environment. This can theoretically be determined by finding the total decay rate of a pollutant in a closed defined background structure, calculation of which contains both mass distribution among environmental media and media specific half- life. HAPs hazardous air pollutants have different kinds of human health effects, carcinogenic and non- carcinogenic, depending upon the chemicals contain concentration and exposure time. Some of them have both toxic and carcinogenic effect. The toxic effect can be acute (short -term severe health effect) or chronic (Long-term persistent health effect). Toxicity is frequently marked in a shorter length of time than the carcinogenic effect. The possible health effects of non-carcinogens range from skin irritation to life- shortening. Carcinogens cause or proliferation the occurrence of malignant neoplasms or cancers. Risk characterization integrates the information on hazard identification, dose response assessment and exposure assessment to develop a qualitative and quantitative assessment of the possibility that any of the hazards related with the chemical will be realized in exposed people. Risk score scheme helps to detect environmental releases of toxic chemicals that are probable to pose larger risk to human health. This system adjusts the amount of chemical that is released [66,67].The cancer risk calculated in the present study suggests the exposure level to be extreme from being safe for population residing for 15 years in the city. In all the three sites, the assessed cancer risk is more for benzene due to its carcinogenicity. Assessed cancer risk for all the individual components (except ethyl benzene) exceeded the threshold value of 1×10^{-6} demonstrating significant cancer risk. A study conducted in Kolkata estimated the ambient air quality at five busy petrol pumps by using Chemical Mass balance software (CMB 8.2) recognized exhaust level from roadway and refueling station. Monitoring of the service station workers revealed that the average exposure level for benzene and toluene were 3.9, and 5.5 fold higher than the ambient air. The integrated life time cancer risk due to benzene, ethyl benzene, formaldehyde and acetaldehyde and overall hazard index due to chronic exposure to some hazardous Volatile Organic Compounds are 1.48E-04 and 2.3 signifying the possibility of cancer as well as chronic health effect on the workers exposed [68].A study conducted in Calcutta estimate the life time cancer risk for the population residing in Calcutta for determination of cancer risk, carcinogenic potency of benzene has been used as 7.3×10^{-6} per µg m^{-3}[26].However one must note that at high concentration linear extrapolation of the data becomes unreliable therefore the estimates are indicative only. Mutagenicity assessment of BTX was performed on two strains of Salmonella typhimurium revealed that Extracts of samples were positive in both tester strains TA98 and TA100 without metabolic activation signifying the existence of direct mutagens in ambient air that can cause both frame-shift and base-pair mutation. The mutagenic response was greater for TA100 than TA98 suggesting greater activity for base-pair mutagenicity than frame-shift mutagenicity and was found to be statistically significant [31].

8. INTERNATIONAL LEVEL HEALTH IMPACT STUDIES OF BTEX

Constituents of smoke haze, including BTEX are known carcinogens the effects of which may not be apparent for years. The significances may be more severe for children for whom the particulates inhaled are high in relation to body weight [70], a fugacity based multimedia mass balance model, TAPL3 has been successfully used to determine whether the pollutant can have a local, regional or global scale impact this model mathematically calculates the environmental persistence; travel distance in air (long range transport potential or LRT) and the percentage distribution of the target pollutant in five well mixed environmental compartment namely air, water, soil, sediment and vegetation. This simulation tool uses a default value for the total emission of 1000kg/h into a single mobile medium (air or water) and returns the total environmental load in the system. In this study the significance of BTEX emission towards human health has been assessed in terms of non-cancer and cancer risk in population due to their inhalation exposure. The increasing lifetime cancer risk for Benzene and ethyl benzene was found to be higher than the tolerable value and range between 3.0×10^{5} and 8.9×10^{6} in three sites, while the non-cancer health risk was found to be within tolerable limit. The concentration of BTEX were found to be quite high in the present study and their levels could be a real hazard to the health of the city residents gives the average daily exposure, individual hazard quotient (HQ) and ILTCR (for 15 years residence time for an individual).According to WHO the lifetime risk of chronic leukemia for benzene exposure of $1\mu/m^3$ is $4.4\text{-}7.6\times10^{-6}$[25, 68]. Whereas ethyl benzene is classified as a group D carcinogen [71].A study conducted in Thailand estimate the cancer risk of BTEX exposure among gasoline station workers The mean BTEX concentration in gas stations was slightly higher than that of the roadside; there was no significant difference in the concentration between inner and outer areas. The mean lifetime cancer risks for workers exposed to benzene and ethyl benzene for 30 years were estimated as 1.75×10^{-4} and 9.55×10^{-7}. The estimated hazard quotients for BTEX compounds were 0.600, 0.008, 0.007 and 0.002, respectively. The most predominant symptoms of workers were headache (61%), fatigue (29%) and throat irritation (11%), respectively. Exposure to benzene and toluene was significantly associated with fatigue ($p<0.05$)[72] during pregnancy for a doubling the concentration of benzene The risk of lymphomas increased by 25% (p for trend = 0.06) [73].Estimated daily average exposure concentration of BTEX (m,p,o) were 1.45E-03, 2.93E-03, 1.01E-03, 1.73E-03, 7.58E-04 respectively and the corresponding hazard quotient were 1.57E-01, 2.39E-02, 3.29E-03, 8.06E-03, 3.53E-03 the integrated life time cancer risk(ILTCR) of benzene was 4.19E-05 the assessed values indicating significant cancer risk[74]. Life time cancer risk for Benzene higher for electrochemical repair and car painting Centre followed by chemical analysis laboratories and sewing work rooms were 1.44E-04, 8.71E-05,<2.43E-06 respectively. The values obtained greater than 1 for benzene representing Hazard Quotient (HQ) only for electrochemical & car painting Centre [57]. The cancer risk of benzene was 1.34E-05, which indicates that benzene has potential cancer risk to exposed population [59]. The mean cancer risk for the urban school children (1.7×10^{-5}) was found to be higher than the sub- urban school children (0.88×10^{-5}) children living with smoking parents had higher risk level (1.7×10^{-5}) then the children living with non-smoking parents (1.08×10^{-5}), overall risk levels were $< 1\times10^{-4}$ [61].

9. CONCLUSION AND RECOMMENDATIONS

The literature scanned revealed that in developed countries the main source of BTEX emissions are industrial followed by motor vehicles etc. but in developing countries like India its emission is mainly by motor vehicles in the ambient air. This could be the reason they have standards of BTEX for industrial areas like OSHA. Similarly in India we have standards for ambient air issued by CPCB. Although literature clearly indicate that its crossing the limiting value. This may be because of fuel quality, vehicle type and above all road condition and transportation planning congestion free roads. Therefore it is recommended that government and policy maker should focus on fuel quality, road maintenance etc. So, based on these observations especially in mega cities like Delhi the traffic planner and policy makers should reassessed the guidelines there is urgent need of more systematic study for the exposure assessment because it is still on higher sides. Therefore, it is a matter of concern that government should take immediate action to control VOCs especially BTEX in urban area Necessary and effective emission reduction strategies are required to be developed in order to curb the surface level of volatile organic compounds and hence ozone pollution to protect human being from various harmful effects.

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