

BTEX in Ambient Air of a Metropolitan City

D. Majumdar (née Som)¹, A. K. Mukherjee², S. Sen¹

¹Department of Chemistry, Calcutta University, Kolkata, India; ²Regional Occupational Health Centre (Eastern), Kolkata, India.
Email: dipanjalisom@gmail.com

Received September 29th, 2010; revised November 11th, 2010; accepted December 20th, 2010.

ABSTRACT

The environmental fate, global warming effect and human health risk from mono aromatic VOCs are of major concerns among many consequences of their anthropogenic emission. In more than a yearlong study (November 2003 to February 2005) of the city air in Kolkata, India at different seasons in three different sites, the seasonal mean benzene and toluene concentrations varied between 13.8 - 72.0 $\mu\text{g}/\text{m}^3$ and 21.0 - 83.2 $\mu\text{g}/\text{m}^3$ respectively along all the sites. The environmental distribution and load of BTEX (Benzene, Toluene, Ethylbenzene and isomers of Xylene) in different environmental compartment was estimated using a multimedia mass balance model, TaPL3. The total environmental load of BTEX together was estimated to be 9.7×10^4 kg. Contribution of Kolkata metropolitan city towards global warming due to environmental emission of BTEX has been estimated as 1.9×10^5 tons of carbon dioxide equivalent per year which is about 1.1% of yearly direct CO_2 emission the city. The consequence of BTEX emission towards human health has been estimated in terms of non-cancer and cancer risk in population due to their inhalation exposure. The cumulative lifetime cancer risk for benzene and ethylbenzene was found to be higher than the acceptable value and range between 3.0×10^5 and 8.9×10^6 in three sites, although the non-cancer health risk was found to be within acceptable limit.

Keywords: Multimedia Mass Balance, Seasonal Variation, Global Warming, Health Risk, Kolkata

1. Introduction

The fate of a chemical in the environment is controlled by its physico-chemical properties, the nature of introduction of the chemical in the environment [1] and also by the environmental conditions. Volatile organic compounds (VOCs) are omnipresent in lower urban atmosphere. Various typical anthropogenic activities like intense transportation, industrial and commercial activities prevailing in urban areas particularly in metropolitan cities [2-4] in addition to natural emissions are responsible for elevated VOC levels in urban air [5].

The mono-aromatic volatile compounds like benzene, toluene, ethylbenzene, xylenes (BTEX), emitted to the ambient air, constantly take part in partitioning and distribution between the major environmental compartments like water, soil, vegetation etc. or it may entail partitioning between phases within an environmental compartment [6].

Multimedia mass balance models are simple mathematical descriptions of the natural environment designed to gain qualitative and quantitative understanding of the environmental distribution and fate of chemicals. These models can be effectively used to describe the fate of the chemicals such as VOCs in different subdivision of en-

vironmental compartments having homogeneous environmental characteristics and chemical concentration by integrating information of multiple and interacting process of partitioning, transport and transformation [1,7-9]. Several models and software packages have been developed and efficiently used for assessing chemical fate in the environment on a regional scale, e.g., EUSES and ChemCAN in Japan [10]; QWASI in West Yorkshire, United Kingdom [11]; TaPL3 in Mumbai, India [12].

Worldwide rapid urbanization, industrialization and consumerism are resulting in increasing emission of CO_2 and other Green House Gases (GHGs) along with VOCs. The most significant increase of energy consumption and GHG emissions are taking place in metropolitan cities which have rapidly expanding populations enjoying higher living standards and material affluence than the people living in rural areas and smaller cities [13]. VOCs are considered as contributors to global warming by Intergovernmental Panel for Climate Change (IPCC) because of their chemical reactivity and their potential to produce tropospheric ozone and other photochemical oxidant. Metropolitan cities thus have significant contribution towards the total national as well as global emission of GHGs including CO_2 and VOCs. Although the yearly CO_2 emission load for Kolkata is reported [13] but

neither a comprehensive VOC emission inventory is available nor the global warming consequences of VOC emission of any city have ever been estimated.

Besides their environmental effects, VOCs also have many harmful effects to human health even at lower concentrations, affecting different target organs e.g. central nervous systems, respiratory system, liver, kidney, reproductive systems etc. [14,15]. The VOCs, in general, have a positive correlation with severe symptoms of asthma among children [16]. Many of these especially benzene has been confirmed as human carcinogen both by International Agency on Research on Cancer (IARC) and American Conference of Governmental Industrial Hygienist (ACGIH).

Risk assessments for the toxic pollutants are widely used in different countries as a regulatory decision-making processes to combat air pollution. In a risk assessment, the extent to which a population is or may be exposed to a certain chemical is determined, and the extent of exposure is considered in relation to the kind and degree of hazard posed by the chemical, thereby permitting an estimate of the potential health risk due to that chemical for the population involved [17]. By performing non-cancer and cancer risk assessment, the extent of the possible health damage of the general population due to environmental exposure to VOCs can be assessed. The human health risk assessment process includes exposure assessment that determines the magnitude and duration of the exposures and risk estimation. The likelihood of adverse effects on direct human exposure via inhalation is understood from risk estimation [18].

In the present study, the ambient seasonal concentration of BTEX in a metropolitan city, namely Kolkata, India, have been measured to estimate the total elevated environmental load of these target VOCs utilizing TaPL3 multimedia mass balance model. Contribution of Kolkata metropolitan city towards global warming due to its environmental load of BTEX has been estimated as carbon dioxide equivalent. Estimation of non-cancer health hazard as well as integrated lifetime cancer Risk (ILCR) due to the inhalation exposure of the general city population towards BTEX was also made.

2. Methodology

2.1. Study Area

Three monitoring sites, was selected geographically for ambient air sampling. All the sites were a combination of commercial and residential area with several small-scale industries scattered intermittently. The details of the three sites, Site N in Northern Kolkata, Site C in Central Kolkata and Site S in Southern Kolkata, are as follows:

Site N: Situated in North Kolkata at ~10 m away from the main arterial road connecting North and South Kolkata at a height of 5 m. Mainly residential and some commercial activities were prevailing in the surrounding area.

Site C: Situated in the Central Kolkata at about 5m height at a distance of ~5 m away from the major road connecting Central Kolkata to the city railway station. There was an open ground with greeneries in front of the sampling site at other side of the road. The surrounding areas were mainly used for commercial purposes along with some residential activities. Minor small scale industrial activity can also be noticed in the adjacent area.

Site S: Located in South Kolkata at a height of about 7 m and ~5 m away from a major road connecting southern and eastern part of the megacity. The area around the sampling site was populated with various small and medium scale industries. Some commercial and residential activities were also noticed in the adjacent area.

Transportation activity was prominent in all the three sites same as in the rest of the city.

2.2. Sampling Period

Air sampling was performed at the selected sites (Site N, C and S) in dry seasons during the period from December 2003 to February 2005. The monitoring were done in winter (December '03 - February '04 & December '04 - February '05), summer (March '04 - June '04) and post monsoon (September '04 - November '04). The monitoring was continued up to the next winter. 15-18 samples per season (except in winter '03 - '04; 9 samples) were collected in each site with a total of 152 samples.

2.3. Sampling Procedure

Air sampling for VOCs were conducted at the selected sites between 9:00 AM and 6:00 PM. VOCs were collected in sorbent tubes containing activated charcoal (60-80 mesh), spread in two compartments (100/50mg) by drawing air through a constant flow low volume pump (SKC, USA) at a rate of 0.1 LPM or less for about 4-5 hours each.

2.4. Determination of BTEX

The charcoal was desorbed in 1 ml of carbon disulfide (CS₂) for 1-1.5 hour and analysed for benzene, toluene, ethylbenzene, and three isomers of xylenes. Quantification was done on a Gas Chromatograph (Perkin Elmer, Auto System XL GC) equipped with a Flame Ionization Detector. Separation of the analytes was achieved by PE 624 (Perkin Elmer) capillary column, isothermally at 100°C. Detector and injector temperature were maintained at 200°C and 180°C respectively.

The samples were quantified against five-point calibration curve prepared from standard pure substances (Aldrich, USA) at different dilutions in CS₂ containing each of the six analytes. Fluorobenzene was used as internal standard to avoid injection error and error from trace benzene content in the solvent.

2.5. Quality Control

Duplicate measurements were done for 10% samples using dual holders of which the analytical results were highly correlated ($r^2 = 0.99$). Sampling flow rates of all the pumps were determined using Ultra-flo Calibrator (SKC Inc. USA) before and after sampling. Field blank test and breakthrough test were done to ensure quality control.

3. Calculations

3.1. Determination of Multimedia Partitioning, Persistence and LRT of BTEX

The percentage distribution of the target pollutant in five well mixed environmental compartment namely air, water, soil, sediment and vegetation can be predicted along with their long-range transport (LRT) potential and overall environmental persistence using TaPL3 model (software copyright 2000, version 3.0, Canadian Environmental Modeling Centre). This simulation tool is a fugacity-based Level III multimedia mass balance model [16] that uses a default value for the total emission of 1000 kg/h into a single mobile medium (air or water) and returns the total environmental load in the system. The probable emission of the target VOCs in the system under examination is estimated from the actual environmental load as calculated from measured concentration in air assuming a linear relationship between the two. Required input for the model used in the simulation for the target pollutant is given in **Table 1**.

3.2. Determination of Global Warming Consequences of BTEX

BTEX are non methane volatile organic compounds (NMVOC) and they have two fold contributions towards climate change [25,26].

1) The primary contribution arises from their indirect chemical effect on the atmosphere. VOCs influence climate through production of organic aerosols and their involvement in photochemistry, *i.e.*, production of O₃ in presence of NO_x and sunlight [27].

2) The secondary contribution is due to the eventual production of CO₂ from the atmospheric degradation of the VOC and determined by the amount of carbon pre-

sent therein.

The CO₂ equivalent emissions arising from 1) is given by:

$$CO_{2\text{primary}} = GWP_{\text{voc}} \cdot m_{\text{voc}} \quad (1)$$

Where, CO_{2primary} is CO₂ equivalent in tons, m_{voc} is the number of tons of the VOC emitted and GWP_{voc} is the indirect Global Warming Potential (GWP) for the particular VOC species. The GWP of a VOC species compares the radiative forcing of a ton of a GHG over a given time period (say, 100 years) to a ton of CO₂ [25]. Estimation of GWPs requires complicated calculation involving powerful models and the values for many VOCs have been reported by the Intergovernmental Panel on Climate Change [27]. Unfortunately, the GWPs of BTEX are not available and an indirect GWP value of 10 is assumed for each of them [26] in our calculation.

The secondary CO₂ equivalent emissions arising from (2) depends on the number of carbon atoms in the VOC, its molecular weight and the mass of the VOC released.

$$CO_{2\text{secondary}} = 44 \cdot n_{\text{voc}} \cdot m_{\text{voc}} / MW_{\text{voc}} \quad (2)$$

Where, n_{voc} is the number of carbon atoms in a molecule of the VOC, MW_{voc} is its molecular weight in g/mole and $CO_{2\text{secondary}}$ is in tons of CO₂ '44' refers to the molecular weight of CO₂.

Thus the total CO₂ equivalent emissions (in tons) arising from the direct release of the VOC is

$$CO_{2\text{equiv}} = CO_{2\text{primary}} + CO_{2\text{secondary}} \quad (3)$$

3.3. Determination of Inhalation Exposure and Risk

In the current study, the non-cancer hazard and integrated life time cancer risk (ILCR) due to the exposure to a few VOCs at their prevailing level were estimated. The daily exposure (E) of an individual due to intake process (considering inhalation only) was calculated from the Equation (1) [18]:

$$E = C * IRa * EDa / BWa \quad (1)$$

The chronic non-cancer hazard index was estimated using daily exposure E. The integrated lifetime cancer risk (ILCR) upon an individual for residing in the area for 15 years was estimated from the effective life time exposure, E_L (Equation (2)).

$$E_L = E * (D/7) * (WK/52) * (YE/YL) \quad (2)$$

The description of the variables used here is tabulated below.

Table 1. Chemical and environmental parameters for running TaPL3 simulation.

Chemical parameters						
VOC pollutant		Benzene	Toluene	Ethylbenzene	Xylene	
molar mass	(g mole ⁻¹)	78	92	106	106	
Vapour Pressure ^a	VP (Pa)	12672.2	3769.3	1276.7	1074.0	
Octanol-carbon partition co-efficient ^a	K _{oc}	55.1	139	228	271	
Octanol-air partition co-efficient ^b	K _{oa}	465	1471	3080	3245	
Octanol-water partition co-efficient ^a	K _{ow}	150	480	1300	1300	
Dimensionless Henry's law constant ^c	K _h	0.289	0.325	0.422	0.357	
Partition co-efficient (dimentionless) ^d	water-air	4.35	3.76	3.02	3.61	
	soil-air	47.7	150.8	315.7	332.6	
	sediment-air	47.7	150.8	315.7	332.6	
	suspended particles-air	473.5	1591.8	4699.6	5586.4	
	Fish-air	23.3	73.6	154.0	162.3	
	aerosol-air	473.5	1591.8	4699.6	5586.4	
	vegetation-air	6.0	12.4	23.2	27.4	
	Half life (h) in ^a	Air	141.8	57.1	47.0	23.3
		Water	267.6	312.0	156.0	420.0
		Soil	4564.8	682.3	156.0	362.4
Sediment		5359.0	2568.0	2772.0	4404.0	
	vegetation ^e	1000	1997.12	1000	1000	
Environmental parameters						
System Area ^f		1785.0	km ²			
Area of water ^f		59.2	km ²			
Vegetation fraction of total area ^f		0.35				
Mixing height		400	m			
Wind velocity		2.0	km h ⁻¹			
Water velocity		0.5	km h ⁻¹			

^aDatabase available with CalTOX™, Version 1.5 [19]. ^b[20] ^c[21]. ^dCalculated [22]; except for fish-air partition coefficient (K_{FA}), K_{FA} = V_L × K_{oa}, where V_L is the volume fraction of lipid in fish. ^eDue to in non-availability of data, half life of 1000 hour has been assumed for benzene, ethylbenzene and xylene in vegetation compartment. Value for toluene was calculated from Foster *et al.* [23]. ^f[24].

Variable	Description	Value	Units
E	Daily Exposure		mg/kg/day
C	Concentration of the pollutant		mg/m ³
IRa	Inhalation rate, adult	0.83*	m ³ /hr
EDa	Exposure Duration, adult	10	hr/d
Bwa	Body Weight, adult	70	kg
D	Days per Week Exposure	7	d
WK	Weeks of Exposure	52	d
YE	Years of Exposure	15	y
YL	Years in Lifetime	75	y

*Ref.: [18].

3.3.1. Calculation of Chronic Non-Cancer Risk

Non-cancer risks were expressed as Hazard Quotient (HQ), which is defined as the ratio between the yearly average daily dose received, E_Y and the response dose, RfD (a level below which adverse health effects are not likely to occur).

This algorithm were used to calculate chronic non-cancer risk (*i.e.*, risk associated with long-term exposures), using chronic RfDs. Summation of HQs for individual contaminants gave Hazard Index (HI).

3.3.2. Calculation of Cancer Risk

Cancer risks was calculated from the Equation (3)

$$\text{Risk} = E_L \left(\text{mg} \cdot \text{kg}^{-1} \cdot \text{d}^{-1} \right) * \text{SF} \left(\text{mg}^{-1} \cdot \text{kg} \cdot \text{d} \right) \quad (3)$$

Where, SF is the slope factor or carcinogenic potency slope.

4. Result & Discussion

4.1. Ambient Level of BTEX and Their Seasonal Variation

Mean VOC concentrations at three monitoring sites dur-

ing December 2003 to February 2005 and their seasonal variation are shown in **Figure 1**. There is hardly any demarcation of areas for distinct activities like residential, industrial, commercial etc. in most part of the Kolkata mega-city and the difference in concentration in all the sites are thus not statistically significant. Toluene was found to be the most abundant component followed by benzene. Seasonal mean concentrations varied between

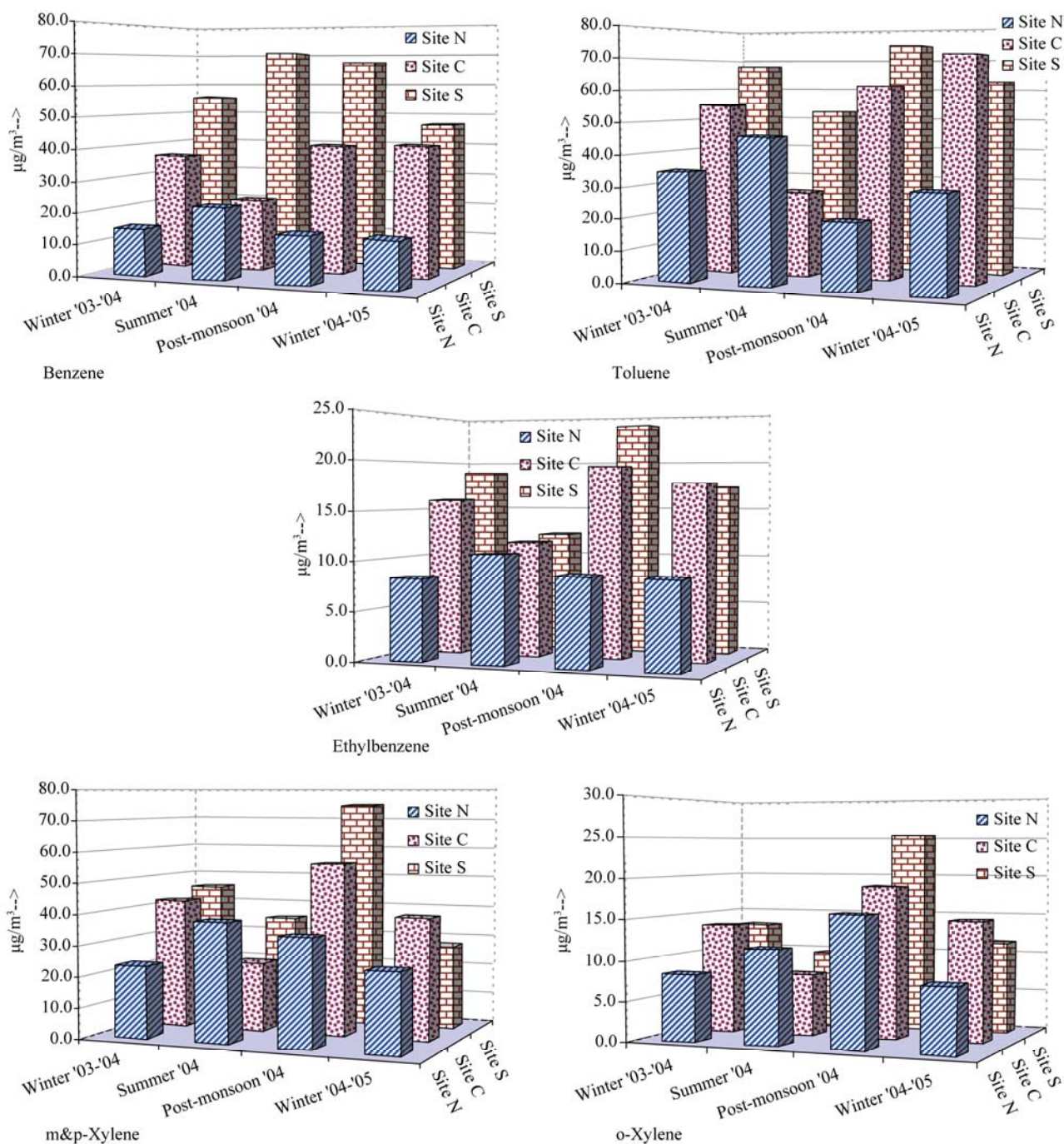


Figure 1. Seasonal levels of BTEX in three monitoring sites in Kolkata City.

13.8 - 72.0 $\mu\text{g}/\text{m}^3$ for benzene, 21.0 - 83.2 $\mu\text{g}/\text{m}^3$ for toluene, 7.6 - 21.6 $\mu\text{g}/\text{m}^3$ for ethyl benzene, 22.1 - 57.3 $\mu\text{g}/\text{m}^3$ for *m*-& *p*-xylene (combined) and 7.8 - 21.2 $\mu\text{g}/\text{m}^3$ for *o*-xylene with overall geometric mean levels of 29.2, 45.4, 13.1, 32.9 and 11.9 $\mu\text{g}/\text{m}^3$ respectively. The highest values observed for benzene and toluene was 177.2 $\mu\text{g}/\text{m}^3$ and 174.9 $\mu\text{g}/\text{m}^3$ respectively during winter '04 - '05, at site S. More than a decade ago, Samanta *et al.* [28] reported enormously high values for BTX (benzene, 192 - 18,816 $\mu\text{g}/\text{m}^3$; toluene, 98 - 3139 $\mu\text{g}/\text{m}^3$ and xylene, 153 - 2037 $\mu\text{g}/\text{m}^3$) in Kolkata atmosphere. Since then some effective measure was taken by the State Pollution Control Board to wind up unauthorized small scale industries responsible for VOC emission in and around Kolkata. More over, the decrease of BTEX level is due to the directives of the Government of India in lowering the permissible limit of benzene up to 3% in metro cities including Kolkata after 2001 and also the mandatory use of Bharat Stage II (equivalent to EURO II) vehicles after year 2002. An overall fairly good correlation ($r^2 = 0.62$ to 0.83) among the BTEX were found except between benzene and *o*-xylene (0.51) indicating a predominant common source, namely vehicular emission. One way analysis of variance (ANOVA) shows that except for benzene, seasonal variation is significant ($p \leq 0.01$). The site-wise toluene to benzene ratio ranged from 1.3 - 2.2 with an overall average of 1.7 which is typical of urban environment.

Table 2 gives a comparative account of the level and seasonal trend obtained in the current study with a few other urban areas worldwide. The city experiences a humid and tropical climate. The temperature measured at different sites during the study period found to vary between 13.5°C to 29.0°C in winter months and 29.0°C to 39.0°C during summer months. Wind speed recorded in all sites during winter months varied between 0.03 to 3.30 m/s and during summer months, 0.10 to 3.70 m/s. Calm conditions prevail frequently during winter months, and are more common in the evening hours. Relative humidity remains quite high throughout the year. The relative humidity varied from 34% to 89% during winter months and 44% to 86% during summer months.

The target VOCs showed higher average level in most cases in winter season compared to summer or post-monsoon may be due to the lower mixing height and less dispersion during winter. The photochemical reactivity of toluene, ethylbenzene and xylenes which leads to the formation of carbonyls through reaction with hydroxyl radical plays important role in their removal during hot tropical summer with bounty of sunlight. Relatively lesser photochemical reactivity of benzene [37] may explain the higher level (though not statistically significant) during winter caused by lowered mixing height and dis-

persion.

4.2. Environmental Distribution of BTEX

The percentage distribution and probable load of BTEX in different environmental compartments for their direct and continuous release in air was estimated using TaPL3 multimedia mass balance model (**Table 3**). Out of the five segments, there was negligible partitioning in vegetation and thus not incorporated in table. Air is expectedly the most favorable compartment of residence for principal part of all the target pollutants with dominant load. A small amount of distribution of these compounds was found in soil followed by water. Trace amount of partitioning was observed in the sediment compartment.

The total environmental load is highest for toluene and xylenes (3.3×10^4 kg both) followed by benzene (2.1×10^4 kg) and ethylbenzene (9.5×10^3 kg). Considering the target VOCs, the total environmental load was calculated as 9.7×10^4 kg. **Table 4** compares the emission rates of the pollutants and their fate in the environment. Estimated hourly emission rate was highest for xylenes followed by toluene, ethylbenzene and benzene. The persistence and long range transport (LRT) were highest for benzene and lowest for xylenes which commensurate with the relative reactivity of the mono-aromatics. The persistence of benzene was found to be 2.5, 3.0 and 6.1 times higher than toluene, ethylbenzene and xylene respectively. This is reflected in the observation that the concentration ratios with respect to benzene *i.e.*, T/B, E/B and X/B emission ratio obtained from the model are 3.9, 1.4 and 9.5 respectively whereas the T/B, E/B and X/B concentration ratio in air is only 1.7, 0.4 and 1.6. The LRT denotes that at least for benzene this city acts as an area source for surrounding suburban and rural areas within 400 km radius. An estimation of yearly emission for BTEX in Kolkata metropolitan city is presented in **Table 4**.

The total estimated emission for BTEX is as high as 1.4×10^4 tons per year which is comparable to the estimated evaporative emission of 1.1×10^5 tons per year for total hydrocarbon reported for Kolkata in emission inventories for VOCs in metro cities [38].

4.3. Global Warming Consequences of BTEX Emission in City Air

The global warming consequences for BTEX emission in the city environment, expressed as CO₂ equivalent estimated using Equations 1, 2 and 3, is also given in **Table 4**. Our study shows that 1.9×10^5 tons of CO₂ equivalents of only BTEX are being emitted per year from Kolkata metropolitan city. The total yearly CO₂ emission of Kolkata city in the year 2000 has been estimated to be 1.7×10^7 tons, which is 2.2% of national CO₂ emission

Table 2. Comparison of average level and seasonal trend with studies in other urban area.

City, country	Reported value (site characteristics)		Comments
	Benzene ($\mu\text{g m}^{-3}$)	Toluene ($\mu\text{g m}^{-3}$)	
Hong Kong, China [29]	4.9 (roadside)	28.8 (roadside)	Different sources for total BTEX in different seasons are indicated.
Pearl River Delta, China [3]	15.4-67.3 (urban-roadside)	28.6-106.9 (urban-roadside)	Autumn (November) BTEX level is 26-56% more than their summer (July) level. Meteorological conditions such as source and characteristics of air mass are the reason for such massive seasonal variation rather than variation in source input or photochemistry.
Delhi, India [30]	12-55 (urban-residential)	10-80 (urban-residential)	Winter VOC level is distinctly higher than summer or monsoon level in general, B/T ratio ranged from 1.04-2.05.
	80-550 (urban-traffic crossing)	18-55 (urban-traffic crossing)	
Shizuoka, Japan [31]	0.478 $\mu\text{g m}^{-3}$ in summer 0.946 $\mu\text{g m}^{-3}$ in winter (industrial urban)	4.339 $\mu\text{g m}^{-3}$ in summer 6.403 $\mu\text{g m}^{-3}$ in winter (industrial urban)	BTEX level in winter was higher than summer. Pollutants were more homogeneously distributed in winter. Seasonal variation was also influenced by emission sources.
Algiers city, Algeria [32]	27.1 (roadside) 9.6 (urban)	39.2 (roadside) 15.2 (urban)	Minor seasonal variation with winter concentration 10% higher than summer. T:B is 1.5-2.1
Hong Kong, China [33]	417 pptv (urban) ($\approx 1.3 \mu\text{g m}^{-3}$)	2765 pptv (urban) ($\approx 10.4 \mu\text{g m}^{-3}$)	Winter levels of toluene and other VOCs were significantly higher than the summer. A strong local/regional source during winter is suggested. The VOC levels are affected by Asian monsoon circulation, the clean maritime inflow air dilutes (reduces) them significantly during summer also resulting low annually averaged VOC level.
United States [34]	1.03 (Urban)	2.38 (Urban)	Higher concentration in cooler season for BTEX. Changes in emission activity, removal rates, or dispersion/dilution/transport may explain the seasonal variation
Delhi, India [35]	48-110 (metropolitan-urban)	85-204 (metropolitan-Urban)	Winter levels are higher than summer. Meteorology, variation in source strength and availability of OH radical were identified to be the controlling factors. T/B ratio varied between 1.8-2.5
São Paulo, Brazil [36]	1.30-11.31 (metropolitan-urban)	2.05-16.92 (metropolitan-urban)	Higher VOC concentration in winter (August) than summer (December). Variation in sources is attributed to be the probable cause.
Kolkata, India [present Study]	29.2 (metropolitan -urban)	45.4 (metropolitan -urban)	Significantly higher winter level due to meteorological factors like lowered mixing height and lesser dispersion and also enhanced photochemical removal of TEX in summer; insignificantly lower summer level for benzene due to less photochemical reactivity, only meteorological factors increases the winter level. T/B ratio ranged from 1.3 to 2.2.

Table 3. Percentage distribution and estimated load of BTEX in environmental compartments.

Environmental compartment	Benzene		Toluene		Ethylbenzene		Xylene	
	%	load (kg)	%	load (kg)	%	load (kg)	%	load (kg)
Air	98.6	2.1×10^4	97.7	3.2×10^4	98.9	9.4×10^3	97.8	3.3×10^4
Water	0.2	5.0×10^1	0.2	7.0×10^1	0.1	1.2×10^1	0.2	7.3×10^1
Soil	1.2	2.5×10^2	2.1	6.9×10^2	1.0	9.0×10^1	1.9	6.4×10^2
Sediment	<0.1	9.6×10^{-1}	<0.1	4.2	<0.1	3.0	0.1	2.3×10^1

Table 4. LRT, persistence and emissions of BTEX in environment.

Parameters	Benzene	Toluene	Ethylbenzene	Xylene
LRT (km)	409	164	135	67
Persistence (day)	8.6	3.5	2.9	1.4
Emission rate (kg h ⁻¹)	102	394	138	968
Yearly emission (tons year ⁻¹)	8.94 × 10 ²	3.45 × 10 ³	1.21 × 10 ³	8.48 × 10 ³
Emission CO ₂ -equivalent (tons year ⁻¹)	1.2 × 10 ⁴	4.6 × 10 ⁴	1.6 × 10 ⁴	1.1 × 10 ⁵

with only 1.6% of population [13]. Thus the CO₂ equivalent of BTEX only represents almost 1.1% of the total emission of Kolkata and 0.002% of national CO₂ emission in addition to the total CO₂ load. It is expected that the total hydrocarbon present in the city air has the potential to increase the level of CO₂ even more. This indicates that the actual global warming consequence of emissions in city air is reasonably higher than the direct CO₂ emission after considering the emission of VOCs.

4.4. Risk Assessment

The concentrations of the BTEX were found to be quite high in the present study and their levels could be a real threat to the health of the city inhabitants. **Table 5** gives the average daily exposure, average life time exposure, Individual Hazard Quotient (HQ) and ILTCR (for 15 years residence time for an individual). Effective life time exposure is maximum for xylene mixture and toluene because of their higher ambient concentration followed by benzene and ethylbenzene.

According to WHO the lifetime risk of chronic leukemia for benzene exposure of 1 µg/m³ is 4.4 – 7.6 × 10⁻⁶ [39] while ethylbenzene is classified as a group D carcinogen [40]. The cancer risk calculated in the current study suggests the exposure level to be far from being safe for population residing for 15 years in the city. In all the three sites, the estimated cancer risk is more for benzene due its high carcinogenicity. Estimated cancer risk for all the individual components (except for ethyl benzene in Site N) exceeded the threshold value of 1 × 10⁻⁶ indicating significant cancer risk. In general, residents of Site S receive higher exposure from the pollutants in comparison to the other two sites and as a result the probability of cancer risk is higher in Site S. Assuming that the carcinogenic effect from different pollutant is additive, the cumulative cancer risk from benzene and ethylbenzene is maximum (3.0 × 10⁻⁵) in Site S, followed by Site C (1.9 × 10⁻⁵) and Site N (8.9 × 10⁻⁶).

In spite of its lower exposure value, benzene gives the highest non-cancer HQ due to its low reference dose for adverse non-cancer health effect. Benzene is closely followed by xylenes in causing non-cancer health hazard.

Table 5. Estimate of individual pollutant exposure, associated non-cancer hazard and cancer risk.

Pollutant	Site	Daily exposure (mg kg ⁻¹ day ⁻¹)	Effective life time exposure (mg kg ⁻¹ day ⁻¹)	Individual HQ	ILCR
Benzene	Site N	1.5E-03	3.0E-04	1.8E-01	8.3E-06
	Site C	3.3E-03	6.6E-04	3.9E-01	1.8E-05
	Site S	5.2E-03	1.0E-03	6.0E-01	2.8E-05
Toluene	Site N	3.1E-03	6.2E-04	2.2E-03	
	Site C	5.1E-03	1.0E-03	3.6E-03	
	Site S	6.0E-03	1.2E-03	4.2E-03	
Ethylbenzene	Site N	8.2E-04	1.6E-04	2.9E-03	6.3E-07
	Site C	1.5E-03	3.0E-04	5.2E-03	1.2E-06
	Site S	1.7E-03	3.5E-04	6.1E-03	1.3E-06
Xylene mixture	Site N	3.6E-03	7.1E-04	1.2E-01	
	Site C	5.0E-03	1.0E-03	1.8E-01	
	Site S	5.7E-03	1.1E-03	2.0E-01	

The individual HQs or the HI for BTEX did not exceed anywhere indicating no serious threat of chronic non-cancer health effect in pollutant specific target organs for the city population.

5. Conclusions

Ambient concentration of Benzene, Toluene, Ethylbenzene and isomers of Xylene (BTEX) have been found to be appreciably high in Kolkata metropolitan city. 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 × 10⁴ kg.

The prevailing benzene and ethylbenzene level is estimated to pose significant cancer risk due to the inhalation exposure to the general city population.

6. Acknowledgements

The authors' sincerest thanks are due to Dr. Anjali Sri-

vastava, Scientist & Head, Kolkata Zonal Laboratory, National Environmental Engineering Research Institute for her interest in the work. Thank is also due to Dr. K. Mukhopadhyay for his help during field work.

REFERENCES

- [1] D. Mackay, W. Y. Shin and K. C. Ma, "Illustrated Handbook of Physical Chemical Properties and Environmental Fate for Organic Chemicals," CRC Press, Florida, 1997.
- [2] C. H. Lai and K. S. Chen, "Characteristics of C₂-C₁₅ Hydrocarbons in the air of Urban Kaohsiung," *Taiwan. Atmospheric Environment*, Vol. 38, No. 13, 2004, pp. 1997-2011.
- [3] X. Wang, S. Guo, J. Fu, C. Chan, S. C. Lee, L. Y. Chan and Z. Wang, "Urban Roadside Aromatic Hydrocarbons in Three Cities of the Pearl River Delta, People's Republic of China," *Atmospheric Environment*, Vol. 36, No. 33, 2002, pp. 5141-5148.
- [4] E. Ilgen, N. Karfich, K. Levsen, J. Angerer, P. Schneider, J. Heinrich, H. E. Wichmann, L. Dunemann and J. Bege-row, "Aromatic Hydrocarbons in the Atmospheric Environment: Part I. Indoor Versus Outdoor Sources, the Influence of Traffic," *Atmospheric Environment*, Vol. 35, No. 7, 2001, pp. 1235-1252.
- [5] T. S. Leong, S. Muttamara and P. Laortanakul, "Influence of Benzene Emission from Motorcycles on Bangkok Air Quality," *Atmospheric Environment*, Vol. 36, No. 4, 2002, pp. 651-661.
- [6] S. E. Manahan, "Environmental Chemistry," CRC Press, Florida, 2004.
- [7] TRIMFaTE, USEPA, "Office of Air Quality Planning and Standards, TRIMFaTE Technical Support Document," *Description of Module*, EPA-453/D-99-002A, Vol. I, Research Triangle Park, NC, 1999.
- [8] TRIMFaTE, USEPA, "Trimfate Technical Support Document, Description of Chemical Transport and Transformation Algorithm," Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA - 453/D-99-002B, Vol. II, 1999.
- [9] E. Webster, J. Hubbarde, D. Mackay, L. Swanston and A. Hodge, "Development of Tools to Improve Exposure Estimation for Use in Ecological Risk Assessment: The Tap13 Upgrade," *Report to environment Canada*, CEMC Report 2003xx, Trent University, Peterborough, 2003.
- [10] K. Kawamoto, M. MacLeod and D. Mackay, "Evaluation and Comparison of Multimedia Mass Balance Models of Chemical Fate: Application of Euses and Chemcan to 68 Chemicals in Japan," *Chemosphere*, Vol. 44, No. 4, 2001, pp. 599-612.
- [11] A. Srivastava and D. Som, "Hazardous Air Pollutants in Industrial Area of Mumbai - India," *Chemosphere*, Vol. 69, No. 3, 2007, pp. 458-468.
- [12] C. Warren, D. Mackay, M. Whelan, K. Fox and Mass, "Balance Modeling of Contaminants in River Basins: Application of The Flexible Matrix Approach," *Chemosphere*, Vol. 68, No. 7, 2007, pp. 1232-1244.
- [13] H. Imura, "The Budgets of GHGs, Urban Air Pollutants and Their Future Emission Scenarios in Selected Mega-Cities in Asia (APN 2002-04)," Final Activity Report, Air Pollution Network, 28 February 2003.
- [14] R. Duarte-Davidson, C. Courage, L. Rushton and L. Levy, "Benzene in the Environment: An Assessment of the Potential Risks to the Health of the Population," *Occupational and Environmental Medicine*, Vol. 58, No. 1, 2001, pp. 2-13.
- [15] V. Muzyka, S. Bogovski, A. Viitak and T. Veidebaum, "Alteration of Heme Metabolism in Lymphocytes and Metal Content in Blood Plasma as Markers of Diesel Fuels Effects on Human Organism," *The Science of Total Environment*, Vol. 286, No. 1-3, 2002, pp. 73-81
- [16] R. J. Delfino, H. Gong Jr., W. S. Linn, E. D. Plizzari and Y. Hu, "Asthma Symptoms in Hispanic Children and Daily Ambient Exposures to Toxic and Criteria Air Pollutants," *Environmental Health perspective*, Vol. 111, No. 4, 2003, pp. 647-656.
- [17] "Principles of risk assessment: a non-technical review," risk assessment workshop, USEPA, Easton, 17-18 March 1985.
- [18] "Air Risk Assessment Work Plan," Air and Radiation Division, Tristate, Risk Assessment Project, USEPA, 1997.
- [19] CalTOX™ Version 1.5, "A Multimedia Total Exposure Model for Hazardous-Waste Sites," Prepared by The University of California, Davis in Cooperation with Lawrence Livermore National Laboratory for the Office of Scientific Affairs Department of Toxic Substances Control California Environmental Protection Agency, Sacramento, California, 1994.
- [20] H. Salem and S. A. Kartz, "Inhalation Toxicology," CRC press, 2001, pp. 443
- [21] DA 2002, "Soil Vapor Extraction and Bioventing," Manual No. 1110-1-4001," Department of the army, US army corps of engineers Washington, DC., EM 1110-1-4001, *Engineering and Design*, Available at-url: http://www.usace.army.mil/publications/eng-manuals/em_1110-1-4001/entire.pdf last accessed on 30th May 2008.
- [22] MSC-E, "POP Model Intercomparison Study. Stage I. Comparison of Descriptions of Main Processes Determining POP Behavior in Various Environmental Compartments," Edited by MSC-E, *Technical Report*, January 2004,
- [23] K. L. Foster, S. Sharpe, E. Webster, D. Mackay and R. Maddalen, "The Role of Multimedia Mass Balance Models for Assessing the Effects of Volatile Organic Compound Emissions on Urban Air Quality," *Atmospheric Environment*, Vol. 40, No. 16, 2000, pp. 2986-2994.
- [24] VISION 2025, "Perspective Plan of KMA: 2025," Kolkata Metropolitan Development Authority, April 2005.
- [25] IPCC 2006, "IPCC Guidelines for National Greenhouse Gas Inventories," Prepared by the National Greenhouse Gas Inventories Programme, H. S. Eggleston, L. Buendia,

- K. Miwa, T. Ngara and K. Tanabe, Eds., IGES, 2006.
- [26] DoE, 2007. Climate Change Consequences Of VOC Emission Controls. AEAT/ENV/R/2475. Report to The Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland ED48749102, Issue 3, September 2007.
- [27] IPCC, "Climate Change 2001: The Scientific Basis," *Third Assessment Report of the Intergovernmental Panel on Climate Change Published for the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, 2001.
- [28] G. Samanta, G. Chattopadhyay, B. K. Mondal, T. Roychowdhuri, P. P. Chowdhury, C. R. Chanda, P. Banarjee, D. Lodh, D. Das and D. Chakraborty, "Air Pollution in Calcutta During Winter - a Three Year Study," *Current Science*, Vol. 75, No. 2, 1998, pp. 123-138.
- [29] K. F. Ho, S. C. Lee, M. Gloria and Y. Chiu, "Characterization of Selected Volatile Organic Compounds, Polycyclic Aromatic Hydrocarbons and Carbonyl Compounds at a Roadside Monitoring Station," *Atmospheric Environment*, Vol. 39, 2002, pp. 57-65.
- [30] A. Srivastava, A. E. Joseph, S. Patil, A. More, R. C. Dixit and M. Prakash, "Air Toxics in Ambient Air of Delhi," *Atmospheric Environment*, Vol. 39, No. 1, 2005, pp. 59-71.
- [31] T. Ohura, T. Amagai and M. Fusaya, "Regional Assessment of Ambient Volatile Organic Compounds in an Industrial Harbor Area, Shizuoka, Japan," *Atmospheric Environment*, Vol. 40, No. 15, 2006, pp. 238-248.
- [32] R. Kerbachi, M. Boughedaoui, L. Bounoua and M. Keddam, "Ambient Air Pollution by Aromatic Hydrocarbons in Algiers," *Atmospheric Environment*, Vol. 40, 2006, pp. 3995-4003.
- [33] H. Guo, K. L. So, I. J. Simpson, B. Barletta, S. Meinardi and D.R. Blake, "C1-C8 Volatile Organic Compounds in the Atmosphere of Hong Kong: Overview of Atmospheric Processing and Source Apportionment," *Atmospheric Environment*, Vol. 41, No. 7, 2007, pp. 1456-1472.
- [34] M. C. McCarthy, H. R. Hafner, L. R. Chinkin and J. G. Charrier, "Temporal Variability of Selected Air Toxics in the United States," *Atmospheric Environment*, Vol. 41, No. 34, 2007, pp. 7180-7194.
- [35] R. R. Hoque, P. S. Khillare, T. Agarwal, V. Shridhar and S. Balachandran, "Spatial and Temporal Variation of Btex in the Urban Atmosphere of Delhi, India," *Science of the Total Environment*, Vol. 392, No. 1, 2008, pp. 30-40.
- [36] R. Miranda and E. Tomaz, "Characterization of Urban Aerosol in Campinas, São Paulo, Brazil," *Atmospheric Research*, Vol. 87, No. 2, 2008, pp. 147-157.
- [37] C. Dutta, D. Som, A. Chatterjee, A. K. Mukherjee, T. K. Jana and S. Sen, "Mixing Ratios of Carbonyls and Btex in Ambient Air of Kolkata, India and Their Associated Health Risk," *Environ Monit Assess*, Vol. 147, 2009, pp. 97-107.
- [38] "Inventory of Evaporative Emissions of Hydrocarbons from Various Sources in Delhi, Mumbai, Chennai and Kolkata," National Environmental Engineering Research Institute, NEERI, 2005.
- [39] WHO, Air Quality Guidelines for Europe, 2nd ed., World Health Organization, Regional Office for Europe, Copenhagen, WHO Regional Publications, European Series, No. 91, 2000. Available at url: <http://www.euro.who.int/>
- [40] IARC, International Agency for Research on Cancer, 2002; IARC Monographs Programme on the Evaluation of Carcinogenic Risks to Humans, 2002.