ROADSIDE BTEX EMISSIONS IN DIFFERENT DEVELOPING COUNTRIES

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ABSTRACT:
Benzene, Toluene, Ethylbenzene and Xylene (BTEX) form an important group of aromatic Volatile Organic Compounds (VOCs), emitted from cars, where BTEX is a known carcinogenic. This review summarizes literature data from the past 10 years on monitoring and analysis of BTEX in the urban and rural atmospheres. This research discussed the following points, sampling locations, sampling methods, analytical techniques, health impacts of BTEX and the chemistry of BTEX in the atmosphere. As a result for this review study, a good framework can be drawn to tackle this issue from the Malaysian perspective.

KEYWORDS:
BTEX, Rural, VOC, Urban.

INTRODUCTION
A dramatic impact on air quality world-wide was created by the rapid urbanization and industrialization over the past decades. Risks on human health can be posed by the ambient air pollutants such as suspended particulate matters and volatile organic compounds that originate from automobile exhaust, combustion exhaust, industry processes and domestic activities [1]. The urban air quality controlled by pollutant emissions, meteorological and geographical conditions, solar radiation, deposition and dispersion parameters [2].
The interest in determining the ambient concentrations of volatile organic compounds (VOCs) due to their significant adverse effects on human health was increased in the past few years [3].

BTEX (benzene, toluene, ethylbenzene, xylenes) are harmful volatile organic compounds (VOCs), which have negative effects on human health, such as headache, eyes irritation, chest tightness, etc. Vehicular emissions are main sources of BTEX, as well as other sources, such as building and furnishing materials emissions, etc. ([4]; [5]).

In order to maintain low ozone levels in urban areas where its formation is under a VOC-limited regime, better management of ambient concentrations of Volatile Organic Compounds (VOCs) is essentially needed. In the urban areas on many developed countries, the significant decrease in traffic-induced VOC emissions resulted in relatively comparable shares of traffic and non-traffic VOC emissions [6].

The major sources of BTEX are automotive exhausts and evaporative emissions from the plastics production, paints, glues, solvents, etc. In indoor environments, a major part of BTEX emissions is directly related to indoor activities such as cooking, heating, smoking, cleaning, and includes also emissions from building materials, varnishes, paints and solvents ([7]; [8]).

Industrial sources of BTEX are, printing and laminating facilities, foundries, electronics, and paint manufacturing units, moreover they also occur at hazardous waste sites [5].

Benzene is known as a carcinogenic compound, which is emitted mainly from petrol-fuelled cars and thus it is found in all urban areas ([9]; [10]; [11]). The relative contributions of light-duty vehicles (LDV) and heavy duty vehicles (HDV) to the total emissions indicated that aldehydes, BTEX, and alkanes are mainly produced by LDV, while HDV dominated emissions of CO, NO\textsubscript{x}, SO\textsubscript{2}, and PM\textsubscript{10} [12].

Reports indicated that mobile sources account for 75–85% of the benzene emissions of which 70% is from exhaust, near heavy road traffic and high emissions are related to the use of gasoline in non-catalytic cars [10].

**HEALTH IMPACTS OF BTEX**

In the urban areas volatile organic compounds may cause adverse human health affects, such as adverse effects on reproductive systems or birth defects, even at parts per billion (ppb) levels. A Study that was carried in United States discovered that ambient VOCs share in 35–55% of the outdoor air cancer risk in the US [13].

World Health Organization (WHO) has estimated that a lifetime exposure of 0.17 μg/m\textsuperscript{3} gives rise to an excess risk of developing leukemia of 1 per 1,000,000 inhabitants based on toxic-kinetic models [9]. In Sweden, relationship between acute myeloid leukemia (AML) and car density was found; the incidence of AML was 5.5 in regions that have more than 20 cars / km\textsuperscript{2}. Low benzene concentrations in ambient air are likely to be dangerous; other
studies have also found an association between traffic density and incidence of leukemia in children [14].

**REVIEW OF PREVIOUS STUDIES**

Research papers that carried out to tackle the emissions of BTEX in different statuses in the last ten years were reviewed; table 1 show summary for the reviewed research papers.

Rommelt, et.al. [14] found that BTX concentrations were measured between 1993 and 1997 in buses and trams in Munich center and along main roads during regular rides. The sampling time was between 07.00 and 00.00 h. the samples were analyzed by GC-FID. The results show that the mean concentrations for Benzene, Toluene and Xylenes over the monitoring period are 15 μg/m³, 42.1 μg/m³ and 37.3 μg/m³, respectively.

Six monitoring campaigns were carried out (over one year) in the Municipality of Copenhagen, Denmark, as part of the project monitoring of atmospheric concentrations of benzene in European towns and homes. In each campaign, measurement of the personal exposure to benzene of 50 volunteers (non-smokers living in non-smoking families) living and working in Copenhagen was done. Simultaneously, benzene in their homes and in an urban network distributed over the municipality was measured. The Radiello diffusive sampler was used to sample 5 days averages of benzene and other hydrocarbons and the samples were analyzed by GC-FID [9].

The annual averages of the geometrical mean values were 5.22, 4.30 and 2.90 μg / m³ for personal exposure, home concentrations and urban concentrations, respectively. The general level of benzene is controlled by tow main parameters in Copenhagen: the emission from traffic and dispersion due to wind speed [9].

Real-world emissions of a traffic fleet on a transit route in Austria were determined in the Tauern tunnel experiment in October 1997. Individual hydrocarbons were sampled by an automated mobile Airmotec GC type HC 1010. Separation and analysis of the BTEX components (BTEX) was done by GC-FID. The results show that BTEX concentrations were 4.5 / 9.4 / 2 / 6.7 μg / m³ [12].

Benzene in gasoline samples and petroleum fractions was determined by GC–FID methods using two different capillary columns. Five calibration solutions of benzene in isooctane, with and without internal standard, were prepared. The approximate concentrations of benzene were 0.1, 0.5, 1.0, 1.5, and 2.0 % (v/v) [15].

Lu et, al. [4], measured BTEX in four hospitals of Guangzhou from 2nd January to 20th March 2004. Collections of samples were carried out in five consecutive daytimes for each hospital. Commercial stainless steel canister was used for collection of BTEX samples and analysis was done by using GC-MSD. Results show that Toluene was the most abundant BTEX.
During the study of [2], a 12 months comprehensive monitoring campaign to assess aldehydes and BTEX concentrations was carried out in the Tijuca district (Rio de Janeiro), where it is an area of commercial activities and a high density of vehicles. BTEX were sampled by drawing air through activated coconut shell charcoal tubes 7 cm long, 4 mm ID, was used for sampling of BTEX, analysis was carried out by GC-MS. Results show that the mean concentrations for benzene, toluene, ethylbenzene, m,p-xylene and o-xylene, were 1.1, 4.8, 3.6, 10.4 and 3.0 µg/m$^3$, respectively [2].

Hsieh et al., [5] measured the BTEX concentrations at four representative night markets and one background location in southern Taiwan. Sampling was done once monthly (non-rainy days) for a period of 14 months and the samples were analyzed by using GC-FID. Results show that BTEX concentrations during night market activities obtained from this study were still lower than the current time weighted average (TWA) values.

Wong et al., [1], measured BTEX concentration inside and outside car park in Hong Kong, the samples were collected in 6-litre fused silica-coated stainless steel canisters equipped with passive air sampling restrictors, then were analyzed using GC-FID. The results show that the BTEX concentrations were 29.4, 36.8, 597 and 87 µg/m$^3$ respectively.

Pilidis et al., [3], carried out monitoring campaign for BTX in Ioannina, a medium-sized Greek city. The samples were collected by using passive sampling tubes which were placed at different points of the city, analyzed by using GC-FID. Measurements were repeated in an exact manner over the four seasons, the results show that benzene levels, at all sampling points, exceed the limits of the EU Directive 2000/69. Correlation found between Benzene levels and traffic density, while BTX ratios present a seasonal variation linked to meteorological conditions.

In Strasbourg (East of France), [7] measured BTEX concentrations in twenty university libraries using Radiello passive sampling systems containing activated charcoal, samples were quantified by GC-PID. The results show that the mean BTEX concentrations were 0.2, 3.8, 0.8, 1.9 µg/m$^3$.

Zalel et al., [6], studied the urban roadside BTEX in Haifa; the data were collected from two monitoring stations. Results show that a large portion of the ambient BTEX concentrations in Haifa nowadays are below the monitoring instruments’ reliable measurement level., thanks to better traffic exhaust control measures.

Liu et al. [13], investigated volatile organic compounds (VOC) at two sites in the largest industrial area Kaohsiung, southern Taiwan, designated for traffic and industry. The samples were collected during rush and non rush hours in summer and autumn seasons, at the two sites simultaneously. VOC groups were found to have the same pattern at both sites: aromatics were most abundant (78–95%) followed by alkanes (2–16%) and alkenes (0–6%). The measured BTEX concentration at the two sites ranged from 69 to 301 ppb.
Halek, et al. [16], conducted a BTEX monitoring campaign in Tehran; the measurements were carried out under different conditions in the indoor environment. Samples were collected by drawing air through charcoal-filled tubes with a portable pump and they were analyzed by using GC-FID. The results show high level of BTEX concentrations especially the concentration of benzene was 2–4 times greater than the maximum levels recommended by many countries.

In Romania, [17], investigated the BTEX emitted from different materials, adhesives, combustion sources or tobacco smoke. The samples were collected by drawing air through active charcoal cartridges and analyzed by using GC-MS. The results show that BTEX concentrations were 60.15, 157.86, 1.5, 2.5 ppm respectively.

Nolasco et al. [18], monitored VOCs emission from road traffic inside a 1 Km long tunnel located at the exit of the Tenerife’s biggest town, Santa Cruz de Tenerife. Samples were taken by grab-sampling in 400 cm³ stainless-steel canister, and were analyzed by using the GC/MS/MS. The preliminary results show that BTEX are the dominant pollutants of the traffic vehicles in the tunnel, moreover, 8.3 kg per kilometer was an estimate for the BTEX concentrations due to the traffic movement.

The BTEX concentration were measured in three typical cities (Guangzhou, Macau and Nanhai), China by [19]. Multi-bed adsorbent tubes were used for air sampling at typical ground level microenvironments. The thermal desorption–gas chromatography–mass selective detector (TD–GC–MSD) technique was used to analyze the BTEX concentrations. The results show that the mean concentrations of BTEX were, respectively, 51.5, 77.3, 17.8 and 81.6 μg/m³ in Guangzhou, 34.9, 85.9, 24.1, 95.6 μg/m³ in Macau, and 20.0, 39.1, 3.0 and 14.2 μg/m³ in Nanhai [19].

Schneider et al. [8], carried out a pilot study to examine BTEX concentrations in 20 homes in Erfurt, Germany. The samples were collected passive sampling device and were analyzed using GC-FID. The results show that mean BTEX concentrations at 1.2m level in the twenty homes were 3.86, 50.13, 3.59, 2.84 μg/m³ respectively.

According to the study of [10], which was carried out in three representative sites with high traffic volume in Algiers, results show that BTEX were the dominant pollutants. The mean concentrations of benzene and toluene were 27 and 39 μg/m³ respectively.

Khoder, [11], monitored VOC’s in two urban areas (Ramsis and Haram) in Cairo and one rural area (Kafr El Akram) in Manoufiah in Egypt. The samples were collected using activated coconut charcoal tubes and analyzed by GC-FID. The results show that the BTEX ratios were (2.01:4.94:1:4.95), (2.03:4.91:1:4.87) and (2.31:2.98:1:2.59) in Ramsis, Haram and Kafr El-Akram, respectively.
Chang et al. [20], investigated non methane hydrocarbon (NMHC), in three roadways in Taiwan. The samples were collected using stainless steel canisters and analyzed by GC-FID. The results show that BTEX concentrations were 2.37, 7.74, 1.45, 3.28 ppbv% respectively.

Rappengluck et al. [21], measured non methane hydrocarbon (NMHC) in two sites (city center and suburban) in Athens. The samples were analyzed by GC-FID. The results revealed that the mean BTEX concentrations in the center of Athens were 11.7, 21.2, 4, 7.8 ppbv respectively.

O'Donoghue et al., [22], studied the difference in pollution exposure between bus and cycling commuters on a route was compared in Dublin, the samples were collected by using a SKC Vac-U-Chamber™ and analyzed by GC-FID. The mean bicycle and bus benzene concentrations are 1.62 and 2.21 ppb respectively.

Rappengluck et al. [23], monitored NMHC in several locations in Munich by using online gas chromatography methods. Low NMHC values compared to other cities worldwide was revealed by the results. The data suggests that fuel evaporation and solvent releases can be added to traffic emissions as sources of summertime NMHC inventories. Furthermore BTEX considered being important ozone precursors in the Munich area.

In twenty eight US states, Sampling campaign to monitor non methane hydro carbon “NHMC” was carried out between 1999-2005. The air samples were collected by canisters and analyzed by GC-FID. The results show that the mean mixing ratios for BTEX concentration in Los Angeles were 480, 1380, 210, 200 pptv respectively [24].

BTEX emissions were monitoring at roadsides by [25], in Hanoi, Vietnam. The samples were collected by SKC charcoal tubes and analyzed by GC-FID. The results show that the geometric mean of hourly BTEX concentrations in a street with high traffic volume, were 65, 62, 15, 43 μg/m³.

Rappengluck et al. [26], monitored volatile organic compounds (VOC’s) in three locations in the metropolitan area of Santiago de Chile. The sampling was carried out by using air canisters and the samples were analyzed by GC-FID. The results show that the medina for BTEX concentrations in Las Condes (LAC) were 0.95, 2.28, 0.52, 1.46 ppbv respectively.

NMHC were monitored in forty three cities by [27]. The samples were collected by stainless steel canister and analyzed by GC-FID. The results show that the maximum BTEX ratios were 10.4, 11.2, 2.7, 10.1 ppbv respectively.

<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>Exposure type</th>
<th>Subject or place</th>
<th>Pollutants</th>
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</table>

**Table 1: Studies on BTEX** (Modified from [28]).
<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>Exposure Type</th>
<th>Duration</th>
<th>B</th>
<th>T</th>
<th>E</th>
<th>X</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rappengluck et al. 1998</td>
<td>Athens</td>
<td>Roadside</td>
<td>City center</td>
<td>11.7</td>
<td>21.2</td>
<td>4</td>
<td>7.8</td>
<td>ppbv</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Suburban</td>
<td>2.5</td>
<td>6.7</td>
<td>1.3</td>
<td>2.1</td>
<td>ppbv</td>
</tr>
<tr>
<td>Romieu et al., 1999</td>
<td>Mexico City</td>
<td>Personal (work shift)</td>
<td>Gas station attendant</td>
<td>310</td>
<td>680</td>
<td>110</td>
<td>490</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Street vendor</td>
<td>77</td>
<td>160</td>
<td>28</td>
<td>128</td>
<td>µg/m³</td>
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<td></td>
<td></td>
<td></td>
<td>Office worker</td>
<td>44</td>
<td>470</td>
<td>17</td>
<td>81</td>
<td>µg/m³</td>
</tr>
<tr>
<td>Jo and Yu, 2001</td>
<td>Taegu, Korea</td>
<td>Personal (7–8 h)</td>
<td>ETS bus driver</td>
<td>28.1</td>
<td>88.7</td>
<td>8.1</td>
<td>30.2</td>
<td>µg/m³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Non-ETS bus driver</td>
<td>14.5</td>
<td>49.5</td>
<td>7</td>
<td>21.4</td>
<td>µg/m³</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>ETS taxi driver</td>
<td>44</td>
<td>141</td>
<td>10.2</td>
<td>37.3</td>
<td>µg/m³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>ETS: Environmental Tobacco Smoke</td>
<td>24.8</td>
<td>80.8</td>
<td>8.8</td>
<td>23.6</td>
<td>µg/m³</td>
</tr>
<tr>
<td>Schmid et al., 2001</td>
<td>Austria</td>
<td>Tunnel</td>
<td>Tauerntunnel</td>
<td>4.5</td>
<td>9.4</td>
<td>2</td>
<td>6.7</td>
<td>µg/m³</td>
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<td>Skov et al., 2001</td>
<td>Denmark</td>
<td>Different positions (5 Days)</td>
<td>Personal Exposure</td>
<td>5.22</td>
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<td>µg/m³</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>indoor</td>
<td>4.3</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>outdoor</td>
<td>2.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barletta et al., 2002</td>
<td>Karachi, Pakistan</td>
<td>Ambient (4–6 h)</td>
<td>Traffic street</td>
<td>16.6</td>
<td>26.8</td>
<td>8.2</td>
<td></td>
<td>µg/m³</td>
</tr>
<tr>
<td>Batterman et al., 2002</td>
<td>Detroit, USA</td>
<td>Vehicle/roadway (2–3 h)</td>
<td>Bus</td>
<td>4.5</td>
<td>10.2</td>
<td>9</td>
<td>2.1</td>
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<tr>
<td>Wang et al., 2002</td>
<td>China</td>
<td>Urban roadside (30 min)</td>
<td>Guangzhou</td>
<td>51.5</td>
<td>77.3</td>
<td>17.8</td>
<td>81.6</td>
<td>µg/m³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Macau</td>
<td>34.9</td>
<td>85.9</td>
<td>24.1</td>
<td>95.6</td>
<td>µg/m³</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Nanhai</td>
<td>20</td>
<td>39.1</td>
<td>3</td>
<td>14.2</td>
<td>µg/m³</td>
</tr>
<tr>
<td>Wong et al., 2002</td>
<td>Hong Kong</td>
<td>Indoor and outdoor</td>
<td>Car Park</td>
<td>29.4</td>
<td>36.8</td>
<td>597</td>
<td>87</td>
<td>µg/m³</td>
</tr>
<tr>
<td>Mukherjee et al., 2003</td>
<td>Kolkata, India</td>
<td>Personal (3–4 h)</td>
<td>Bus driver</td>
<td>527.3</td>
<td>472.8</td>
<td></td>
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<td>µg/m³</td>
</tr>
</tbody>
</table>
BTEX CHEMISTRY

The important of non-methane hydrocarbons (NMHCs) as a group of VOCs in the urban areas because of their reaction with the hydroxyl radical (OH), which plays a critical role in atmospheric photochemical reactions and the potential health effects associated with prolonged exposure to such compounds as benzene ([22]; [24]).

When nitrogen oxides (NOx) exist, VOC’s plays a vital role in the formation of photochemical smog in the sunlit atmosphere through their photochemical degradation pathways. Various secondary compounds can be formed due to these processes, e.g. ozone (O3), peroxycarboxylic nitric anhydrides (PANs), hydrogen peroxide (H2O2) and in general organic hydrogen peroxides (ROOH), and a broad range of aldehydes RCHO are produced. Short-lived intermediate products occur such as hydroxyl radicals (OH), hydrogen peroxy radicals (HO2) and organic peroxy radicals (RO2). The enhanced formation of aerosols that increase turbidity of the atmosphere, is another characteristic of the photochemical processes that induced by VOC [29].
The stable structure of benzene where six atoms of carbon are connected with three double bonds in conjugation made benzene less reactive molecule. On the other hand toluene and even more the isomers of xylene exhibit intense photochemical activity, due to their ability to give stable free radicals by photolysis. Toluene and xylene are less abundant comparing to benzene because during high insulation periods, they are photo-destructed and react with other atmospheric constituents [3].

A sharp decrease in urban VOC concentrations followed the introduction of three-way catalyst and evaporative canisters in modern vehicles, due to the large share that automotive sources used to have in VOC emissions [6].

VOCs have been measured using variety of analyses: inventory evaluation, monitoring changes of atmospheric levels to infer changes in emissions, source reconciliation studies, evaluation of photochemical models, indirect determination of air mass history or radical concentrations and investigations of the seasonal cycle of photochemistry [29].

CONCLUSION
From the literatures, it can be concluded that most of the studies use the gas chromatography technique to analyze the samples and to measure the BTEX concentrations. Previous studies show clear link between exposures to BTEX and the negative health impacts such as headache, eyes irritation, chest tightness). Concentrations of BTEX in urban areas were greater than the concentrations in rural areas due to heavier traffic volume.

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