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# BTEXs in Indoor and Outdoor Air Samples: Source Apportionment and Health Risk Assessment of Benzene

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## Abstract

Level of benzene, toluene, ethyl benzene, m,p-xylene and o-xylene (BTEXs) was measured in several indoor and outdoor air samples. Five indoor air samples were from motor vehicle workshops and three samples were from gasoline filling stations and the rest were ambient air samples. They were collected using a 1L Tedlar® bag. BTEX analysis was performed with Thermal Desorption (TD) - Gas Chromatography Mass Spectrometer (GCMS). The concentration of ΣBTEXs in indoor (ID1 to ID5) were 864.29, 115.32, 655.79, 72.99, 96.05 µg/m$^3$ respectively. ΣBTEXs in outdoor (OD1 to OD6) samples were, 367.45, 85.12, 50.29, 159.94, 46.02, 68.57 µg/m$^3$ respectively. Calculated LADD value in indoor and outdoor air samples ranged in the scale of 0.27–3.42 and 0.16–1.88 µg/kg/d respectively. Concentrations of all indoor and outdoor samples surpassed the cancer risk (CR) limit for benzene but were below HQ (<1) for non-cancer risk impact. In conclusion, areas within petroleum stations and motor vehicles workshops may pose hazardous cancer risk and non-cancer risk through BTEXs exposure to workers and non-workers.

**Keywords:** Benzene; Toluene; Ethyl benzene; Xylene; BTEX; Air pollution; Source identification; Risk evaluation; Malaysia; Developing country

## 1. Introduction

BTEX refers to Benzene, Toluene, Ethyl benzene and three isomers of Xylene and they are referred by World Health Organization (WHO) as hazardous air pollutants (HAPs) [1]. Humans who are exposed to BTEX for a long period of time have high risk to chronic disease, such as cancer [2]. For example, WHO [3] classified benzene as carcinogenic to humans, though no safe level of exposure is recommended yet. Synder [4] indicates that exposure in the range of 13.0 to 45.0 µg/m3 (4.07–14.11 ppm) could yield 1 cancer in 10,000 exposed people. Meanwhile, toluene, ethyl benzene and xylenes are also classified as potential carcinogens to humans [5].

The human exposure to benzene, toluene, ethyl benzene and xylenes were from inhalation of contaminated air either from naturally-occurring compounds in crude oil or from primary man-made sources into the environment such as through emissions from motor vehicles, aircraft exhaust, fuel filling stations and cigarette smoke [6]. Most benzene exposure for non-smoker is derived from vehicle exhaust or petrol vapour emissions [7]. WHO [3] stated that the exposure can occur either occupationally or domestically from continuous usage of petroleum products, including motor fuels and solvents. Increasing number of vehicles especially in urban area increase human exposure to BTEXs. Moreover, many sources of BTEXs such as fuel stations and workshops are located in urban area.

Indoor and outdoor exposure of BTEXs was correlated with specific sources. Several research [8, 9] have pointed out that BTEXs level in residential indoor air closed to a petrol filing station or an industrial areas are higher. Workers who are exposed directly to BTEX from a specific source will face health risks [10-12]. Therefore, health risk assessment is important to evaluate the hazards and adverse impacts of pollutants such as BTEXs to human health [13]. Determination of gases in ambient air required specific techniques for sampling and analysis. Application of Tedlar® bag for whole air sampling was an established sampling method i.e. EPA TO-15. Similarly, direct analysis of BTEX in Thermal Desorption (TD) coupled with Gas Chromatography Mass Spectrometer (GCMS) is a standard procedure as well. This procedure is easy, rapid and green since no solvent is involved in the extraction [14].

In this study, concentrations of BTEXs in several indoor and outdoor locations were measured and their possible sources were identified. Estimation of health risk related to benzene exposure was calculated and compared with other related studies.

## 2. Material and Method

### 2.1 Sampling

A total of 11 sampling sites were selected in areas of Serdang, Selangor. Among the samples, three indoor locations belong to automobile and motorcycle repair shops; three in the vicinity of petroleum fuel refill stations; one from roadside, one at the faculty and one at a residential hostel (Universiti Putra Malaysia). The sampling period was August- September 2015.

## 2.2 Sampling method

Personal Air Sampler (PAS, Supelco) was set at 100 ml/min flowrate. The pump was calibrated using Air Flow Calibrator (Go Cal, Sensidyne). 1L of Tedlar bag (Supelco) was used to collect the air. With approximately 8-10 minutes of sampling time 800-1000 ml of air could be collected. From this 500 ml of air was pumped through the TD system for the BTEXs analysis.

## 2.3 Analysis with TD-GCMS

Air samples were directly pumped using the automated controller (CIA Advantage, Markes) onto the TD System (Unity, Markes). The system was equipped with a cool, Air Toxic Analyser Trap U-T15ATA-2S (Markes, UK) to concentrate the BTEXs before further desorption to the GC-MS system.

Separation of gases (BTEXs) was done using a gas chromatography Agilent 6890N (Agilent, USA) and detected by Agilent 5975C (Agilent, USA) Mass Selective Detector. DB-624 (J&W Scientific, USA) capillary column (60 m length, 0.32 mm i.d, 1.80 µm film thickness) was used for the separation. Parameters setting for TD and GCMS are shown in Table 1.

| **Desorption parameters** | |
|---|---|
| Desorption temperature | 280°C for VOCs |
| Desorption time | 30 min for VOCs |
| Split flow | Splitless |
| Flow path temperature | 150°C |
| Line-purge | 1 min |
| Trap-purge | 3 min |
| Sampling valve | 0.5 L |
| **GC-MS parameters** | |
| Temperature program | Initial 40°C(4min), 4°C/min to 220°C (2min) |
| Inlet temperature | 200°C |
| Auxiliary temperature | 280°C |
| MS Quad | 150°C |
| MS Source | 230°C |
| Scan mass range | 35-300 amu |

**Table 1:** TD and GC-MS parameters.

## 2.4 Quality Assurance/ Quality Control

Multiple points calibration was performed in order to create quantification curve for BTEXs. Gas standard 10 ppm (MESA, USA) was diluted proportionally with purified air in pre-clean 10 L Tedlar® bag for the calibration purposed. Limit of detection (LOD) was calculated based on 3 standard deviation of the lowest calibration (1 ppb). Good correlation was observed for all compounds as shown in Table 2.

| Compound Name | Formula | Correlation coefficient $R_2$ | LOD (ppb) |
|---|---|---|---|
| Benzene | y = 3E+06x - 4E+06 | 0.9975 | 0.08 |
| Toluene | y = 2E+06x + 6E+06 | 0.9979 | 0.07 |
| Ethylbenzene | y = 2E+06x + 2E+06 | 0.9959 | 0.02 |
| m,p-Xylene | y = 3E+06x + 7E+06 | 0.9920 | 0.02 |
| o-Xylene | y = 1E+06x + 2E+06 | 0.9917 | 0.02 |

**Table 2:** QA/QC studies on BTEX measurements.

## 3. Results and Discussion

### 3.1 BTEXs level

**3.1.1 Indoor air:** Concentration of individual component of BTEXs in indoor and outdoor samples was quantified (Table 3). The highest ΣBTEXs concentration for indoor air was found in ID1 (864.29 μg/m$^3$), followed by ID3 (655.79 μg/m$^3$), ID2 (115.32 μg/m$^3$), ID5 (96.05 μg/m$^3$) respectively and the lowest was in ID4 (72.99 μg/m$^3$). The highest concentration in ID1 and ID2 revealed that motorcycle workshops with gasoline vapours are a principle source of BTEXs. Many researchers have found out that motorcycles especially with two-stroke engines produced more VOCs from incomplete burning of fuel in the engines [15, 16]. Car workshop A (ID3) was also detected with high concentration of BTEXs in comparison to sites ID4 and ID5. Toluene was the most abundant compound in all sites except ID5. Toluene/benzene (T/B) ratio for all indoor sites (1.58- 2.20) indicated that gasoline fuel was the principle emission source. Ratio of T/B was always used as an indicator of vehicular emission [16, 17] and according to a study by Lan and Binh, T/B ratio of 2 indicated mainly a vehicular emission from petrol fuel in Malaysia.

| Sample Description | | Benzene | Toluene | Ethyl Benzene | m,p-Xylene | o-xylene | ΣBTEXs |
|---|---|---|---|---|---|---|---|
| | | Concentration (μg/m$^3$) | | | | | |
| *Indoor* | | | | | | | |
| ID 1* | Motorcycle workshop A | 153.56 | 332.21 | 111.83 | 122.88 | 143.81 | 864.29 |
| ID 2 | Motorcycle workshop B | 25.12 | 57.69 | 5.47 | 11.94 | 15.10 | 115.32 |
| ID 3* | Car workshop A | 98.62 | 191.79 | 109.63 | 120.20 | 135.55 | 655.79 |
| ID 4 | Car workshop B | 12.17 | 25.31 | 5.09 | 11.09 | 19.33 | 72.99 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ID 5 | Car workshop C | 12.55 | 19.90 | 9.24 | 23.65 | 30.71 | 96.05 |
| *Outdoor* | | | | | | | |
| OD 1* | Petrol station A | 48.77 | 101.79 | 57.92 | 70.34 | 88.63 | 367.45 |
| OD 2 | Petrol station B | 19.15 | 37.69 | 3.15 | 8.50 | 16.63 | 85.12 |
| OD 3 | Petrol station C | 9.9 | 19.91 | 3.95 | 3.29 | 13.24 | 50.29 |
| OD 6 | Roadside, UPM | 7.79 | 33.81 | 31.00 | 28.25 | 59.09 | 159.94 |
| OD 7 | Faculty of Environmental Studies, UPM | 7.45 | 32.51 | 0.58 | 0.67 | 4.81 | 46.02 |
| OD 8 | Residence College, UPM | 5.44 | 51.63 | 1.41 | 3.10 | 6.99 | 68.57 |

*Collected close to the fuel source.

**Table 3:** BTEXs concentration (µg/m$^3$) in indoor and outdoor samples.

**3.1.2 Outdoor air:** Among the outdoor samples collected, OD1 was detected with the highest ΣBTEXs (367.45 µg/m$^3$), followed by OD6 (159.94 µg/m$^3$), OD2 (85.12 µg/m), OD8 (68.57 µg/m$^3$), OD3 (50.29 µg/m$^3$), and OD7 (46.02 µg/m$^3$) respectively. Toluene was found the most abundant compound in all samples except in the case of OD6 where o-Xylene was the highest. T/B ratio for outdoor samples (OD1-OD3) revealed a ratio of 2 indicating gasoline as a source. A ratio of 2.2 was also observed by Lan [16] in roadside ambient air of Kuala Lumpur. High T/B ratio of >4-10 for outdoor samples (OD6-OD8) indicates additional sources such as industrial emission in those areas.

Benzene level in outdoor samples was found high in all petrol stations sites (OD1>OD2>OD3), followed by OD6 (roadside), OD7 (Faculty) and OD8 (Residential). The result clearly indicated outdoor benzene risk in the following order petrol stations> roadside> faculty> residential area.

**3.1.3 Benzene health assessment:** Health risk estimation for benzene in indoor and outdoor sites was based on Lifetime Average Daily Doses (LADD), cancer risk (CR) and hazard quotient (HQ). Calculation of LADD, CR and HQ for indoor and outdoor samples was based on Edokpolo et al. [18]. All parameters for the calculation were based on United State Environment Protection Agency (US EPA) recommendation value. According to the US EPA, a cancer risk above $1 \times 10^{-6}$ is critical, as it significantly increases carcinogenic potential in humans. A hazard quotient (HQ) is a measure of potential overall hazard risk. A HQ of ≥ 1 is considered as an “adverse non-carcinogenic effect of concern”; while a value of ≤ 1 is within acceptable limit.

| **Sample** | **LADD (µg/kg/d)** | **Cancer Risk (CR)** | **Hazard Quotient (HQ)** |
|---|---|---|---|
| *Indoor* | | | |
| ID 1 | 3.42 | $9.34 \times 10^{-5}$ | 0.40 |
| ID 2 | 0.56 | $1.53 \times 10^{-5}$ | 0.07 |
| ID 3 | 2.20 | $6.00 \times 10^{-5}$ | 0.26 |
| ID 4 | 0.27 | $7.40 \times 10^{-6}$ | 0.03 |
| ID 5 | 0.28 | $7.63 \times 10^{-6}$ | 0.03 |
| *Outdoor* | | | |
| OD 1 | 1.88 | $5.15 \times 10^{-5}$ | 0.22 |
| OD 2 | 0.74 | $2.02 \times 10^{-5}$ | 0.09 |
| OD 3 | 0.38 | $1.05 \times 10^{-5}$ | 0.04 |
| OD 4 | 0.23 | $6.23 \times 10^{-6}$ | 0.03 |
| OD 5 | 0.22 | $5.96 \times 10^{-6}$ | 0.03 |
| OD 6 | 0.16 | $4.35 \times 10^{-6}$ | 0.02 |

**Table 4:** Calculated benzene health risk.

Table 4 shows the results of calculated LADD, CR and HQ for indoor (ID1-ID5) and outdoor (OD1-OD6) air samples. Indoor samples for ID1 showed the highest LADD (3.42 µg/kg/d), followed by ID3 (2.20 µg/kg/d), ID2 (0.56 µg/kg/d), ID5 (0.28 µg/kg/d) and ID4 (0.27 µg/kg/d). All samples from indoor air exceeded the cancer risk guideline ($> 1 \times 10^{-6}$) indicating cancer risk to workers. ID1 and ID3 are air samples collected from motorcycle and car workshops with one of the highest risk value of $9.34 \times 10^{-5}$ and $6.00 \times 10^{-5}$ respectively. However, HQ results (<1) from all indoor samples represent less effect of non-cancer risk to the workers based on benzene level.

CR value for all outdoor samples were also higher than the recommended limit. Petrol stations (OD1-OD3) were calculated with a value of $5.15 \times 10^{-5}$, $2.02 \times 10^{-5}$ and $1.05 \times 10^{-5}$ respectively. However, the results were lower than in a study by Moolla et al. [12] in a diesel station bus depot. Meanwhile, OD4-OD7 indicated CR value of $6.23 \times 10^{-6}$, $5.96 \times 10^{-6}$ and $4.35 \times 10^{-6}$ respectively. Benzene cancer risk results in ambient roadside, faculty and residential area were also high if one considers the study of Garg et al. [19] in India. The CR results for outdoor samples suggest that all samples close to fossil fuel or vehicles were at cancer risk. HQ results for outdoors samples with <1 suggested non-cancer risk of benzene in all sampling sites.

## 4. Conclusion

In summary, BTEX was prevalent in both indoor and outdoor samples in Serdang, Malaysia. The highest concentrations were recorded always at sites close to petroleum products e.g. petrol stations, automobile workshops. The toluene/benzene ratios confirm this finding. Staggeringly, health risk calculations based on LADD, CR and HQ indicate that Malaysians are at risk both in indoor and outdoor from benzene exposure. The current results suggest for more intense sampling throughout urban environment in Malaysia for risk assessment with BTEX pollution.

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