



## ORIGINAL ARTICLE

# Ambient Air Measurement of Benzene, Toluene and Xylene Within a Nigerian Petroleum Products Depot and Its Host Environment Using Carbon Adsorption and GC-FID Techniques

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### Abstract

Health effects of benzene, toluene and xylene emissions from a Nigerian Petroleum Products depot make stringent adherence to maximum allowable concentration very important. The storage facilities and distribution network and other installations of petroleum products depot are significant sources of benzene, toluene and xylene therefore ambient air of the depot requires observation and assessment. The ambient air concentrations of BTX were been measured within Pipelines and Product Marketing Company, Mosimi Depot and its immediate environment. Air samples were collected on granular activated charcoal through low volume air sampler and extracted with carbon disulphide (CS<sub>2</sub>) by desorption process. The extracted solutions were subjected to Flame Ionization Detection analysis in a gas chromatograph (Model: HP 6890) using a capillary column HP 5MS with length, inner diameter and particle size set at 30 m × 0.25 mm × 0.25 μm. The gas chromatograph was powered with chemstation RevA09.01 [1206] software to determine the concentrations of each of the identified VOCs species. The concentrations of benzene, toluene, p xylene, m xylene and o xylene ranged between 0.0104 - 0.0711, 0.0019 - 0.0998, 0.0010 - 0.0022, 0.0014 - 0.0026 and 0.0006 - 0.0019 mg/m<sup>3</sup> respectively. The mean values were 0.0277, 0.0389, 0.0013, 0.0019 and 0.00010 mg/m<sup>3</sup>, respectively. On the average, the observed concentrations did not exceed the tolerance (air concentrations) limits set for Nigeria environment by the National Environmental Standards and Regulations Enforcement Agency (NESREA).

**Keywords:** BTX, VOCs, Interspecies Ratio, Local Air Quality, Health Risk

### Introduction

The growing interests in determining ambient level of aromatic Volatile Organic Compounds were due to its roles in the atmosphere and at ground level. VOCs play important role in formation of Ozone and as precursors of Photochemical smog which are detrimental to human health and ecosystem. By virtue of their vapour pressure benzene, toluene and xylene are classified as

volatile organic compounds (As organic compounds having saturated vapour pressure greater than 10-1 mmHg at 25°C) (Shirley, 1991). They are aromatic VOCs pollutants in the air. Thus, if not properly controlled they could find their way easily into the ecosystem and atmosphere (Muhibbu-Din, 2017). VOCs are commonly encountered by people as they go about their daily routine for both indoor and outdoor (Ojiodu et al., 2012, Muhibbu-din, 2017).

Studies have shown VOCs enter human blood stream through inhalation, ingestion, eye and skin contact (ATSDR, 2001). Long term monitoring of these toxic aromatic VOCs emissions from Industrial site and facilities confirm significant exposure to inhabitants, workers, general public and host environment of these areas (Muhibbu-Din, 2017; Sulemanov, 1997). Though benzene is the most volatile of aromatic hydrocarbon and found to be most toxic in full range of petroleum products (Akeredolu and Sonibare, 1997). Evans et al stated further that toluene is the compound generally found at highest concentration. Benzene is found to be toxic to bone marrow (Lamb et al., 1980) and carcinogenic causing leukemia in man (Benard, 1983). In general, Exposure to benzene may increase morbidity and mortality rate (Ralph and Stephen, 1981). About 40% of benzene inhaled by mammals is eliminated unchanged in expired air while the remainder is converted to benzene oxide which may convert to phenol (Akeredolu and Sonibare, 1997). Adverse effects on the Central Nervous System are the critical health concern following human exposure to toluene and xylene vapours.

Symptoms of their exposure progress from fatigue, headache, depression, memory loss, irritation of the upper respiratory tracts, disturbance of vision, dizziness, nausea, collapse and coma while direct contact with them may result in intense burning of skin and eyes. (ATSDR, 2000). In Nigeria, these hazardous air pollutants are subjected to regulatory requirement under Federal Ministry of Environment which supervise the activities of Nigeria's pollution regulatory body called National Environmental Standard and Regulatory Agency (NESREA). The Agency set benzene, toluene and xylene (and its isomers) emission limits as 0.05 mg/m<sup>3</sup>, 0.05 mg/m<sup>3</sup>, 0.02 mg/m<sup>3</sup> respectively for petroleum based and chemical industries air emission guidelines as enshrined in National Environmental Standard and Regulation act, 2009. This study is to find out if VOCs emission from Mosimi depot is at allowable level and health risk its pose to local population.

## **Materials and Methods**

### ***Study Area and Description of Sampling Site***

Mosimi depot is one of the subsidiaries of Nigeria National Petroleum Corporation, located at Sagamu, Ogun state. The basic activities in Mosimi Depot are; reception of petroleum products such as, PMS, DPK, and AGO from Atlas Cove and local refineries. The Petroleum products are pumped to both Ibadan and Ore depots. Sagamu is within the tropical humid climatic zone of Nigeria, which is generally characterized by high rainfall and high relative humidity. The average monthly rainfall for the study area ranges between 7.1 mm in the month of January to 208.3 mm in the month of June.

The mean annual temperature is 26°C; although with some variations over time. The mean diurnal minimum temperature varies from 21.8 °C in December to 24.34 °C in April while the mean diurnal maximum temperature varies from 33.92 °C to 37.1 °C at the onset of the wet season (March and April) (Akanni, 2000). It is situated at latitude 6° 45'22 61" and 6° 45'64 02" North; Longitude 3° 33'07 56" and 3° 32'57 61" East at an elevation of 283ft above sea level.

### ***The Sampling System***

This is made up of low volume air sampler (Model: NEGRETTI 1000TM), sampling sorbent tubes (adsorption column) and adsorbent media (activated charcoal). The air sampler is a chargeable battery powered device (capable of operating on battery for up to 10 hours) through which ambient

air were sucked via adsorbent media. 15g of granular activated carbon was filled in the adsorption tube with glass wool on one side of the adsorption tube. Air samples were pumped through at a fixed flow rate of 12.0 litres per minute. The adsorption column is a glass tube of length 20.0cm and 4.0cm in diameter. The lower end of adsorption column is a glass tube of length 7.0 cm with a diameter of 0.70cm. It was corked at the top with rubber while glass wool was used at the base as a support for adsorbent (activated charcoal).

The lower end of the adsorption column was connected to the to the air sampler. Sampling period that was adopted is 8 (eight) hours .The sampling system was assembled at various locations where sampling was carried out. After sample collection in the field, the adsorbed activated charcoals was placed in sampling bottles and were preserved in ice blocks in a cooler before being taken to the refrigerator where they were kept until extraction and analysis time.

### ***Extraction Procedure***

Each sample was placed in the thimble of soxhlet extractor fitted to a reboiler flask containing about 75 ml of carbondisulphide (CS<sub>2</sub>) that is solvent that was used for extraction. The flask was heated by heating mantle with a thermostat for temperature regulation of 50°C. The condenser for extraction was connected to CHURCHILL chiller which was maintaining the cooling fluid at preset temperatures in the range of -5°C to 0°C. On attainment of this temperature; heating mantle was switched on and was regulated to a convenient point of 50°C.

The sample extraction set-up was run last for about 4 hours for complete extraction. The extract was collected in a sampling bottle and was preserved in a refrigerator. Before further use, the soxhlet extractor and flask were cleaned .The process was repeated for every other sample. For every run, new thimble was used in order to prevent contamination.

### ***Sample (Chromatographic) Analysis***

The quantitative determination of extracted solutions was analyzed with Gas Chromatography (Model: HP 6890) fitted with a Flame Ionizations Detector (GC-FID). The capillary column was HP 5MS with length, inner diameter and particle size set at (30 m×0.25 mm×0.25 µm) .It was attached to the injection port. The flow rate of carrier gas (hydrogen) was 1.0 mL/min; the hydrogen pressure and compressed air were set at 22psi and 28psi respectively. The injection temperature was split injection set at 150°C, the detector temperature at 320°C, and the oven temperature was programmed at 50°C with the 1st ramped 5°C/min to 150°C and 2nd ramped at 10°C/min to 250°C. A 1mL aliquot of the final solution was injected in the GC (split ratio; 20: 1).

Calibration standards were supply and used for calculation of concentrations from chromatography peaks. Calibration standard was first run thereafter sample was run and quantified by ChemStation software. The sampling collection and quantitative analysis describe above is consistent with ANSI/ASTM procedure.

## **Result and Discussion**

### ***Benzene concentration***

The concentration of benzene, toluene, ethyl benzene and xylene were measured for air basin of Mosimi PPMC depot. Benzene concentrations were recorded at various locations within and around the depot. Concentration of 0.0711 mg/m<sup>3</sup> was recorded at Slop tank area (located at east of the depot) was found to be the highest among sampling locations considered as shown in Figure 1.



Figure 1: Map of study Area indicating Sampling Site (Source: Google Earth)

Table 1: Comparison of Average Measured VOCs Species Concentrations with Ambient Air Quality Standards

| SN | VOCs SPECIES  | NESREA air emission guidelines for petroleum based and chemical industries (mg/m <sup>3</sup> ) | PPMC MOSIMI DEPOT SAMPLED (average measured concentration) (mg/m <sup>3</sup> ) |
|----|---------------|---|---|
| 1  | Benzene       | 0.05  | 0.0277  |
| 2  | Toluene       | 0.05  | 0.0389  |
| 3  | Ethyl benzene | 0.02  | 0.0029  |
| 4  | p-Xylene      | 0.02  | 0.0013  |
| 5  | m-Xylene      | 0.02  | 0.0019  |
| 6  | o-Xylene      | 0.02  | 0.0010  |

Source: NESREA (2009)

Its location may be a contributing factor to high benzene concentration obtained. Other contributing factors may be ascribe to evaporative emissions from pipelines, Tank farm 21 and four Slop tanks because of low height, presence of sludge from Tank Farm 22 ( that has not be cleared) not too far from Slop Tanks, variability of wind speed and so on contribute to high

concentration of benzene in the Slop Tanks area. The Workshop area is located less than 1km from the loading gantry and also in the east of the depot. The benzene concentration of 0.0595 mg/m<sup>3</sup> (second highest) was obtained at that site. The contributing sources to the concentration obtained may be due to proximity to loading gantry and decanting point and slop pit at the front, pumping pit at the back and bolster pump pit by the side of workshop. The location is characterized with high variable strong wind speed. At Tank farms area, benzene concentration was found to be 0.0181 mg/m<sup>3</sup>. This value is low when compared to concentrations earlier discussed. It is located in west of the depot. Thus observation here could be attributed to good height of the Tank farms (emission takes place at the top roof of tank), no spillage or leakage of petroleum products as at the time of sampling was observed and prevailing wind direction prevent emissions depositing to the ground level. The benzene concentration observed at Gate1 is 0.0166 mg/m<sup>3</sup>.

The Gate 1 was characterized with high variable of wind speed. The contributing source may include loading gantry (due to proximity to Gate 1), vehicular emissions from loading trucks and other vehicle as they move into PPMC premises. At Gate 2, the concentration of benzene is 0.0102 mg/m<sup>3</sup>. The contributing sources could be from separator pit, waste water from the depot and tank farms that contain remnants of DPK (Dual Purpose Kerosene). Low wind speed was experienced during air sampling. The benzene concentration observed outside PPMC Mosimi depot include one at marketer's block and the second at Otiyejuvillage (behind PPMC Area Office) are 0.0104 mg/m<sup>3</sup> and 0.0077 mg/m<sup>3</sup> respectively. For marketer's block, the contributing sources might include vehicular emissions and presence haulage (where excess products are drawn from loading truck) and emissions from the depot. Variable wind speed was experienced during air sampling. Marketer's block host good number of people and various kinds of vehicle at a time. Level of benzene concentration observed at Otiyeju village was at of 0.0077 mg/m<sup>3</sup>. This low level observed could be attributed to her far distance from the contributing sources. The village is located at a distance right behind area office of PPMC and east of the depot. The prevailing wind directions do not favour influx VOCs and may have limits VOCs species from getting deposited to the village.

Comparing the sampled average concentrations of benzene as against local standard as shown in Table 1 and Figure 2. The mean concentration of benzene is lower when compared to NESREA (air emission guidelines for petroleum based and chemical industries) standard. This implies that benzene emissions from PPMC Mosimidepot are within allowable limits and that operational routine of the depot can be said to be safe for workers, host environment and general public.

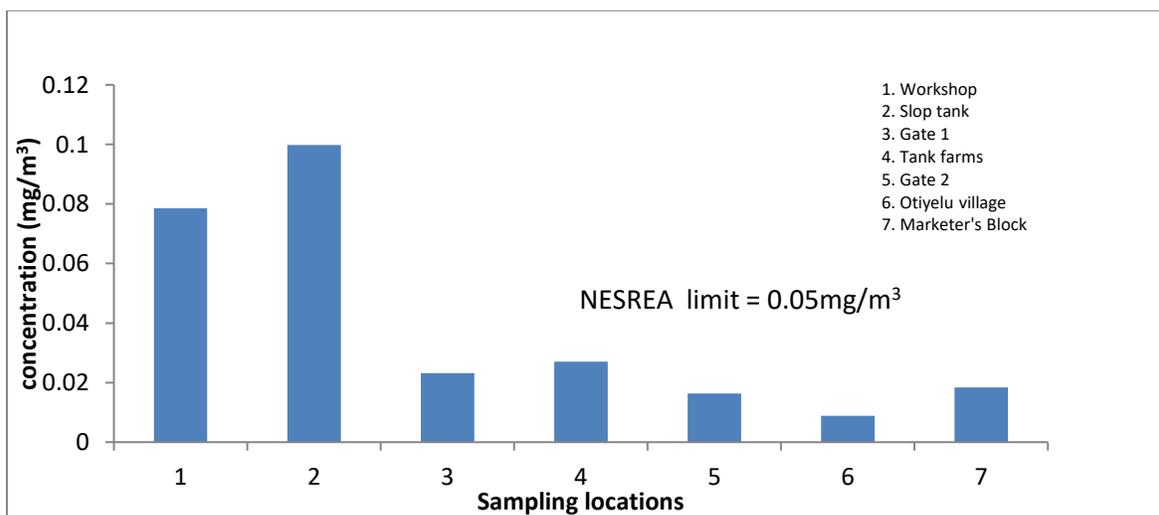


Figure 2: Benzene concentrations as obtained from Mosimi Petroleum Products Depot and its environment

### **Toluene concentration**

Among VOCs species observed, toluene concentrations is the most abundance VOCs species in all sampling locations. The maximum observed toluene concentration was 0.0998 mg/m<sup>3</sup> at Slop tank area. The occurrence of maximum concentration at Slop Tank area could be traced to explanations proffer to benzene concentrations. Within PPMC depot, toluene concentrations were in descending order of Slop tank area (0.0998 mg/m<sup>3</sup>), Workshop area (0.0785 mg/m<sup>3</sup>), Gate1 area (0.0232 mg/m<sup>3</sup>), Tank Farm area (0.0208 mg/m<sup>3</sup>), Gate 2 area (0.0163 mg/m<sup>3</sup>) as shown in Figure 3. Beyond PPMC Mosimi Depot premises toluene concentration decreases (marketer's block area: 0.0183 mg/m<sup>3</sup> and Otiyeju village: 0.0089 mg/m<sup>3</sup>) due to wash down of little or low dispersed hydrocarbon vapour from the depot as shown in Figure 3.

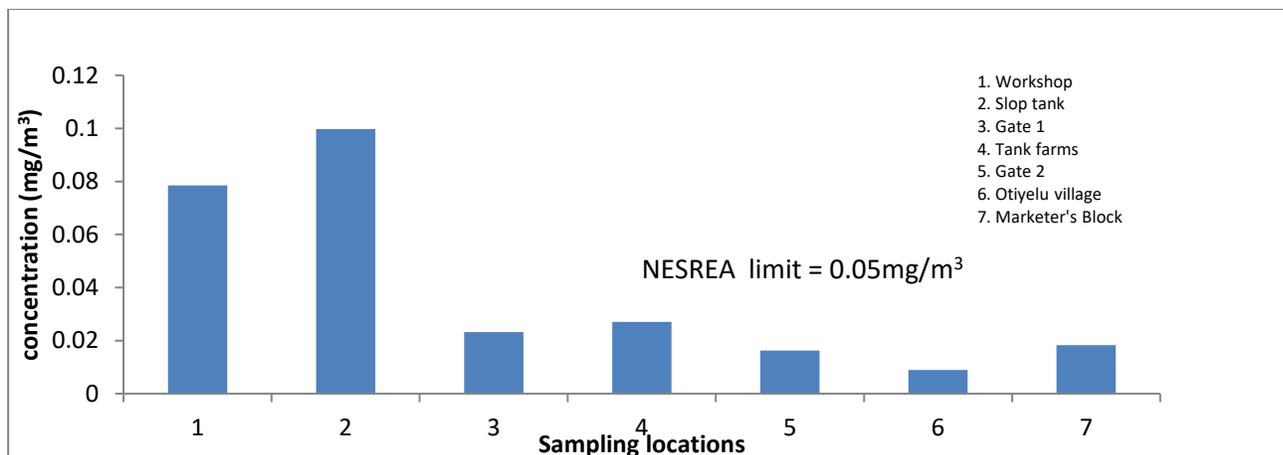


Figure 3: Toluene concentrations as obtained from Mosimi Petroleum Products Depot and its Environment

Comparing the sampled average concentrations of toluene as against local standard as shown in Table 1. The mean concentration of toluene is lower when compared to NESREA (air emission guidelines for petroleum based and chemical industries) standards. This indicate that toluene emissions from PPMC Mosimidepot are within allowable limits and that operational routine of the depot can be said to be safe for workers , host environment and general public.

### **Xylene concentrations**

The GC/FID analysis identified three isomers of xylene. They are para-xylene (p-xylene), meta-xylene (m-xylene) and ortho-xylene (o-xylene). Unlike the earlier findings with benzene and toluene levels in terms of spatial distribution, Trace level of xylene concentration was observed. Among the three isomers of xylene, m-xylene is the most prominent. M-xylene detected at Slop Tank area was seen to be highest (0.0028 mg/m<sup>3</sup>), followed by 0.00256 mg/m<sup>3</sup> at Workshop area. The lowest concentration of m-xylene was 0.0007 mg/m<sup>3</sup> at Otiyeju village as shown in Figure 4. P-xylene concentration is next to m-xylene in descending order of distributions. The highest detected was at Slop Tanks area with concentrations of 0.0022 mg/m<sup>3</sup> with the least at Otiyeju village with concentration of 0.0004 mg/m<sup>3</sup> as indicated in Figure 5. The least among the xylene isomer is o-xylene with highest concentration observed at Slop Tanks area and least concentration was observed to be 0.0011 mg/m<sup>3</sup> at Otiyeju village as shown in Figure 6. All xylene isomers detected are extremely at low value probably due to their exposure to photochemical reactions.

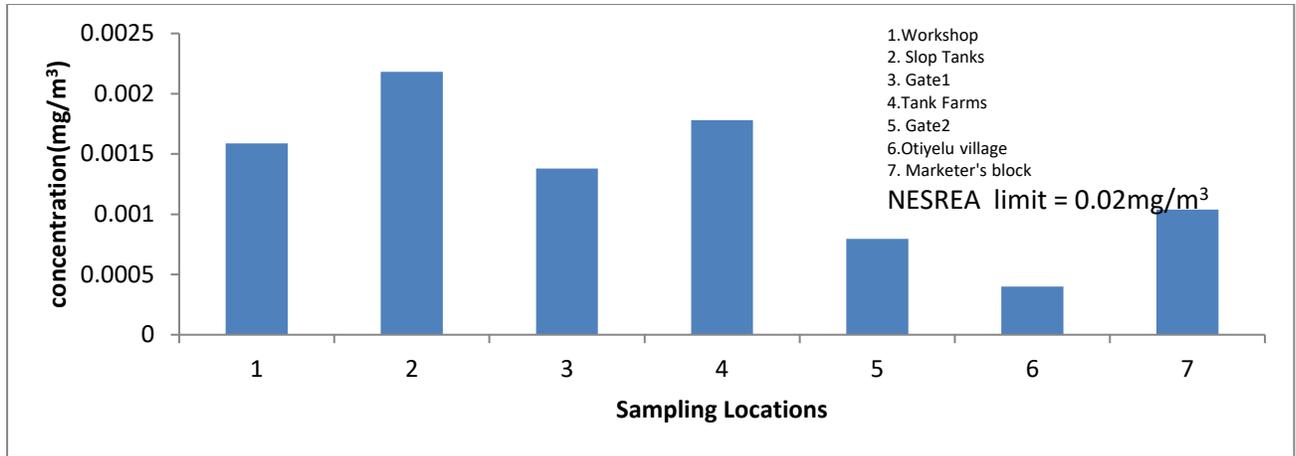


Figure 4: p-xylene Concentrations as Obtained from Mosimi Petroleum Products Depot and its Immediate Environment

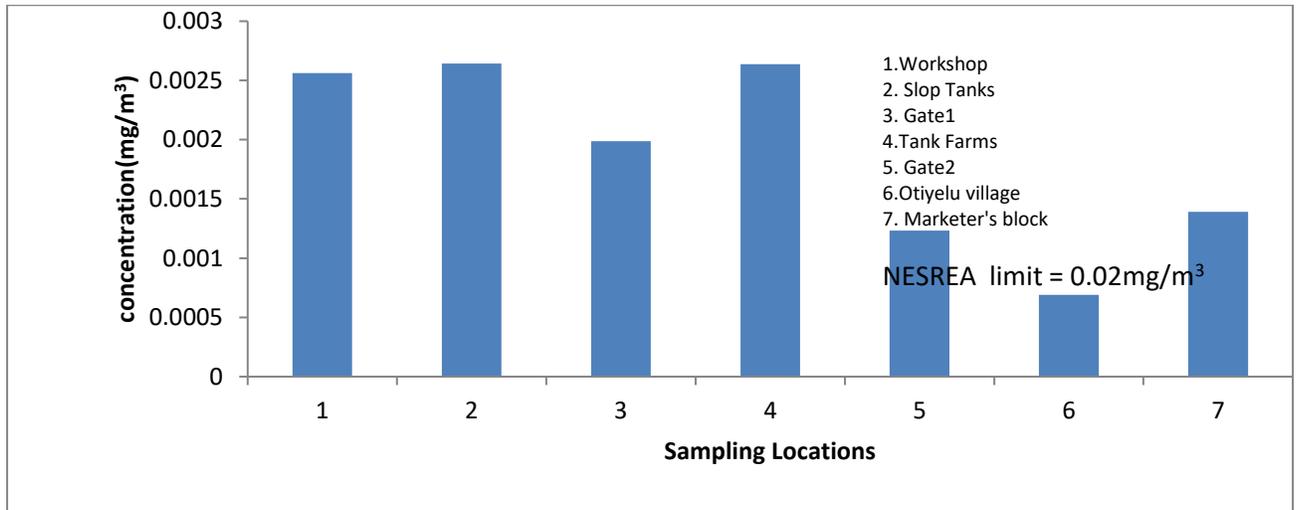


Figure 5: m-xylene Concentrations as Obtained from Mosimi Petroleum Products Depot and Immediate Environment

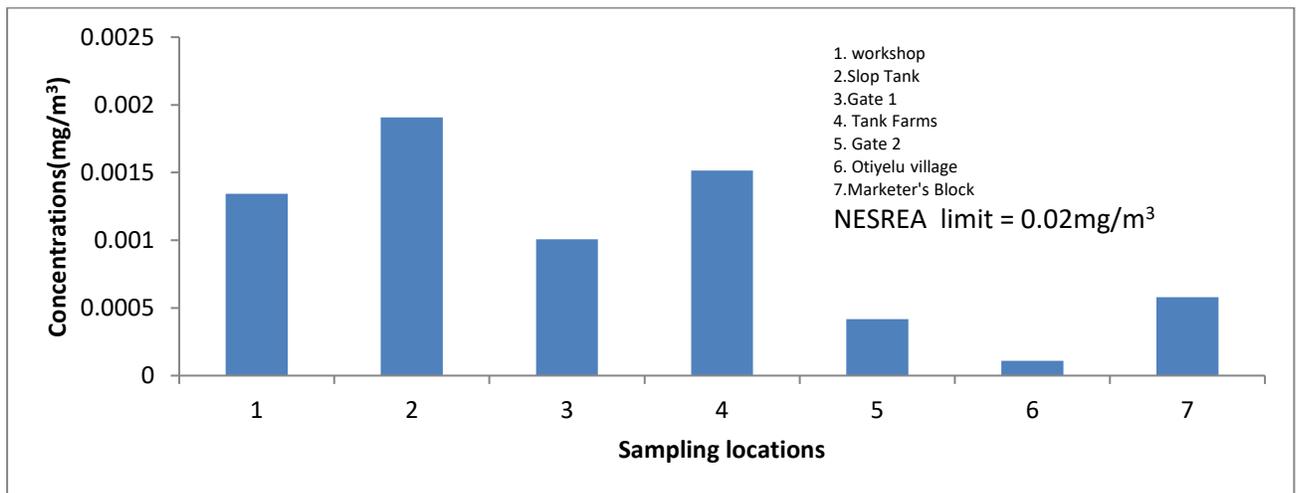


Figure 6: o-xylene Concentrations as Obtained from Mosimi Petroleum Products Depot and its Immediate Environment

Comparing the sampled average concentrations of xylene isomers as against local standard as shown in Table 1. The mean concentrations of xylene isomers are lower when compared to NESREA (air emission guidelines for petroleum based and chemical industries) standards. This indicate that xylene emissions from PPMC Mosimidepot are within allowable limits and that operational routine of the depot can be said to be safe for workers, host environment and general public.

### VOCS Interspecies Ratio as Observed at Nigerian Petroleum Depot and its Host Environment

Considering the T/B ratios observed at PPMC, Mosimi depot from Table 2. It can be inferred that T/B ratios for most of the locations are comparable, steady and suggested that they have multiple sources at a time. They are mostly influenced by emissions from multiple and similar sources from the depot. T/B ratio of the market's block has the highest value with 1.7698 (this is as a result of multiple vehicular emission sources couple with emission sources from the depot) while Otiyelu village has the lowest value with 1.1500. This can be attributed to its distance from numerous point sources.

Low values of X/B ratios were observed for all locations. This clearly indicate higher benzene concentrations and suggest that more reactive VOCs species have been exposed to photochemical degradation and their concentrations decreases quickly in ambient air basin of Mosimi depot. The decrease ratios X/B can be a measure of age of air mass (Nelson and Quigley, 1983). The small X/B ratios further revealed the fact that photochemical reactions were active. Overall, these ratios suggested that VOCs species of Mosimi depot have similar multiple sources and photochemical reactions are active in the site investigated.

Table 2: Interspecies ratio of VOCs species as observed at PPMC Mosimi Depot

| S/N | Location            | Toluene/benzene | m+p-<br>Xylene/Benzene | o-<br>Xylene/Benzene | Xylene/Benzene |
|-----|---------------------|-----------------|------------------------|----------------------|----------------|
| 1   | Workshop            | 1.3191          | 0.0697                 | 0.0227               | 0.0923         |
| 2   | Slop Tanks          | 1.4026          | 0.0678                 | 0.0268               | 0.0946         |
| 3   | Gate 1              | 1.3951          | 0.2026                 | 0.0607               | 0.2933         |
| 4   | Farm tanks          | 1.4968          | 1.4968                 | 0.0838               | 0.3282         |
| 5   | Gate 2              | 1.5954          | 0.1986                 | 0.0409               | 0.2395         |
| 6   | Otiyelu<br>Village  | 1.1500          | 0.1413                 | 0.0140               | 0.1552         |
| 7   | Marketer's<br>Block | 1.7698          | 0.2346                 | 0.0560               | 0.2905         |

### Conclusion

This study about benzene, toluene and isomers of xylene concentrations in the ambient air of Mosimi Petroleum Products depot and its host environment was carried out to understand the compositions and concentrations distribution of aromatic VOCs with respect to locations. It was observed that the industrial site might not only encounter emission from industrial sources alone but also influence by traffic sources within the vicinity. Among VOCs species identified, Toluene concentrations were found to be most abundant and xylene concentrations were least. Characteristics ratio revealed that VOCS species at PPMC Mosimi depot and host environment are of similar origin and that photochemical reactions are active within and around the depot

There have been no previous results or records in the literature for PPMC Mosimi depot to compare with. However, the average measured concentrations did not exceed the tolerance air

concentrations limit sets for Nigeria environment by National Environmental Standards and Regulations Enforcement Agency (NESREA). The averaged measured concentration of VOCs species sampled at PPMC Mosimi depot and Host Environment conform to local standard. There is a complex relationship between the VOCs species observed and possible emission sources. The clarification of that relationship requires the use of receptor modeling.

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