Evaluation of interactions between Benzene and Toluene Species in the Air Basin of a Nigerian Petroleum Products Depot

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Abstract:

Benzene and Toluene species concentrations relationship and interaction were determined in the air basin of Pipelines and Products Marketing Company Mosimi Depot, Sagamu, Nigeria .This study evaluates the status level of these air pollutants emitted from Mosimi Petroleum depot industrial area using active sampling and gas chromatography fitted with flame ionization detector ; Model : HP 6890. Air samples were collected over granular activated charcoal with 10-18 mesh using a low volume air sampler. The Model: Negretti 1000 [tm] sampler was placed at human breathing height of 1.5m for a sampling period of eight hours at different sampling location. Desorption process was carried out on the used activated charcoal using solvent extraction method with carbondisulphide as the solvent. The extracted solutions were subjected to gas chromatography fitted with flame ionization analysis. The gas chromatography was powered with chem-station REV A09.01 [1206] software to determine the concentration of each of the benzene and toluene species present. The concentrations of benzene ranged between 0.0104 and 0.0711 mg/m^3 while that of toluene ranged between 0.0019 and 0.0998 mg/m^3 within Pipelines and Products Marketing Company in Mosimi depot and host environment. The Pearson's correlation of benzene and toluene is 0.998 while concentrations ratios ranged between 1.32 and 1.77 which indicate both species are have a relationship and are of multiple similar sources.

Keywords: Air pollutants; Benzene species; Toluene species; interaction; Emission; Petroleum Depot

1. Introduction

Benzene and Toluene in the air are major components and most abundant species of aromatic Volatile Organic Compounds (VOCs) (Muhibbu-din, 2017). They significantly affect the chemistry of the atmosphere and human health. They played important roles in photo-oxidation and promote the formation of toxic secondary pollutants (tropospheric ozone and peroxy acetyl nitrate) and enhance greenhouse effects (Finlayson-pitts and Pitts, 2000). The reaction of benzene and toluene in ambient air with Hydroxyl (OH) and nitrate (NO_3^-) radicals serves as dominant degradation processes for aromatic VOCs in the atmosphere which result to products that contribute to the formation of secondary organic aerosol (SOA) by nucleation and condensation (Muhibbu-din, 2017; Brocco et al., 1997). These two aromatic VOCs influence both gas phase pollutants and particle phase pollutants directly. They have ecotoxicological effects ranging from carcinogenesis to neurotoxicity (Cetin et al., 2003) on human and atmosphere above a certain dose. The operation of Nigeria Petroleum Products Depot, Mosimi, facilities are associated with emissions of benzene and toluene which mainly originated from distribution network (valves, pumps, pipelines, flange), loading and dispensing processes, storage (farm) tanks, Equipment leaks and wastewater area. Long-term monitoring of toxic aromatic VOCs pollutants from petroleum depot industrial facilities most especially at the loading gantry confirms significant exposure to workers, residents around the industrial site and the host environment/community (Muhibbu-din, 2017; Suleinavov, 1997). Benzene, Toluene and any other VOCs enter human body stream through inhalation, ingestion and skin (ATSDR, 2001). Short-term exposure (within 24 hours) causes people to develop sign and symptoms such as drowsiness, dizziness, rapid irregular heartbeats, headache, tremors, confusion and unconsciousness. Long-term exposure (a year or more) to benzene have harmful effects on bone marrow, cause anemia, cancer and even death. Women who breathe in high level benzene for months have irregular menstrual period and decrease in size of their ovary (ATSDR, 2015). Repeated exposure to toluene also causes headache, sleeplessness, impaired ability to think, confusion, memory loss and death if the emission continues. Long term exposures have effect on reproductive system, nervous system, liver and kidney damage. Studies in human and animal expose to toluene general indicate that toluene is not carcinogenic. Toluene is less toxic than benzene (ATSDR, 2015).

A study of VOCs in Nigerian atmosphere by Ojiodu *et* al. (2011) revealed 40% of aromatic VOCs among total VOCs identified in high traffic within Benin City. Akeredolu and Sonibare (1997) investigated a Nigerian refinery and its immediate environment and found that toluene is the most abundant VOCs emissions with 0.434 mg/m^3. The aim of this study is to evaluate the relationship and interaction level of benzene and toluene emissions in the airshed of Pipelines and Products Marketing Company (PPMC) Mosimi Depot by active sampling and gas chromatography fitted with flame ionization (GC-FID) analysis. This study was carried out within and around Pipelines and Products Marketing Company (PPMC) Mosimi Depot, Sagamu, Nigeria.

2. Materials and Methods

2.1 Study Area and Description of Sampling Site

Mosimi depot is one of the subsidiaries of Nigeria National Petroleum Corporation (NNPC), located at Sagamu, Ogun State, Nigeria. 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℃; although with some variations over time. The mean diurnal minimum temperature varies from 21.8 ℃ in December to 24.34 ℃ in April while the mean diurnal maximum temperature varies from 33.92 ℃ to 37.1 ℃ at the onset of the wet season (March and April) (Akanni, 2000). It is situated at latitude 6^0 45’22 61’’ and 6^0 45’64 02’’ North; Longitude 3^0 33’07 56’’ and 30 32’57 61’’ East at an elevation of 283ft above sea level.

All units of the depot were categorized into seven locations as follows; Workshop area, Slop Tanks area, Gate 1, Tank Farms , Gate 2, Otiyelu Village and Marketer’s Block. Each unit was deployed with sampling system over the survey period as shown in Figures 1 and 2. The sampling system was placed at human breathing height of 1.5 m for a sampling period of eight (8) hours at different sampling units. The survey period was every day of the sampling campaign.

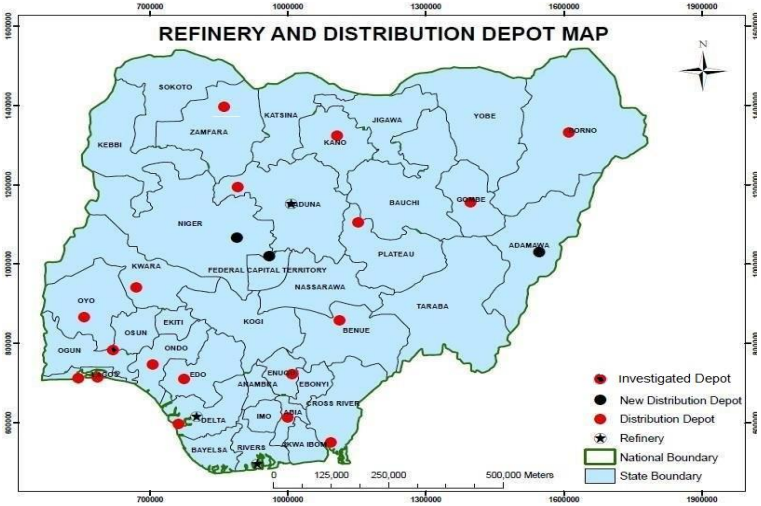


Figure 1: Map of study area indicating sampling area

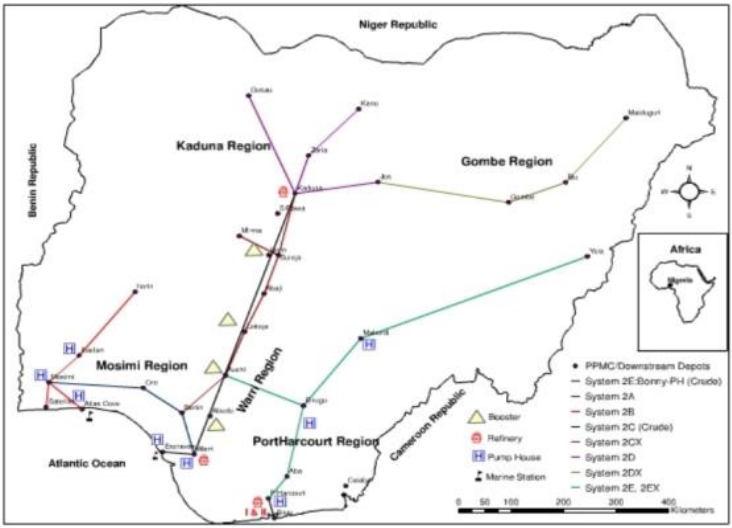


Figure 2: A map showing NNPC pipeline network (Nigeria) revealing the Mosimi Pipeline.

2.2 Sampling locations

2.2.1 The Sampling System

This is made up of low volume air sampler, 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 was sucked via adsorbent media. 15g of 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 was eight hours. The sampling system was assembled at various locations where sampling was carried out.After sample collection in the field, the used activated charcoals were 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.

2.2.2 Extraction Procedure:

Each sample was placed in the thimble of Soxhlet extractor fitted to a reboiler flask containing about 75 ml of carbon disulphide (CS_2) 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 sample. For every run, new thimble was used in order to prevent contamination.

2.2.3 Chromatographic Sample Analysis:

The quantitative determination of extracted solutions were analyzed with Gas Chromatography (Model: HP 6890) fitted with a Flame Ionization 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 22 psi and 28 psi respectively. The injection temperature was split injection set at 150 ℃, the detector temperature at 320 ℃ and the oven temperature was programmed at 50 ℃ with the 1st ramped 5 ℃/min to 150 ℃ and 2nd ramped at 10 ℃/min to 250 ℃. A 1mL aliquot of the final solution was injected in the GC (split ratio; 20: 1). Calibration standards were supply by the Laboratory which was used for calculation of concentrations from chromatography peaks. Calibration standard was first run thereafter sample was run and quantifies by chem.-station software. The sampling collection and quantitative analysis describe above is consistent with ANSI/ASTM procedure (ANSI/ASTM D-1605-60).

3. Results and Discussion

3.1 Benzene Concentrations

The concentrations of benzene and toluene species were measured for air basin of Mosimi PPMC depot were summarized in Table 1. Benzene concentrations were recorded at various locations within and around the depot. A Concentration of 0.0711 mg/m^3 was recorded at Slop Tanks area (located at the east of the depot) was found to be the highest among sampling locations considered. Its location may be a contributing factor to high level benzene concentration obtained. Other contributing factors may be ascribed 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 was located less than 1km from the loading gantry and also in the east of the depot. The benzene concentration of 0.0595mg/m^3 (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 the workshop. The location is characterized by high variable strong wind speed.

At Tank farms area, benzene concentration was found to be 0.0181mg/m^3. This value is low when compared to concentrations earlier discussed. It is located in the west of the depot. Thus observation here could be attributed to the good height of the Tank farms (emission takes place at the top roof of the 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^3. The Gate 1 was characterized with the 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^3.The contributing sources could be from separator pit, wastewater 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 Otiyeju village (behind PPMC Area Office) are 0.0104mg/m^3 and 0.0077 mg/m^3 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 hosts a 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^3. 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 limited VOCs species from getting deposited to the village.

3.2 Toluene Concentrations

Between the two VOCs species observed, toluene concentrations are the most abundance VOCs species in all sampling locations. The maximum observed toluene concentration was 0.0998 mg/m^3 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^3), Workshop area (0.0785 mg/m^3), Gate1 area (0.0232 mg/m^3), Tank Farms area (0.0208 mg/m^3), Gate 2 area (0.0163 mg/m^3). Beyond PPMC Mosimi Depot premises toluene concentration decreases (Marketer's block area: 0.0183 mg/m^3 and Otiyeju village: 0.0089 mg/m^3) due to washing down of little or low dispersed hydrocarbon vapour from the depot.

Table 1: Measured Concentrations (mg/m^3) of Benzene and Toluene species at Mosimi PPMC Depot

S/N	LOCATION	BENZENE	TOLUENE
1	Workshop	0.0595	0.0785
2	Slop Tanks	0.0711	0.0998
3	Gate 1	0.0166	0.0232
4	Tank farm	0.0181	0.0271
5	Gate 2	0.0102	0.0163
6	Otiyelu Village	0.0077	0.0089
7	Marketer's block	0.0104	0.0183

3.3 Benzene and Toluene Species Correlation Analysis:

In this research, Pearson's correlation (2- tailed) analysis was employed for Benzene and Toluene emissions to determine their strength of association or co-occurrence. The statistical package for social science software (SPSS version 25.00, SPSS, Chicago, IL, USA) was used. It always takes a value between -1 and +1 indicating perfect correlation. A correlation close to or equal to zero indicates no relationship between variables. A positive correlation coefficient indicates a positive relationship and a negative correlation indicate a negative relationship between variables. The correlation coefficients between benzene and toluene species were computed using Microsoft Excel software. Below are the Pearson correlation results as indicated in Table 2. The Pearson's r is 0.998 (value close to 1).

This indicate a very strong positive relationship between the co-occurrence of benzene and toluene. This means that changes in benzene emissions is strongly related to toluene emission and vice versa suggesting that their primary sources of origin are similar. The sig. (2-tailed) value is 0.000 (value less than 0.05) which show that relationship between benzene and toluene is statistically significant. This implies that increase or decrease in benzene emission is significantly related to increase or decrease in toluene emission. Overall, the determined correlations support the conclusion that benzene and toluene emission from PPMC Mosimi depot have a relationship between them and are of similar origin.

Table 2: Correlations results of Benzene and Toluene

Correlations	Benzene	Toluene
Benzene Pearson Correlation	1	.998**
Sig. (2 - tailed)		.000
N	7	7
Toluene Pearson Correlation	0.998**	1
Sig. (2 - tailed)	0.000	
N	7	7

** Correlation is significant at 0.01 levels (2- tailed)
Pearson correlation of benzene and toluene species = 0.998
P-value = 0.000 and N= number of variable for both benzene and toluene

3.4 Concentrations ratio of Benzene and Toluene as observed at PPMC Mosimi Depot:

Concentration ratios of benzene and toluene were taken as an indication to compare their emission sources. Because of the varying reaction rates of benzene and toluene with hydroxyl radical (OH^-), these ratios provide information about characteristic of air at the sampling site. It also gives information to infer on source(s) origination. Benzene and Toluene are chief constituents of hydrocarbon vapour in the air basin of PPMC Mosimi depot. They have atmospheric life times of 12.5 and 2.4 days respectively and therefore they are relatively stable in the atmosphere (Muhibbu-din, 2017; Prinn et al., 1987). They do not disperse easy into the environment after release.

Several studies concluded about number and type of contributing sources using toluene to benzene (T/B) ratio. Higher T/B ratios (value exceeding one) indicate the presence of multiple contributing sources (Muhibbu-din, 2017; Gelencsér, Siszler and Hlavay, 1997). Lee et al (2002)suggested that T/B ratios increased with increasing traffic volume, industrial emission and other sources. Considering the T/B ratios as observed at PPMC, Mosimi depot from Table 3. 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 1.77 (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 1.15. This can be attributed to its distance from numerous point sources. Overall these ratios suggested that benzene and toluene emission of Mosimi depot have similar multiple sources in the site investigated.

Table 3: Concentrations ratio of Toluene/Benzene specie as observed at PPMC Mosimi Depot.

Location	Toluene/Benzene
workshop	1.32
Slop tanks	1.40
Gate 1	q.40
Tank farm	1.50
Gate 2	1.60
Otiyelu village	1.16
Marketer's block	1.76

4. Conclusion

Benzene and Toluene emission in the ambient air of PPMC Mosimi depot was carried out to understanding their existing level with respect to locations. It was observed that the emissions might not only come from industrial sources but also little influence from vehicular sources within the vicinity. Toluene was found to be more abundant than benzene. Extremely low concentrations were observed for both aromatic species probably due its geographical location and large volume of natural air. Extreme low concentrations indicate that both aromatic species emissions do not have negative impacts on human health and on environment. It was evident that PPMC Mosimi depot contributes to concentration level of benzene and toluene in the air basin of the depot. Benzene and Toluene emission from PPMC Mosimi depot have a relationship between them and are of similar multiple sources of origins in the site investigated.

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6. Conflict of Interest

The author declares that there is no conflict of interests regarding the publication of this manuscript.

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Abbreviation

m3	cubic meter
GC-FID	Gas Chromatography Fitted With Flame Ionization Detector
g	Gram
µm	Micrometer
mg/m3	Milligram per cubic meter
ml	Millimeter
mm	Millimeter
NNPC	Nigeria National Petroleum Corporation
PPMC	Pipelines and Products Marketing Company