CHEMICAL ENGINEERING | RESEARCH ARTICLE

Assessment of the contribution of hazardous air pollutants from Nigeria’s petroleum refineries to ambient air quality. Part 1

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Abstract: This study investigated the contribution of anthropogenic emission of benzene from petroleum refineries to the Nigerian’s ambient air quality with the view of understanding the impact of petroleum production facilities on host airshed. The Activities of the four existing and 22 proposed petroleum refineries in Nigeria were obtained from the Department of Petroleum Resources and these were combined with emission factors of different units at the refineries to estimate benzene emissions. No-control-measure option (worst case scenario) was assumed because of lack of information on control efficiency of the refineries. The study revealed that two of the existing refineries in one of the oil-producing cities in Nigeria released a total of $10.01 \times 10^{11}$ tons/year of benzene into the ambient air of the city, apart from additional $2.35 \times 10^{13}$ tons/year anticipated to be released from three of the proposed refineries into the ambient air of the same host community. If operated at full capacity, the estimated benzene emission from the four existing refineries stood at $5.50 \times 10^{13}$ tons/year while the 22 proposed refineries have the capacity of releasing additional $16.73 \times 10^{13}$ ton/year. On the overall, the contribution of benzene from refineries on yearly basis to Nigerian airshed was estimated to be $22.24 \times 10^{13}$ tons. These concentrations if not checked could lead to devastating environmental issues. Some mitigating measures were suggested to control and subsequently abate benzene emission from these refineries.

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PUBLIC INTEREST STATEMENT
This study investigates the impact of hazardous air pollutants from existing and proposed petroleum refineries in Nigeria to its ambient air quality. The petroleum refineries considered in this study are all located in the southern part of Nigeria except one while the hazardous air emission of interest is benzene. Benzene emission from all the refineries were assessed using the emission factor approach. From this study, appropriate control measure must put in place so as to reduce the hazardous effect of benzene on the host communities.
Subjects: Combustion; Environmental Health; Pollution

Keywords: refineries; benzene; emission; petroleum; airshed

1. INTRODUCTION

Globally, anthropogenic air pollution has been an important issue of concern for many years due to its adverse effects on plants, animals, environment and human health. Continuous increase in the level of air pollution emission has been reported to be the consequence of increasing population, industrialization, density of traffic, and space heating (Benaissa et al., 2019; Coskun et al., 2011; Edokpolo et al., 2015; Odekanle et al., 2017; Riyadh et al., 2020). Recently, due to continuous increase in crude oil production in the Niger Delta of Nigeria, emission of various gaseous hydrocarbons has become worrisome and called for urgent attention. Apart from various petroleum explorations and exploitations, other crude oil production activities such as transportation and gas flaring and venting also emit hazardous air pollutants which adversely affect ambient air quality of the region (Sonibare et al., 2007).

Hazardous Air Pollutants (HAPs) also refer to as Volatile organic compounds (VOCs) are one of the important air emissions. They are defined as organic chemical compounds which can evaporate easily under normal conditions of temperature and pressure. These pollutants are emitted to the atmosphere from both anthropogenic and natural sources. Benzene is found in ambient air as a result of burning fuels, such as coal and petrol. Benzene is also common in unleaded fuel, where it is added as a substitute for lead, allowing smoother running of petrol engines. Benzene concentrations in fuel were once as high as 20%, but are now reduced to <1% in many countries, due to harmful health impacts (Sonibare et al., 2007). It forms an important group of aromatic volatile organic compounds (VOCs) been emitted because of its role in the troposphere chemistry and the risk of deleterious effects on human health. Each year industrial facilities discharge pollutants into the environment, releasing large amounts of pollutants leading to respiratory, neurological and reproductive disorders, and cancers. The World Health Organization (WHO) and International Agency for Research on Cancer (IARC) classify benzene as a group one carcinogen (World Health Organization, 2000). Prolonged exposure to high concentrations of benzene causes leukaemia in humans (Edokpolo et al., 2014) while less severe health impacts can occur at lower concentrations, causing headaches, nausea, drowsiness and even unconsciousness (Mulenga & Siziya, 2019; Nordlinder & Ramnass, 1987). The WHO has not set a standard for ambient Benzene concentrations, stating that there is no safe level of exposure. Many countries use an annual average standard of 3.6 μg m⁻³ (Nordlinder & Ramnass, 1987).

Among many chemical industries, petroleum refineries have been identified as large emitters of great amount of benzene (Akeredolu & Sonibare, 2004). This is due to the fact that recently, the use of benzene in manufacturing processes has been reduced by replacement with less hazardous compounds (Nordlinder & Ramnass, 1987) and therefore, benzene could now be considered as exclusive by-product of petroleum production and refining operations. Benzene, an hazardous air pollutant is a typical component of crude petroleum and its derivatives. During refining operations, apart from storage tanks, pipes with different flanges, valves, pumps and compressors are required for the transportation of crude oil and its products from one location to the other. All these equipment coupled with the volatility of benzene and the prevalent atmospheric condition could be a potential source of benzene emission within refinery facilities. Nigeria is presently a major emitter of these hazardous air pollutants which comes from a number of sources with the petroleum refinery facilities (Akeredolu & Sonibare, 2004; Obanijesu et al., 2009).

Various studies have shown some degree of attempts to provide information on the environmental impacts of petroleum production facilities in a community by investigating some criteria pollutants from the existing refineries. Emission of SO₂ above the permissible limits from the petroleum operation areas of Niger Delta of Nigeria has been reported (Obanijesu et al., 2009). CO and NO₂ emissions around six flow stations have also been monitored and estimated using Air
Quality Index (Sonibare et al., 2010). The study reported that at 60 meter distance around petroleum production facilities, children and elderly as well as people with underlining health issues should not be allowed into the facilities except adequate inhalation preventive measure is taken. Similar study investigated VOC emission from petroleum facilities in Nigeria and reported that the Southern part of the country is at a great risk of VOC’s emission from petroleum refinery (Sonibare et al., 2007). Also, the health risk resulting from benzene exposure in petroleum refineries has also been estimated using the Hazard Quotient (HQ) at 50% (CEXP50) and 95% (CEXP95) exposure levels (Edokpolo et al., 2014) and the study suggested a potential cancer risk for exposure to benzene in all the scenarios. Majority of these and other previous studies have concentrated on the impact of the existing petroleum refineries on ambient air quality [11, 14]

However, the Federal Government of Nigeria has recently licensed and approved the operation of additional 22 refineries (apart from the four existing ones) in the country. Monumental increase in the emission of air pollutants to the ambient air from both the existing and proposed refineries is therefore envisaged. As part of research effort to assess the contribution of various anthropogenic activities to local atmospheric pollution load across the country, the need to project the impacts of the proposed refineries on air quality of the community and coupled with the peculiarity of benzene in terms of its health effects, this study aims to estimate the emission of benzene from both the existing and the proposed refineries using emission factor approach. Activities data were obtained from the country’s Department of Petroleum Resources for both the existing and proposed refinery. This was used together with the emission factor obtained in literature to estimate the emission rate of benzene into the ambient air. This study is considered necessary for the enhancement of preparedness and proactiveness on the part of Environmental Regulatory Agency prior to the full operation of the proposed refineries. The study will also provide better understanding of the impact of petroleum production facilities on ambient air quality of host airshed.

2. METHODOLOGY

2.1. Study area

All the petroleum refineries examined in this research (except one) are concentrated in the southern part of Nigeria as shown in Figure 1. They are located in Kaduna, Rivers, Delta, Akwa Ibom, Cross River, Ogun, Ondo, Edo, Anambra, Bayelsa, and Lagos, with the following land areas 46,053 km², 11,077 km², 17,698 km², 7,081 km², 20,165 km², 16,981 km², 15,500 km², 17,802 km², 4,844 km², 10,773 km² and 3,577 km², respectively.

2.2. Determination of benzene emissions from different sources at the refinery

Figure 2 is the flowchart, showing the procedures involved in the estimation of benzene emission from the refineries, while Tables 1 and 2 show the names of the existing and proposed refineries along with their capacities, years of production/issue of license, locations and coordinates. The activities of both the existing and proposed petroleum refineries in Nigeria were obtained from the Department of Petroleum Resources (Department of Petroleum Resource (DPR), 2001, Department of Petroleum Resource DPR, 2004, Department of Petroleum Resource DPR, 2010) and combined with emission factors of different units at refinery (RTI: Research Triangle Institute, 2015) to calculate Benzene emissions as:

Emission rate (E) (ton/annum) = PQ D / 100

(1)

Where, P = annual operating rate of the refinery; Q = emission factor (kg/unit); D = % control efficiency. Due to a lack of information on the level of efficiency of the control devices, control efficiency was assumed to be zero (Mulenga & Siziya, 2019; Vargas-Elizondo, 2020) and thus Eq. (1) became:

Emission rate (E) (ton/annum) = PQ

(2)
With this no-control-measure, it is assumed that the emission is a worst case scenario although, it is expected that the higher the control efficiency, D, the lower the emission rate.

Total benzene emissions from the refineries were determined as the sum of emission from point and area sources.
| S/N | Name of Refinery                             | Capacity (bbl/dy) | Date of issue | State   | Longitude & Latitude       |
|-----|---------------------------------------------|-------------------|---------------|---------|---------------------------|
| 1   | Kaduna Refining & Petrochemical Company     | 110 000           | 1980          | Kaduna  | 10.15900 N,8.13390E      |
| 2   | Port Harcourt Refining Company I            | 60 000            | 1965          | Rivers  | 4.85810 N,6.92090E       |
| 3   | Port Harcourt Refining Company II           | 150 000           | 1989          | Rivers  | 4.85810 N,6.92090E       |
| 4   | Warri Refining & Petrochemical Company      | 125 000           | 1978          | Delta   | 5.53250 N,5.89870E       |

Source: (Department of Petroleum Resource (DPR), 2001)
| S/N | Name of Refinery                                      | Capacity (bbl/day) | Date of issue | State            | Coordinates     |
|-----|-------------------------------------------------------|--------------------|---------------|------------------|-----------------|
| 1   | Amakpe International Refinery                        | 12 000            | 2004          | Akwa Ibom        | 4.93000 N,7.87220E |
| 2   | Amexum Corporation                                   | 100 000           | 2009          | Cross River      | 6.16700 N,8.66010E   |
| 3   | Antonsio Oil                                         | 27 000            | 2009          | Ogun             | 6.90750 N,3.58130E   |
| 4   | Chase Wood Consortium Nigeria Limited                | 70 000            | 2004          | Akwa Ibom        | 4.93000 N,7.87220E   |
| 5   | Clean Water Refinery                                 | 60 000            | 2004          | Rivers           | 4.85810 N,6.92090E    |
| 6   | Gasoline Associate & International Limited Refinery  | 100 000           | 2009          | Ogun             | 6.90750 N,3.58130E   |
| 7   | Ilaje Refinery & Petrochemicals                      | 100 000           | 2004          | Ondo             | 6.89590 N,4.89360E    |
| 8   | Niger Delta Refinery & Petrochemical Limited         | 100 000           | 2004          | Delta            | 5.53250 N,5.89870E    |
| 9   | NSP Refineries and Oil Services Limited              | 120 000           | 2004          | Rivers           | 4.85810 N,6.92090E    |
| 10  | Ode Aye Refinery Limited                             | 100 000           | 2004          | Ondo             | 6.89590 N,4.89360E    |
| 11  | Ologbo Refinery Company Nigeria Limited              | 12 000            | 2010          | Edo              | 6.54380 N,5.89870E    |
| 12  | Orient Petroleum Resources Limited                   | 55 000            | 2004          | Anambra          | 6.27580 N,7.00680E    |
| 13  | Owena Oil & Gas Limited                              | 60 000            | 2004          | Ondo             | 6.89590 N,4.89360E    |
| 14  | Qua Petroleum Refinery Limited                       | 100 000           | 2004          | Akwa Ibom        | 4.93000 N,7.87220E    |
| 15  | Rehoboth Natural Resources Limited                   | 12 000            | 2008          | Bayelsa          | 4.86780 N,5.89870E    |
| 16  | Resources Refinery & Petrochemical Limited           | 100 000           | 2004          | Akwa Ibom        | 4.93000 N,7.87220E    |

(Continued)
| S/N | Name of Refinery                                      | Capacity (bbl/day) | Date of issue | State   | Coordinates          |
|-----|------------------------------------------------------|-------------------|---------------|---------|----------------------|
| 17  | Rivgas Petroleum & Energy Limited                    | 30 000           | 2004          | Rivers  | 4.85810 N,6.92090E    |
| 18  | Sapele Refinery Limited                              | 100 000          | 2004          | Delta   | 5.53250 N,5.89870E    |
| 19  | South West Refinery & Petrochemical Company          | 100 000          | 2004          | Ogun    | 6.90750 N,3.58130E    |
| 20  | Starrex Petroleum Refinery                           | 100 000          | 2004          | Rivers  | 4.85810 N,6.92090E    |
| 21  | Total Support Limited                                | 12 000           | 2004          | Cross River | 6.16700 N,8.66010E   |
| 22  | Union Atlantic Petroleum Refinery                    | 100 000          | 2002          | Lagos   | 6.60800 N,3.62180E    |

Source: (Department of Petroleum Resource DPR, 2004, 2010; NNPC: Nigeria National Petroleum Corporation, 2008)
3. RESULTS AND DISCUSSION

A total of 26 identified petroleum refineries (both existing and proposed) in Nigeria were considered for benzene emissions assessment in this study.

The Annual emission calculated from the emission factors of benzene—a hazardous air pollutant from the four existing refineries are presented in Table 3. The benzene emissions were 3.75–1.50 × 10^{13} tons/yr with a mean of 5.92 × 10^{11} tons/yr for Warri Refinery, 1.80–7.23 × 10^{12} tons/yr with a mean of 2.86 × 10^{11} tons/yr for Port Harcourt Refinery I, 4.50–1.81 × 10^{13} tons/yr with a mean of 7.15 × 10^{11} for Port Harcourt Refinery II and 3.30–1.32 × 10^{13} tons/yr with a mean of 5.23 × 10^{11} tons/yr for Kaduna Refinery. Figure 3 shows the sum of benzene emissions from the process unit at four refineries with Port Harcourt Refinery II having the highest emission of benzene because of its highest production capacity as compared to others. The minimum and maximum benzene from these refineries were from their cooling towers and the storage tanks, respectively. This was an indication that with certain temperature can instigate the emission of benzene from storage tank, while at lower temperature (as observed from the cooling tower), emission of benzene and diffusion of benzene was reduced.

| S/N | Process/Equipment | Warri Refinery (125 000 bbl/dy) | Port Harcourt Refinery I (60 000 bbl/dy) | Port Harcourt Refinery II (150 000 bbl/dy) | Kaduna Refinery (110 000 bbl/dy) |
|-----|-------------------|-------------------------------|------------------------------------------|------------------------------------------|-------------------------------|
| 1   | Storage Tanks     | 1.50 × 10^{13}               | 7.23 × 10^{12}                           | 1.81 × 10^{13}                           | 1.32 × 10^{13}               |
| 2   | Boilers and Process Heater firing fuels | 1.01 × 10^{6}               | 4.83 × 10^{5}                           | 1.21 × 10^{6}                           | 8.86 × 10^{5}               |
| 3   | Combustion Engines firing various fuels | 8.54 × 10^{8}               | 4.11 × 10^{8}                           | 1.03 × 10^{9}                           | 7.51 × 10^{8}               |
| 4   | Turbines firing various fuels | 8.85 × 10^{6}               | 4.25 × 10^{6}                           | 1.06 × 10^{7}                           | 7.79 × 10^{6}               |
| 5   | CCU Catalyst Regenerator | 4.11 × 10^{11}               | 1.97 × 10^{11}                           | 4.93 × 10^{11}                           | 3.61 × 10^{11}               |
| 6   | CRU Catalyst Regeneration vent | 9.13 × 10^{4}               | 4.38 × 10^{4}                           | 1.10 × 10^{5}                           | 8.03 × 10^{4}               |
| 7   | Flare             | 4.11 × 10^{2}               | 1.97 × 10^{2}                           | 4.93 × 10^{2}                           | 3.61 × 10^{2}               |
| 8   | Diesel Fired Emergency Engines | 1.24 × 10^{8}               | 5.93 × 10^{7}                           | 1.48 × 10^{8}                           | 1.09 × 10^{8}               |
| 9   | Delayed Coking Unit | 1.92 × 10^{5}               | 9.22 × 10^{4}                           | 2.30 × 10^{5}                           | 1.69 × 10^{5}               |
| 10  | Controlled Coke Calcining | 1.32 × 10^{8}               | 6.35 × 10^{7}                           | 1.59 × 10^{8}                           | 1.16 × 10^{8}               |
| 11  | Effluents         | 7.25                          | 3.48                                    | 8.71                                    | 6.38                         |
| 12  | Diesel Combustion factor (internal & external Combustion) | 1.79 × 10^{5}               | 8.76 × 10^{4}                           | 2.19 × 10^{5}                           | 1.61 × 10^{5}               |
| 13  | Crude/Atmospheric Distillation | 6.34 × 10^{6}               | 3.04 × 10^{6}                           | 7.61 × 10^{5}                           | 5.58 × 10^{5}               |
| 14  | Vacuum Distillation | 2.11 × 10^{4}               | 1.01 × 10^{4}                           | 2.53 × 10^{4}                           | 1.86 × 10^{4}               |

(Continued)
Table 4. Total benzene emission at each of the existing refineries in Nigeria

| S/N | Process/Equipment | Warri Refinery (125,000 bbl/dy) | Port Harcourt Refinery I (60,000 bbl/dy) | Port Harcourt Refinery II (150,000 bbl/dy) | Kaduna Refinery (110,000 bbl/dy) |
|-----|-------------------|---------------------------------|------------------------------------------|------------------------------------------|-------------------------------|
| 15  | Coking            | $2.96 \times 10^6$            | $1.42 \times 10^6$                      | $3.55 \times 10^6$                      | $2.60 \times 10^6$           |
| 16  | Hydrocracking     | $9.17 \times 10^6$            | $4.40 \times 10^6$                      | $1.10 \times 10^7$                      | $8.07 \times 10^6$           |
| 17  | Catalytic cracking/FCCU | $7.03 \times 10^6$                  | $3.37 \times 10^6$                      | $8.43 \times 10^6$                      | $6.18 \times 10^6$           |
| 18  | Catalytic reforming/CRU | $4.43 \times 10^7$                  | $2.13 \times 10^7$                      | $5.32 \times 10^7$                      | $3.90 \times 10^7$           |
| 19  | Hydrotreating/ Hydrides sulphurization | $2.61 \times 10^6$                  | $1.25 \times 10^6$                      | $3.13 \times 10^6$                      | $2.29 \times 10^6$           |
| 20  | Alkylation        | $2.11 \times 10^5$            | $1.01 \times 10^5$                      | $2.53 \times 10^5$                      | $1.86 \times 10^5$           |
| 21  | Isomerization     | $3.51 \times 10^6$            | $1.69 \times 10^6$                      | $4.22 \times 10^6$                      | $3.09 \times 10^6$           |
| 22  | Polymerization    | $8.44 \times 10^6$            | $4.05 \times 10^6$                      | $1.01 \times 10^7$                      | $7.43 \times 10^6$           |
| 23  | Controlled Asphalt Blowing | $7.41 \times 10^7$                        | $3.62 \times 10^7$                      | $8.89 \times 10^7$                      | $6.52 \times 10^7$           |
| 24  | Loading           | $7.63 \times 10^1$            | $3.66 \times 10^1$                      | $9.15 \times 10^1$                      | $6.71 \times 10^1$           |
| 25  | Cooling Towers    | 3.75                            | 1.80                                    | 4.50                                    | 3.30                         |
| 26  | Wastewater        | $1.13 \times 10^7$            | $5.47 \times 10^6$                      | $1.36 \times 10^7$                      | $9.96 \times 10^6$           |
| TOTAL |               | $1.54 \times 10^{13}$         | $7.43 \times 10^{12}$                   | $1.86 \times 10^{13}$                   | $1.36 \times 10^{13}$        |

Figure 3. Total Benzene emission at each of the existing refineries in Nigeria

For the 22 proposed refineries, the expected benzene emissions on an annual basis were as presented in Table 4 with Amakpe International Benzene emissions ranging $3.61 \times 10^{-1}$–$1.44 \times 10^{12}$ tons/yr with a mean of $5.69 \times 10^{10}$ tons/yr, for Amexum Corporation; Gasoline Association and International Limited Refinery; Ilaifa Refinery and Petrochemicals; Niger Delta Refinery Petrochemical Limited; Ode Aye Refinery Limited; Qua Petroleum Refinery Limited; Resource Refinery and Petrochemical Limited; Sapele Refinery Limited; South West Refinery and Petrochemical Company; Starrex Petroleum Refinery and Union Atlantic Petroleum Refinery the Benzene emissions were $3.00–1.21 \times 10^{13}$ tons/yr with a mean of $4.78 \times 10^{13}$ tons/yr at each of the refineries because they all have the same capacity.
Table 4. Estimated Benzene Emission (tons/yr) for proposed refineries

| S/N | Process/Equipment | Amakpe International (12 000 bbl/dy) | Amemum Corporation (100 000 bbl/dy) | Antonsio Oil (27 000 bbl/dy) | Chase Wood Consortium Nig. Ltd (70 000 bbl/dy) |
|-----|-------------------|------------------------------------|-----------------------------------|-----------------------------|---------------------------------------------|
| 1   | Storage Tanks     | $1.44 \times 10^{12}$            | $1.21 \times 10^{11}$            | $3.25 \times 10^{12}$     | $8.43 \times 10^{12}$                      |
| 2   | Boilers and Process Heater firing fuels | $9.66 \times 10^7$ | $8.05 \times 10^5$ | $2.17 \times 10^5$ | $5.64 \times 10^5$ |
| 3   | Combustion Engines firing various fuels | $8.02 \times 10^7$ | $6.84 \times 10^8$ | $1.85 \times 10^8$ | $4.80 \times 10^8$ |
| 4   | Turbines firing various fuels | $8.49 \times 10^5$ | $7.08 \times 10^6$ | $1.92 \times 10^6$ | $4.95 \times 10^6$ |
| 5   | CCU Catalyst Regenerator | $3.94 \times 10^{10}$ | $3.29 \times 10^{11}$ | $8.87 \times 10^{10}$ | $2.30 \times 10^{11}$ |
| 6   | CRU Catalyst Regeneration vent | $8.76 \times 10^7$ | $7.30 \times 10^6$ | $1.97 \times 10^6$ | $5.11 \times 10^6$ |
| 7   | Flare             | $3.94 \times 10^1$      | $3.29 \times 10^2$      | $8.87 \times 10^1$      | $2.30 \times 10^1$ |
| 8   | Diesel Fired Emergency Engines | $1.19 \times 10^7$ | $9.88 \times 10^7$ | $2.67 \times 10^7$ | $6.92 \times 10^7$ |
| 9   | Delayed Coking Unit | $1.84 \times 10^9$ | $1.54 \times 10^9$ | $4.15 \times 10^9$ | $1.08 \times 10^9$ |
| 10  | Controlled Coke Calcining | $1.27 \times 10^7$ | $1.06 \times 10^8$ | $2.86 \times 10^7$ | $7.41 \times 10^7$ |
| 11  | Effluents         | $6.96 \times 10^{-1}$ | $5.80$ | $1.57$ | $4.06$ |
| 12  | Diesel Combustion factor (internal & external Combustion) | $1.75 \times 10^4$ | $1.46 \times 10^5$ | $3.94 \times 10^6$ | $1.02 \times 10^6$ |
| 13  | Crude/ Atmospheric Distillation | $6.09 \times 10^1$ | $5.07 \times 10^6$ | $1.37 \times 10^6$ | $3.55 \times 10^6$ |
| 14  | Vacuum Distillation | $2.03 \times 10^1$ | $1.69 \times 10^6$ | $4.56 \times 10^5$ | $1.18 \times 10^5$ |
| 15  | Coking           | $2.84 \times 10^5$ | $2.37 \times 10^6$ | $6.39 \times 10^5$ | $1.66 \times 10^5$ |
| 16  | Hydrocracking    | $8.80 \times 10^1$ | $7.34 \times 10^6$ | $1.98 \times 10^6$ | $5.14 \times 10^6$ |
| 17  | Catalytic cracking/FCCU | $6.75 \times 10^5$ | $5.62 \times 10^6$ | $1.52 \times 10^6$ | $3.93 \times 10^6$ |
| 18  | Catalytic reforming/CRU | $4.26 \times 10^5$ | $3.55 \times 10^7$ | $9.58 \times 10^5$ | $2.48 \times 10^5$ |
| 19  | Hydrotreating/Hydro sulphurization | $2.50 \times 10^5$ | $2.08 \times 10^6$ | $5.63 \times 10^5$ | $1.46 \times 10^5$ |
| 20  | Alkylation       | $2.03 \times 10^5$ | $1.69 \times 10^5$ | $4.56 \times 10^5$ | $1.18 \times 10^5$ |
| 21  | Isomerization    | $3.37 \times 10^5$ | $2.81 \times 10^6$ | $7.59 \times 10^5$ | $1.97 \times 10^5$ |
| 22  | Polymerization   | $8.10 \times 10^5$ | $6.75 \times 10^6$ | $1.82 \times 10^6$ | $4.73 \times 10^6$ |
| 23  | Controlled Asphalt Blowing | $7.11 \times 10^5$ | $5.93 \times 10^7$ | $1.60 \times 10^7$ | $4.15 \times 10^7$ |
| 24  | Loading          | $7.32 \times 10^2$ | $6.10 \times 10^1$ | $1.65 \times 10^1$ | $4.27 \times 10^1$ |
| 25  | Cooling Towers   | $3.61 \times 10^{-1}$ | $3.00$ | $8.10 \times 10^{-1}$ | $2.10$ |
| 26  | Wastewater       | $1.09 \times 10^6$ | $9.05 \times 10^6$ | $2.44 \times 10^5$ | $6.34 \times 10^5$ |
| TOTAL |                  | $1.48 \times 10^{12}$ | $1.24 \times 10^{11}$ | $3.34 \times 10^{12}$ | $8.66 \times 10^{12}$ |
The emissions were $1.57\times10^{12}$–$3.25\times10^{12}$ tons/yr with a mean of $1.28\times10^{11}$ tons/yr for Antonsio Oil, for Chase Wood Consortium Nigeria Limited the emissions were $2.10\times10^{12}$–$8.43\times10^{12}$ tons/yr with a mean of $3.33\times10^{11}$ tons/yr for Clean Water Refinery, $3.60\times10^{12}$–$1.44\times10^{13}$ tons/yr with a mean of $5.69\times10^{11}$ tons/yr for NSP Limited Service Refinery, $3.61\times10^{12}$–$1.44\times10^{13}$ tons/yr with a mean of $5.69\times10^{11}$ tons/yr for Ologobo Refinery Company Nigeria Limited, $1.65\times10^{12}$–$6.63\times10^{12}$ tons/yr with a mean of $2.62\times10^{11}$ tons/yr for Orient Petroleum Resources Limited, $1.80\times10^{12}$–$7.23\times10^{12}$ tons/yr with a mean of $2.86\times10^{11}$ tons/yr, $3.61\times10^{12}$–$1.44\times10^{13}$ tons/yr with a mean of $5.69\times10^{11}$ tons/yr for Rehoboth Natural Resources Limited and Total Support Limited while the emission were $1.74\times10^{12}$–$3.62\times10^{12}$ tons/yr with a mean of $1.43\times10^{11}$ tons/yr for Rivgas Petroleum and Energy Limited. **Figure 4** shows the total emissions at each of the proposed refineries with NSP Limited Service Refinery having the maximum emission while the minimum expected emissions were at Amakpe International, Ologobo Refinery Company Nigeria Limited, Rehoboth Natural Resources Limited and Total Support Limited. This occurred as a result of the production capacity of these refineries.

The process unit with maximum benzene emission was from storage tanks while the cooling towers and the effluents unit emit the minimum.

Apparently, two of the existing refineries located in Rivers State (Port Harcourt Refineries I and II) release a total of $10.01\times10^{11}$ tons of benzene into the ambient air of Port Harcourt City annually. This was thought to result in the elevation of the concentration of the hazardous organic pollutant in ambient atmosphere creating unfriendly environment for the residents of one of the most populous Nigerian city. Benzene emissions are hardly localized with the confinement of the point of release and thus can easily travel through plume where the emissions become fractionated with distance from the source. Advection and diffusion transport can also aid the movement of the emission far away from the sources to create environmental nuisance in a nearby surrounding (Kassomenos, Karakitsios, Pilidis et al., 2004a; Mulenga & Siziya, 2019; Sonibare et al., 2007).

Additionally, three of the proposed refineries (Clean Water Refinery, Rivgas Petroleum and Energy Service and Starrex Petroleum Refinery) are located in Rivers State. It would be therefore anticipated that these three refineries, when fully operational, would have the capacity to release additional $2.35\times10^{13}$ tons of benzene to the atmosphere yearly. Another concern is the
localization of all the 26 refineries. As shown in Figure 1, the location of these refineries suggests that the Southern part of the country would be greatly affected and the situation if not checked, will have adverse effects on human health as well as water, soil and vegetation of the area. The benzene concentration gradients across the study areas are pointers to the fact that petroleum refineries are major sources of increased benzene in ambient air-both indoor and outdoor. It thus sufficed to infer that states with petroleum refineries will likely experience higher exposure to benzene compare to states without petroleum refineries.

Results of similar previous studies from other countries showed lower emission of benzene from petroleum refineries (Edokpolo et al., 2015). Benzene emission from modern refineries in Italy has been reported to be less than 3 mg/m³ (Basso et al., 2011). Similar studies in Bulgaria also reported reduced emission of benzene (Mirkova et al., 1999). The reason behind the discrepancy could be attributed not only to the fact that the estimation in this study was done with “no-control-measure option”, but also to the level of infrastructural developments of the countries where the refineries are domiciled. Italy and Bulgaria could be regarded as developed nations with more sound and strict environmental regulation compared with Nigeria- a developing nation having high level of non-compliance with environmental guidelines. Report by (Sonibare et al., 2007) conducted in 2007 (13 years ago) revealed that the four existing refineries emitted a total of 147,212 ton/annum VOC into the ambient air. This concentration is much lower that the results of this present study. This could be said to be an indication of the obsolete nature of majority of the petroleum refinery facilities.

Previous research have also not only revealed a direct correlation between benzene ambient concentration and proximity to petroleum industries (Na et al., 2001); but also noticed a decline ambient concentration of benzene as the concentration released to the atmosphere decreases (Gibergans-Baquena et al., 2020; Kajihara et al., 2003). The effects of exposure to high level of benzene on human health, water, soil and vegetation (Guo et al., 2004; Johnson et al., 2003; Kim et al., 2001; Ofebea, 2018) provide sufficient evidence for the implementation of necessary control measure in both existing and proposed refineries.

The Benzene emissions from each of the refineries were found to the far more than occupational exposure limits (Table 5) set by various US organizations. This poses a serious health risk to both the personnel working within the refineries and residents of the communities.

Source: (Nordlinder & Ramnnas, 1987)

It is important to note that, of all the common aromatic (BTEX), Benzene has the longest atmospheric lifetime of 9.4 days (Rao et al., 2004). This indicates that benzene has potential to travel a longer distance from the source of release than any other common aromatic component. Based on this and possibility of diffusion, Benzene is not retained within the source of release but

| Regulatory Body                                      | Exposure limits (µg/m³) tons/m³ |
|-----------------------------------------------------|---------------------------------|
| American Conference of Governmental Industrial Hygienists (ACGIH), USA | 1600 1.6 × 10⁻⁹               |
| Occupational Safety and Health Administration (OSHA), USA          | 3250 3.25 × 10⁻⁹               |
| National Institute for Occupational Safety and Health (NIOSH), US | 325 3.25 × 10⁻¹⁰                |
| Safe Work Australia (SWA)                                  | 3250 3.25 × 10⁻⁹               |
rather transported beyond point of release. Apart from wind speed and wind direction, operating temperature is another major parameter that influences the release of Benzene and other BTEX (Aiswarya & William, 2017; Kassomensas, Karakitsios, Pilidis et al., 2004b).

Benzene emissions above 100 ton/annum has been considered as highly unfriendly (Sonibare et al., 2007), however, with reasonable available control technology, either destructive or recovery great proportion can be curtailed (Borowski, 2020; Khan & Kr, 2000). Identification of the potential benzene emission sources in the proposed refineries, right from the design stage can play a vital role in choosing the appropriate control technology (Basso et al., 2011; Mirkova et al., 1999). Recovery approach allows for the recovered benzene to be used as raw material in other manufacturing sector. Destructive approach could involve catalytic combustion process with the use of activated carbon (Dwivedi et al., 2004; Sonibare et al., 2007). Storage tanks should be properly covered; there should be avoidance of cracks and leakages from tanks and pipes. All effluents should be well treated before discharge and most importantly, adequate regulation must be put in place by the government to minimize benzene emission.

4. CONCLUSION
The focus of this study was to assess the potential contribution of Nigerian’s petroleum refineries emission to ambient composition of benzene. Using emission factor approach, benzene emission from both existing and proposed refineries was estimated. The existing refineries release about 5.50 × 10^13 tons/year of Benzene while the proposed refineries have the potential adding 16.73 × 10^13 tons/year, when fully operational. The consequence of this is that 22.24 × 10^13 tons of Benzene will be released to Nigerian airshed yearly. Benzene emission of this magnitude is considered unfriendly not only to the southern region of the country which will be more affected, but Nigeria as a whole, bearing in mind the hazardous nature of the hydrocarbon pollutant. It is concluded that with adequate appropriate control measures, great proportion of the estimated benzene emission could be curtailed.

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ACRONYMS
BTEX Benzene, Toluene, Ethyl benzene and Xylene
HAPs Hazardous Air Pollutants

VOCs Volatile Organic Compounds
WHO World Health Organization
IARC International Agency for Research on Cancer
CO Carbon monoxide
NO2 Nitrogen dioxide
FRCCU Flame Catalytic Cracking Unit
CRU Catalytic reforming Unit
ACGIH American Conference of Governmental Industrial Hygienists
OSHA Occupational Safety and Health Administration
NIOSH National Institute for Occupational Safety and Health
SWA Safe Work Australia
RTI Research Triangle Institute

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