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Outdoor Air Quality and Acid Rains within Warri Refinery and Its Environs

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Authors' contributions

This work was carried out in collaboration between all authors. Author UEA designed the study and performed the statistical analysis. Author IAA wrote the protocol and the first draft of the manuscript. Author OOA managed literature searches. Authors AFA and TAA managed the analyses of the study and literature searches. All authors read and approved the final manuscript.

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ABSTRACT

The focus of the research was to assess the impact of the Warri Refinery operations on the outdoor air quality within the refinery and its environs. The Warri Refining and Petrochemical Company (WRPC) is an industrial complex of the Nigeria National Petroleum Corporation (NNPC) downstream sector, located between Ekpan and Ubeji communities of Delta state of Nigeria. Outdoor air quality within the refinery, Ubeji and Ekpan communities were checked for the concentration of hydrogen sulphide, carbon dioxide, toluene, benzene and perchloroethylene. The results from the study revealed the presence of benzene, toluene and hydrogen sulphide within the outdoor air of the refinery and its environs in almost constant concentrations. However, these gases/vapours are present in concentrations lower than the Federal Environmental Protection Agency (FEPA) listed limits. Also, rain water samples from within the refinery, Ubeji and Ekpan communities were collected for three consecutive years during the raining season and the water samples checked for acidity. There were complaints by some residents of the environs about frequent eye irritation which they link to the rather heavy gaseous emissions. The results from the

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study also further underscores the need for continuous monitoring of outdoor air quality especially in settlements and rural communities bordering areas with high industrial activities.

Keywords: Outdoor; Ekpan; Ubeji; pollution; downstream.

1. INTRODUCTION

The Warri Refining and Petrochemical Company (WRPC) is located between Ekpan and Ubeji communities of Delta state of Nigeria at a surface location of 366,140.12 meters Easting and 174,200.08 meters in Northing. Rapid urbanization and industrialization of Warri and its environment between 1968 and 1990 brought about the contamination of the river, estuaries, creeks and air in the vicinity [1]. Nigeria has vast crude oil and gas deposits and attempts to explore and exploit it have left the country with unique vulnerabilities [2]. The Niger Delta is host to three of Nigeria's four refineries which generates large quantities of effluents daily [3]. Refinery operations are also accompanied by a lot of atmospheric emissions with a potential to contaminate or pollute the air in the neighbourhood.

To underscore the relevance and threats posed by a negligence of the environment June 5 every year is set aside and marked as World's Environment Day [4]. The June 1992 Earth Summit in Rio de Janeiro, Brazil, focused on international agreements to deal with threats occasioned by environmental pollution [5].

The petroleum industry remains one of the most important sectors in the world. The relevance of the petroleum industry notwithstanding its activities leave behind it trails of numerous environmental impact on the host communities. Nigeria being an oil producing country, the activities of crude oil exploitation, petroleum refining, distribution and marketing all have their attendant environmental consequences.

Air pollution is a ranking aspect of environmental pollution, the problems of acid rain and global warming has emerged as some of the more important environmental issues in recent times [6]. The primary cause of acid rain is industrial and automotive air pollution.

Air pollution is defined as the discharge of dust sooth, gaseous oxides, hydrocarbons, volatile organic compounds (VOCs), heavy metals into the atmosphere from several chemical/industrial sources and processes [7]. Volatile organic compounds (VOCs) are gases or vapours emitted by various solids and liquids, many of which have short and long-term adverse effects on human health and the environment. VOCs from petroleum are toxic and foul the air, and some like benzene are extremely toxic, carcinogenic and cause DNA damage. Benzene often makes up about 1% of crude oil and gasoline. Benzene is present in automobile exhaust [8]. Depending on the quantities discharged, air contamination or pollution results. Contamination is an increase in some substance above its natural range [9].

Outdoor air emissions include gases, fumes. particulates, dusts and odours that arise from process activities (e.g. boiler operations) and transportation. Fossil fuel combustion (natural gas, liquid petroleum gas, light oil, diesel, heavy oil) are principal sources of emission in petroleum refining operations. Motor vehicle emissions is one of the leading causes of air pollution with China, United States, Russia, Mexico, and Japan being the world leaders in air pollution emissions, and principal stationary pollution sources to include chemical plants, coal-fired power plants, oil refineries, petrochemical plants, incinerators, e.t.c. [10].

Many of the production processes of an oil refinery and petrochemical plants involve the use of volatile hydrocarbons as basic raw materials as well as end products. Inevitably, processes with volatile hydrocarbons result in their evaporation into the atmosphere. Some of the sources of air pollution in WRPC are as follows:- the torch or flare of the oil refinery which is always alight whenever the refinery is in operation is a major source of emission of CO_x, SO_x and NOx and other combustion products into the atmosphere; stack/chimney of several industrial furnaces/boilers in the process plants also emits CO_x, SO_x and NO_x and other combustion products into the atmosphere; venting operations (from pressure controlling devices) discharge hydrocarbons into the atmosphere; blow-down operations release Liquefied Petroleum Gas and VOCs into the atmosphere; evaporation of volatile hydrocarbons into the atmosphere during loading of tankers at the Pipeline and Products Marketing

Company (PPMC) section of WRPC; oily open-air wastewater treatment plants of the refinery all constitute significant sources of the emission of volatile organic compounds into the atmosphere, [11]. Common indoor air quality related health complaints are headaches, burning eyes, dry throat, respiratory irritation, fatigue, dizziness and neurological effects such as disorientation and mental confusion [12]. Older people are majorly exposed to diseases induced by air pollution. Those with heart or lung disorders are under additional risk. Children and infants are also at serious risk.

2. MATERIALS AND METHODS

2.1 Acid Rains: Tests / Checks for Acid Rains in Settlements within the Range of 5 - 10 Km Radius of the Refinery

Significance: The emission of hydrogen sulphide, the oxides of sulphur, nitrogen and carbon from chemical and industrial processes leads to the formation of acid rains. Acid rain is harmful to natural vegetation, wear out limestone deposits and statues, aids corrosion of rooftops and leaching of minerals from soil.

Materials: Mettler Toledo pH meter, distilled water, ethanol, buffer solutions of pH 4, 7 and 9.

Methods: Rain water samples within the refinery, Ubeji and Ekpan communities were collected for three years consecutively during the raining season and tested for acidity. The measurement was done when the refinery flare and plants were in sustained operation. A calibrated Mettler Toledo pH meter was used in taking the measurement.

- the pH meter electrode was cleaned using ethanol and then distilled water
- the power to the pH meter was turned on
- the pH meter was calibrated using buffers 4, 7 and 9
- the calibrated pH meter electrode was dipped into sample and the reading was taken

2.2 Measurement of Outdoor Air Quality around the Refinery and Settlements within 5 Km Radius of the Refinery

Significance: Hydrogen sulphide is an odourous and toxic gas with an unpleasant smell that forms sulphuric acid with water. It is a precursor of acids rains. The hydrogen sulphide in the air sample was oxidized by zinc oxide in the detector tubes yielding zinc sulphide and water

Benzene is toxic and has been identified as a carcinogen. It presence is undesirable in ambient air. The benzene vapour in the air sample was oxidized by chromate/sulphuric acid reagent in the detector tubes.

Toluene is an analogue of benzene and under certain conditions de-methylate yielding benzene. Gaseous and hydrocarbon vapours are major air pollutants. The toluene vapour in the air sample was oxidized by iodine pentaoxide/sulphuric acid reagent in the detector tubes.

Perchloroethylence a chlorocarbon is an ozone depleting gas. Because of its unsaturation it could easily transform to a chlorofluorocarbon, notable for attacking the ozone layer. Its presence is undesirable in the atmosphere. The perchloroethylene vapour in the air sample was oxidized by iodine in fuming sulphuric acid reagent in the detector tubes.

Carbon dioxide. Concentrations of CO_2 higher than its natural composition of 0.03% is undesirable in the atmosphere, carbon dioxide being a major greenhouse gas is implicated for global warming. The CO_2 in the air sample was absorbed by moist potassium hydroxide reagent in the detector tubes.

Materials: AUER Gas Tester (manual pump), AUER H_2S (1 – 200ppm) detector tubes PR 826, AUER Toluene detector tube (5-1000 ppm) PR 828, AUER Benzene detector tubes PR 807, Perchloroethylene (10 – 500 ppm) detector tubes PR 840, AUER CO_2 (0.1 – 7%) detector tubes PR 817.

Methods:

- The pump (aspirator) was tested and confirmed to be in good working condition by expelling the air in its bellow and its ability to suck in air on releasing the bellow.
- Tips at both ends of detector tube were broken with the tip-breaker on the pump
- The detector tube was inserted tightly into the pump following the guide arrow on the detector tube. Arrow on tube pointing towards the pump.

- The pump was operated about 10 times to saturate the detector tube with the ambient air.
- The broken ends of the detector tube were tightly sealed with tape.
- The reading was taken after 10 minutes for perchloroethylene and after 5 hours for the other gases/vapours.

3. RESULTS AND DISCUSSION

3.1 Acid Rains

The results in Table 1 clearly shows the consistent nature of acid rains especially within the perimeters of the refinery for the three years under review. Within the refinery the pH ranged from 4.70 to 4.95. The pH of the rain water from Ekpan community ranged from 6.10 to 6.20 while the pH of the rain water from Ubeji community ranged from 6.20 to 6.45. In the measurement of pH of rain water Ondo township rain was set up as control, the pH ranged from 6.50 to 6.65. FEPA /WHO set limit for pH of domestic and drinkable water is 6.5 to 8.5. The rain water from within the refinery, Ekpan and Ubeji communities fell short of the listed limits. Ondo township rain water pH averaged 6, 58 a marginal pass above the 6.5 limit.

The pH profile of the rain water from within the refinery, Ekpan and Ubeji communities is due to the heavy emission of CO_2, SO_2 and NO_2 all of which are acidic oxides from the refinery's operation and heavy vehicular emission. On one-to-one interactions, some WRPC staff and residents within Ekpan and Ubeji communities complained of eye irritation from time to time, a condition which might not be unconnected with heavy flue gas emission, vehicular emission and hydrocarbon vapors that pervade the neighbourhood.

3.2 Outdoor Air Quality within the Refinery, Ubeji and Ekpan Communities

Benzene, toluene and hydrogen sulphide were detected in Refinery outdoor air. Hydrogen sulphide concentration was almost constant for the measurements taken in the morning, afternoon and evening ranging from 9 to 12 ppm. FEPA has no listed limits for Hydrogen sulphide, however H_2S is an odourous gas and has the potential of contributing to acid rains. Its presence in ambient air reduces natural air quality.

Benzene was detected but in concentrations of less than toxic in the measurements taken in the morning, afternoon and evenings. FEPA listed limits for benzene in ambient air is 1500 µg/m^3 (147 ppm). The detector tube used for this test

Table 1. Acid rain test

	Refinery rain water (pH)	Ekpan rain water (pH)	Ubeji rain water (pH)	Ondo rain water (pH)	FEPA /WHO limits for (pH) of domestic water
2012	4.95±.0.03	6.20±.0.05	6.45±.0.13	6.50±.0.04	
2013	4.70±.0.13	6.15±.0.04	6.20±.0.14	6.60±.0.5	6.5 - 8.5
2014	4.80±.0.02	6.10±.0.05	6.30±.0.13	6.65±.0.03	

Table 2. Refinery outdoor air

Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	*FEPA µg/m^3*
Hydrogen Sulphide (H_2S) 1-200 ppm	9	10	12	No listed limits
Toluene ($C_6H_5CH_3$) 5-1000 ppm	20	20	25	2000 (141 ppm)
Benzene (C_6H_6) (Tox/Ex)	Less than tox. Level	Less than tox. Level	Less than tox. Level	1500 (147 ppm)
Perchloroethylelene ($Cl_2C=CCl_2$) 10-500 ppm	BDL	BDL	BDL	No listed Limits
Carbon dioxide (CO_2) 0.1-7% vol.	BDL	BDL	BDL	No listed Limits

Tox. = Toxic, Ex. = Extremely toxic, BDL = Below Detection Limit

registered the presence of benzene in the region of less than toxic level which is below 100 ppm Benzene toxicity is between 100 – 2500 ppm while extreme toxicity starts from above 2500 ppm [13]. A study of benzene exposure of 200 California commuters found an average exposure of 13 ppb while driving to and from work in San Fransisco Bay region [14]. Exposure to air pollution from benzene emission from automobile and tobacco smoking has been estimated to surpass that from all stationary industry in the United State [15].

Toluene was detected in almost constant concentrations ranging from 20 to 25 ppm for the measurements taken in the morning, afternoon and evenings. The values are below FEPA listed limits for toluene is 2000 µg/m^3 (141 ppm) in ambient air The concentrations of carbon dioxide and perchloroethylene in the ambient air were below detection limit within the refinery, Ekpan and Ubeji Communities. The slightly higher concentration of toluene in Refinery's ambient air can be attributed tot the fact that the refinery operations is the primary source of emission while vehicular emission is a secondary source.

Again, benzene, toluene and hydrogen sulphide were detected in Ekpan outdoor air. Hydrogen sulphide concentration was almost constant for the measurements in the morning, afternoon and evening ranging from 10 to 12 ppm. FEPA has no listed limits for Hydrogen sulphide. Benzene was detected in concentrations of less than toxic level in the measurements taken in the morning, afternoon and evening. FEPA listed limits for benzene in ambient air is 1500 µg/m^3 (147 ppm). Toluene was detected in almost constant concentrations of 15 ppm for the measurements taken in the morning, afternoon and evenings only as was in the case for benzene. The values are below FEPA listed limits for toluene in ambient air is 2000 µg/m^3 (141 ppm). The slightly higher concentration of benzene and toluene in Ekpan ambient air can be attributed to both refinery operations and much heavier emissions from vehicular traffic in Ekpan which is a more densely populated area than Ubeji.

Benzene, toluene and hydrogen sulphide were detected in Ubeji outdoor air. Again, hydrogen sulphide concentration was almost constant for the measurements in the morning, afternoon and evening at 10 ppm. Benzene was detected in concentrations of less than toxic level in the measurements taken in the afternoon and evenings only. FEPA listed limits for benzene in ambient air is 1500 µg/m^3 (147 ppm).

Table 3. Ekpan outdoor air quality

Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	*FEPA µg/m^3*
Hydrogen Sulphide (H_2S) 1-200 ppm	11	12	10	No listed Limits
Toluene ($C_6H_5CH_3$) 5-1000 ppm	15	15	15	2000 (141 ppm)
Benzene (C_6H_6) (Tox/Ex)	Less than tox. Level	Less than tox. Level	Less than tox. Level	1500 (147 ppm)
Perchloroethylelene ($Cl_2C=CCl_2$)10-500 ppm	BDL	BDL	BDL	No listed Limits
Carbon dioxide (CO_2) 0.1-7% vol.	BDL	BDL	BDL	No listed Limits

Tox. = Toxic, Ex. = Extremely toxic, BDL = Below Detection Limit

Table 4. Ubeji outdoor air quality

Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	*FEPA µg/m^3*
Hydrogen Sulphide (H_2S) 1-200 ppm	10	10	10	No listed limits
Toluene ($C_6H_5CH_3$) 5-1000 ppm	BDL	BDL	20	2000 (141 ppm)
Benzene (C_6H_6) (Tox/Ex)	Less than tox. Level	Less than tox. Level	Less than tox. Level	1500 (147 ppm)
Perchloroethylelene ($Cl_2C=CCl_2$) 10-500 ppm	BDL	BDL	BDL	No listed Limits
Carbon dioxide (CO_2) 0.1-7% vol.	BDL	BDL	BDL	No listed Limits

Tox. = Toxic, Ex. = Extremely toxic, BDL = Below Detection Limit

Toluene was detected in concentrations of 20 ppm in the measurements taken in the evening only as was in the case of benzene. The values also did not exceed FEPA listed limits for toluene in ambient air. The presence of benzene and toluene in Ubeji ambient air can be attributed to both refinery operations and heavy emissions from vehicular traffic which builds up in the afternoon and evenings.

4. CONCLUSION

The occurrence of acid rains detected within the refinery and its environs could be partly attributable to heavy CO_2 emission from the industrial complex and emission of oxides of sulphur (sulphur being a constituent of all crude oil types), hydrogen sulphide and oxides of nitrogen occasioned by refining crude oil, The results of the air quality monitored reveals the presence of benzene, toluene and hydrogen sulphide within the outdoor air of the refinery and its environs in almost constant concentrations whenever the refinery is in operation The dynamics of weather in the open atmosphere however ameliorates challenges from outdoor air contamination or pollution. It is noteworthy, that the gases/vapours detected are present in concentrations that do not exceed FEPA listed limits. There were complaints by some residents of the environs about occasional eye irritation which they link to the rather heavy gaseous emissions. The results from the study also further underscores the need for continuous monitoring of indoor and outdoor air quality especially in settlements and rural communities bordering areas with high industrial activities.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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