

Original Research Article**Outdoor Air Quality and Acid Rains within Warri Refinery and Its Environs****ABSTRACT**

The focus of the research was to assess the impact of the Warri Refinery operations on the outdoor air quality of 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 that 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. 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 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

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 Easting and 174,200.08 in Northing.

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 [1]. The June 1992 Earth Summit in Rio de Janeiro, Brazil, focused on international agreements to deal with threats occasioned by environmental pollution [2].

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.

John, et al consider air pollution 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[3]. The primary cause of acid rain is industrial and automotive air pollution.

Pattel defined "air pollution" 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 [4]. 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 [5].

Depending on the quantities discharged, air contamination or pollution results. Contamination is an increase in some substance above its natural range [6].

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. Segal considers motor vehicle emissions as 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.[7].

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 NO_x 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 LPG 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, [8].

All these facts indicate that several types of emission sources contribute to the concentration levels of pollutants in the ambient air. 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 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 [3].

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 and the atmospheric condition was prevailing. 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

88 **2.2** Measurement of outdoor air quality around the refinery and settlements within 5km radius of
89 the refinery.

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

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

96 **Toluene** is an analogue of benzene and under certain conditions de-methylate yielding benzene
97 which is toxic and has been identified as a carcinogen. Gaseous and hydrocarbon vapours are
98 major air pollutants. The toluene vapour in the air sample was oxidized by iodine
99 pentaoxide/sulphuric acid reagent in the detector tubes.

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

104 **Carbon dioxide.** Concentrations of CO₂ higher than its natural composition of 0.03% is
105 undesirable in the atmosphere, carbon dioxide being a major greenhouse gas implicated for
106 global warming. The CO₂ in the air sample was absorbed by moist potassium hydroxide reagent
107 in the detector tubes.

108 **Materials:**

AUER Gas Tester (manual pump), AUER H₂S (1 – 200ppm) detector tubes PR 826, AUER Toluene detector tube (5-1000ppm) PR 828, AUER Benzene detector tubes PR 807, Perchloroethylene (10 - 500ppm) detector tubes PR 840, AUER CO₂ (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 open suction end of the detector tube was tightly sealed with tape.
- The reading was taken after 5 hours.

3. RESULTS AND DISCUSSION

3.1 Acid Rains

Table 1 . Acid Rain Test

	Refinery	Ekpan Rain	Ubeji Rain	Ondo Rain	FEPA /WHO
	Rain	Water (pH)	Water	Water	Limits for (pH) of
	water (pH)		(pH)	(pH)	Domestic water

2012	4.95	6.20	6.45	6.50	6.5 - 8.5
2013	4.70	6.15	6.20	6.60	
2014	4.80	6.10	6.30	6.65	

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127 The results in Table 1 above clearly shows the consistent nature of acid rains especially
 128 within the perimeters of the refinery for the three years under review. Within the refinery the pH
 129 ranged from 4.70 to 4.95. The pH of the rain water from Ekpan community ranged from 6.10 to
 130 6.20 while the pH of the rain water from Ubeji community ranged from 6.20 to 6.45. In the
 131 measurement of pH of rain water Ondo township rain was set up as control, the pH ranged from
 132 6.50 to 6.65. FEPA /WHO set limit for pH of domestic, usable and drinkable water is 6.5 to 8.5.
 133 The rain water from within the refinery, Ekpan and Ubeji communities fell short of the listed
 134 limits. Ondo township rain water pH averaged 6.58, a marginal pass above the 6.5 limit.

135 The pH profile of the rain water from within the refinery, Ekpan and Ubeji communities is due
 136 to the heavy emission of CO₂, SO₂ and NO₂ all of which are acidic oxides from the refinery's
 137 operation and heavy vehicular emission. On one-to-one interactions, some WRPC staff and
 138 residents within Ekpan and Ubeji communities complained of eye irritation from time to time, a
 139 condition which might not be unconnected with heavy flue gas emission, vehicular emission and
 140 hydrocarbon vapors that pervade the neighbourhood.

141 3.2 Outdoor Air Quality within the Refinery, Ubeji and Ekpan communities

142 **Table 2. Refinery Outdoor Air**

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Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	FEPA $\mu g/m^3$
Hydrogen Sulphide (H ₂ S) 1-200ppm	9	10	12	No listed limits
Toluene (C ₆ H ₅ CH ₃) 5-1000ppm	20	20	25	2000
Benzene (C ₆ H ₆) (Tox/Ex)	Less than tox. Level	Less than tox. level	Less than tox. Level	1500
Perchloroethylelene (Cl ₂ C=CCl ₂)10- 500ppm	BDL	BDL	BDL	No listed limits
Carbon dioxide (CO ₂) 0.1-7% vol.	BDL	BDL	BDL	No listed limits

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

145 Benzene, toluene and hydrogen sulphide were detected in Refinery outdoor air. Hydrogen
 146 sulphide concentration was almost constant for the measurements taken in the morning,
 147 afternoon and evening ranging from 9 to 12 ppm. FEPA has no listed limits for Hydrogen
 148 sulphide, however H₂S is an odourous gas and has the potential of contributing to acid rains. Its
 149 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 $\mu\text{g}/\text{m}^3$. Toluene was detected in almost constant concentrations ranging from 20 to 25 ppm for the measurements taken in the morning, afternoon and evenings, FEPA listed limits for toluene in ambient air is 2000 $\mu\text{g}/\text{m}^3$. 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 to the fact that the refinery operations is the primary source of emission while vehicular emission is a secondary source.

Table 3. Ekpan Outdoor Air Quality

Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	FEPA $\mu\text{g}/\text{m}^3$
Hydrogen Sulphide (H_2S) 1-200ppm	11	12	10	No listed limits
Toluene ($\text{C}_6\text{H}_5\text{CH}_3$) 5-1000ppm	15	15	15	2000
Benzene (C_6H_6) (Tox/Ex)	Less than tox. Level	Less than tox. level	Less than tox. Level	1500
Perchloroethylene ($\text{Cl}_2\text{C}=\text{CCl}_2$)10- 500ppm	BDL	BDL	BDL	No listed limits

Carbon dioxide (CO ₂) 0.1-7% vol.	BDL	BDL	BDL	No listed limits
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Tox. = Toxic, Ex. = Extremely toxic, BDL = Below Detection Limit

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 12ppm. 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 evenings. FEPA listed limits for benzene in ambient air is 1500 $\mu\text{g}/\text{m}^3$. 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. FEPA listed limits for toluene in ambient air is 2000 $\mu\text{g}/\text{m}^3$. The slightly higher concentration of benzene and toluene in Ekpan ambient air can be attributed to both refinery operations and much heavy emissions from vehicular traffic in Ekpan which is a more densely populated area than Ubeji.

Table 4. Ubeji Outdoor Air Quality

Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	FEPA $\mu\text{g}/\text{m}^3$
Hydrogen Sulphide (H ₂ S) 1-200ppm	10	10	10	No listed limits
Toluene (C ₆ H ₅ CH ₃) 5-1000ppm	BDL	BDL	20	2000
Benzene (C ₆ H ₆)	Less than tox.	Less than tox.	Less than	1500

(Tox/Ex)	Level	level	tox. Level	
Perchloroethylene (Cl ₂ C=CCl ₂)10- 500ppm	BDL	BDL	BDL	No listed limits
Carbon dioxide (CO ₂) 0.1-7% vol.	BDL	BDL	BDL	No listed limits

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

176 Benzene, toluene and hydrogen sulphide were detected in Ubeji outdoor air. Again,
 177 hydrogen sulphide concentration was almost constant for the measurements in the morning,
 178 afternoon and evening at 10 ppm. Benzene was detected in concentrations of less than toxic level
 179 in the measurements taken in the afternoon and evenings only. FEPA listed limits for benzene in
 180 ambient air is 1500 µg/m³. Toluene was detected in concentrations of between 15 to 20 ppm in
 181 the measurements taken in the afternoon and evenings only as was in the case of benzene. FEPA
 182 listed limits for benzene in ambient air is 2000 µg/m³. The presence of benzene and toluene in
 183 Ubeji ambient air can be attributed to both refinery operations and heavy emissions from
 184 vehicular traffic which builds up in the afternoon and evenings.

185 4. CONCLUSION

186 The occurrence of acid rains detected within the refinery and its environs could be partly
 187 attributable to heavy CO₂ emission from the industrial complex and emission of oxides of
 188 sulphur (sulphur being a constituent of all crude oil types), hydrogen sulphide and oxides of
 189 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.

REFERENCES

1. Luke O . World Environment Day: Our carbon economy. The Guardian, June 10, 2008, p79
2. United Nations: Earth Summit Convention on Climate Change 3-14 June 1992. United Nations. 1992.
3. John M and Robert C Fay. Chemistry, Prentice Hall Inc., New Jersey, USA. 1995. p 608.
4. Pattel P.N. Unpublished lecture notes on environmental chemistry, University of Nigeria, Nsukka.1990.
5. Wikipedia. http://www.wikipedia.org/wiki.carbon_black.htm. accessed 21/05/2012
6. Willard B. The effects of waste disposal on the coastal waters of Southern California . *Journal of Environmental Science and Technology*. 1982. Vol 16 No. 4 p 226a

- 211 7. Segal R. Greenhouse effect, how it affects us, our transportation. Pollution affects us.
212 <http://webpage.pace.edu/jb44525>. 2011.
- 213 8. Amuho U. E, Audit of Warri Refinery process units for sources of water and air
214 pollution. 2012.
- 215 Oil refinery. [http://en.wikipedia/wiki – oil refinery](http://en.wikipedia/wiki_oil_refinery)