

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 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 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 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 is 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 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 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

89 - the power to the pH meter was turned on

90 - the pH meter was calibrated using buffers 4, 7 and 9

91 - the calibrated pH meter electrode was dipped into sample and the reading was taken

92 **2.2 Measurement of outdoor air quality around the refinery and settlements within 5km**
93 **radius of the refinery.**

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

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

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

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

107 **Carbon dioxide.** Concentrations of CO₂ higher than its natural composition of 0.03% is
108 undesirable in the atmosphere, carbon dioxide being a major greenhouse gas is implicated for

109 global warming. The CO₂ in the air sample was absorbed by moist potassium hydroxide reagent
110 in the detector tubes.

111 **Materials:**

112 AUER Gas Tester (manual pump), AUER H₂S (1 – 200ppm) detector tubes PR 826, AUER
113 Toluene detector tube (5-1000ppm) PR 828, AUER Benzene detector tubes PR 807,
114 Perchloroethylene (10 - 500ppm) detector tubes PR 840, AUER CO₂ (0.1 – 7%) detector tubes
115 PR 817.

116 **Methods:**

- 117 - The pump (aspirator) was tested and confirmed to be in good working condition by
118 expelling the air in its bellow and its ability to suck in air on releasing the bellow.
- 119 - Tips at both ends of detector tube were broken with the tip-breaker on the pump
- 120 - The detector tube was inserted tightly into the pump following the guide arrow on the
121 detector tube. Arrow on tube pointing towards the pump.
- 122 - The pump was operated about 10 times to saturate the detector tube with the ambient air.
- 123 - The broken ends of the detector tube were tightly sealed with tape.
- 124 - The reading was taken after 10 minutes for perchloroethylene and after 5 hours for the
125 other gases/vapours..

126

127 **3. RESULTS AND DISCUSSION**

128 3.1 Acid Rains

129 **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	6.5 - 8.5
2013	4.70±.0.13	6.15±.0.04	6.20±.0.14	6.60±.0.5	
2014	4.80±.0.02	6.10±.0.05	6.30±.0.13	6.65±.0.03	

130

131 The results in Table 1 above clearly shows the consistent nature of acid rains especially
132 within the perimeters of the refinery for the three years under review. Within the refinery the pH
133 ranged from 4.70 to 4.95. The pH of the rain water from Ekpan community ranged from 6.10 to
134 6.20 while the pH of the rain water from Ubeji community ranged from 6.20 to 6.45. In the
135 measurement of pH of rain water Ondo township rain was set up as control, the pH ranged from
136 6.50 to 6.65. FEPA /WHO set limit for pH of domestic and drinkable water is 6.5 to 8.5. The
137 rain water from within the refinery, Ekpan and Ubeji communities fell short of the listed limits.
138 Ondo township rain water pH averaged 6,58 a marginal pass above the 6.5 limit.

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

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

Table 2. Refinery Outdoor Air

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 (141 ppm)
Benzene (C ₆ H ₆) (Tox/Ex)	Less than tox. Level	Less than tox. Level	Less than tox. Level	1500 (147ppm)
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

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

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

151 sulphide, however H₂S is an odourous gas and has the potential of contributing to acid rains. Its
152 presence in ambient air reduces natural air quality

153 Benzene was detected but in concentrations of less than toxic in the measurements taken
154 in the morning, afternoon and evenings. FEPA listed limits for benzene in ambient air is 1500
155 µg/m³ (147 ppm). The detector tube used for this test registered the presence of benzene in the
156 region of less than toxic level which is below 100ppm Benzene toxicity is between 100 –
157 2500ppm while extreme toxicity starts from above 2500ppm [13]. A study of benzene exposure
158 of 200 California commuters found an average exposure of 13ppb while driving to and from
159 work in San Fransisco Bay region [14]. Exposure to air pollution from benzene emission from
160 automobile and tobacco smoking has been estimated to surpass that from all stationary industry
161 in the United State [15]

162 Toluene was detected in almost constant concentrations ranging from 20 to 25 ppm for the
163 measurements taken in the morning, afternoon and evenings. The values are below FEPA listed
164 limits for toluene is 2000 µg/m³ (141 ppm) in ambient air The concentrations of carbon dioxide
165 and perchloroethylene in the ambient air were below detection limit within the refinery, Ekpan
166 and Ubeji Communities. The slightly higher concentration of toluene in Refinery's ambient air
167 can be attributed tot the fact that the refinery operations is the primary source of emission while
168 vehicular emission is a secondary source.

169
170 **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 ₂ S) 1-200ppm	11	12	10	No listed Limits
Toluene (C ₆ H ₅ CH ₃) 5-1000ppm	15	15	15	2000 (141 ppm)
Benzene (C ₆ H ₆) (Tox/Ex)	Less than tox. Level	Less than tox.Level	Less than tox. Level	1500 (147 ppm)
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

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 evening. FEPA listed limits for benzene in ambient air is 1500 $\mu\text{g}/\text{m}^3$ (147ppm). 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 $\mu\text{g}/\text{m}^3$ (141ppm). 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.

Table 4. Ubeji Outdoor Air Quality

Gas/Vapour	9 -10 am	2 – 5 pm	6 – 7 pm	<i>FEPA</i> $\mu g/m^3$
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 (141 ppm)
Benzene (C ₆ H ₆) (Tox/Ex)	Less than tox. Level	Less than tox. Level	Less than tox. Level	1500 (147 ppm)
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

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

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 $1500 \mu\text{g}/\text{m}^3$ (147 ppm). 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.

REFERENCES

- 211 1. Eborge A.B.M. (1995), Water Pollution in Nigeria. Biodiversity and Chemistry of Warri
212 River. Ben Miller Books, Nig. Ltd. Warri
- 213 2. Nduka, K and Orisakew, E (2007). Heavy metal levels and physiochemical quality of
214 potable water supply in Warri, Nigeria. *Annalt. Di.Chem.*97: 86 – 87
- 215 3. T .V Otokunefor and C. Obiukwu (2005) Impact of Refinery Efluent on the
216 physicochemical properties of a water body in the Niger Delta. *Applied Ecology and*
217 *Environ. Research* 3(1) 61 – 72.
- 218 4. Luke O . World Environment Day: Our carbon economy. The Guardian, June 10, 2008, p79
- 219 5. United Nations: Earth Summit Convention on Climate Change 3-14 June 1992. United
220 Nations. 1992.
- 221 6. John M and Robert C Fay. Chemistry, Prentice Hall Inc., New Jersey, USA. 1995. p 608.
- 222 7. Pattel P.N. Unpublished lecture notes on environmental chemistry, University of Nigeria,
223 Nsukka.1990.
- 224 8. Wikipedia. http://www.wikipedia.org/wiki.carbon_black.htm. accessed 21/05/2012
- 225 9. Willard B. The effects of waste disposal on the coastal waters of Southern California .
226 *Journal of Environmental Science and Technology*. 1982. Vol 16 No. 4 p 226a
- 227 10. Segal R. Greenhouse effect, how it affects us, our transportation. Pollution affects us.
228 <http://webpage.pace.edu/jb44525>. 2011.
- 229 11. Amuho U. E, *Audit of Warri Refinery process units for sources of water and air pollution*.
230 2012.
- 231 12. Cadbury Schweppes (1997): *Guide to Environmental Management, Uk*. Indoor and and
232 outdoor air quality p 1.10a-1.10b – 10.
- 233 13. Benzene Test, *Instruction for use* : (AUER Benzene detector tube PR807).

- 234 14. South Coast Air Quality Manage. Dist 1989. *In-Vehicle Characterisation Sudies in the South*
235 *Coast Air Basin. Los Angeles, CA.* South Coast Air Quality Manage. Dist
- 236 15. Lance A.W, [2007]: Human exposure to volatile organic pollutants: Implications for Indoor
237 Air studies. *Annu Rev Energy Environ*, 2006 26: 269 – 301.