Original Paper

Flare Pollution Loads and Carbon-Dioxide Effect on Rainwater Acidity in Niger-Delta: A Review, Investigation and Model for

Safe Living Quarter

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Abstract

Carbon-dioxide does not only affect climate change, but also contribute tremendously in acidification of rain water. Hazard identification and risk assessment are fundamental components of effective risk management, specifically in sensitive areas where adverse effects can have significant consequences. This study provides novel methodology for environmental and safety assessment of flared gases in sensitive areas such as residential homes. Distancing Sampling Technique (DST) was used to investigate the sensitivity of rain water pH at distances away from flare site in order to develop a Risk Management Model for sensitive regions. First, a review on rain water acidity was made around flaring and non-flaring areas in Niger-Delta states, which revealed Moderate-High acidity effect around flaring zones and no effect on non-flaring zone. Secondly, Flared Gas Quantification, pH Experimental Evaluation (PEE) and Risk Assessment Matrix (RAM) were the three systematic approaches used respectively to quantify, measure and evaluate the effects of CO_2 and other flare pollutants around the area of study. An average of 809,300,000 Mscf of associated petroleum gases were flared around the oil and gas producing areas in Delta State, causing a release of around $43x10^{6}$ tons of CO₂ from 2012-2022. Experimental results showed the range of pH from 4.56 \pm 0.06 to 5.10 \pm 0.06 for the 33 samples of harvested rainwater in Kwale community, Delta state causing a deviation of 16.38 to 30.05% from standard. The developed and validated model suggests 4.81KM radius as the safe distance for human habitation from flare sites. Based on these findings, carbon-capture and sequestration projects must be activated in Niger-Delta to curb the menace.

Keywords

Acid rain, Distance sampling, Standard Deviation, Risk Matrix, CO₂ sequestration

1. Introduction

The need to address risk issues in a continuously evolving environment, coupled with improved information and communication technologies has led to the development of several techniques, hazard identification and risk assessment methods (Villa & Cozzani, 2015). Risk analysis by dynamic approach have been an evolving method for identifying, assessing, and quantifying increasing risk in a system with uncertainty, real-time changing environment, and system complexity (Bucelli, et al., 2018; Villa & Cozzani, 2015).

A systematic approach for defining safe residential quarters due to pollution by flared gases around flare regions are still lacking. Nduka, J. et al. (2008), collected rainwater samples from Portharcourt and Warri, which are two major oil and gas industrial areas in Niger-Delta, to determine the water pH, while control samples were collected from Awka in Anambra state, which was non-oil and gas hub. The samples were collected up to 115m from a reference point in a triangular equilibrium using clean plastic basins. The pH readings are as follows: Portharcourt (4.71,4.94,4.93); (5.04,5.73,4.91): Warri (4.81,4.70,6.15);(4.79,4.80,4.72): Awka (6.04,5.88,5.75); (6.00,5.10,5.96). The pH of rainwater in Portharcourt and Warri, were highly acidic due to industrial activities (gas flaring) while the pH of Awka acting as control is within acceptable range.

Odjugo, P. & Osemwenkhae, E. (2009), determined the effects of gas flaring on crops grown in Niger-Delta. The results of their work reveals that the flare affects extends beyond 110 meters from the flare location and therefore advised on further studies to validate the claim. Atuma, M. I., & Ojeh, V. (2013), examined the effect of flared gases on soil and casava productivity from five sites in Ebedei, Ukwani LGA of Delta State in Niger-Delta. The soil samples were harvested at varying depths and distances ranging from 0 - 20cm and 50m - 250m respectively from the bund wall of the flares. Critical analysis using multiple regression and paired t-test methods shows wide acidity variation in the results obtained in flaring area to those from the controlled site (non-flaring area). However, the researchers did not attempt to model a safe threshold for human habitation in those areas due to adverse effects of rain acidity.

In this research, Environmental assessment of risk of CO_2 and other flare pollutants was investigated by evaluating the pH of rainwater around Delta state, a region in Niger-Delta, which was conducted 2KM from flare sites for two consecutive years. The study was aimed at providing simple methodology for safety and environmental assessment of flared gases in sensitive areas at defined distances from flare sites followed by measuring the pH of the water and modelling safe human quarters. pH is an incredible parameter that plays a key role in assessing water quality. In environmental sampling and monitoring, the pH value indicates the pollution index of the water, which has potential adverse effect on the environment, people and ecosystem. On the light of the above, the present work on impact assessment focuses more on the influence of flared gases on rainwater acidity at specific intervals up to 2KM.

Niger-Delta region of Nigeria has proven natural gas reserves of 203.16 Trillion Cubic Feet (TCF) and crude oil reserves of 36.89 billion barrels (bb) and between 400 TCF-600 TCF of undiscoverable natural gas reserves. This is estimated to be within 7.7% -15.5% of global quantity of undiscoverable natural gas resources. Judging by the trend, some considerable amount of the associated gases when produced would be flared leading to huge economic loss and consistently endangering human health, ecosystem and general environment.

Acid rain and most environmental pollutant have been widely attributed to impact of gas flaring especially in the Niger Delta region of Nigeria (Elijah 2022; Ebong, et al., 2022; Nwankwo & Ogagarue, 2011). Gas flaring does not only affect climate change but also pollutes the environment, with utmost effect to inhabitant in close proximity to flare sites. Hazard identification, risk assessment and mitigation plan are keys for prevention of chances of diseases, calamities and mishaps in sensitive areas.

2. Review of Literature

Rainwater is water fallen as rain that has not collected soluble matter from the soil and is therefore soft. It is also a surface water obtained from rain fall, which is an excellent source of domestic water for rural areas and dispersed population (Anyata, 2008; Odume, 2022). Water is essential for the environment, human health, food security and sustainable development, whose quality is an indispensable requirement for healthy living (Schiller, 1982; Adeyeye, et al., 2019). It becomes a problem to humanity, ecosystem and the environment when the physical and chemical balances of the water chemistry are altered due to natural or anthropogenic activities.

Acid rain is a normal rain acidified by certain air pollutants. Rain water acidification is a serious environmental problem of trans-boundary nature caused by the oxides of sulfur and nitrogen and worsened by increasing amount of carbon-dioxide in the atmosphere (Singh & Agrawal, 2007). Whereas the normal rain cleanses, supports, enriches life and the environment, acid rain dirties and damages life, ecosystem and the environment (Abbasi, et al., 2013). Acid rain is considered by many as one of the grave environmental threat of our time caused by air pollution that have led to fish extinction and forest dieback (Grennfelt et al., 2020).

Acidic rain poisons our water bodies and lowers the soil pH. Lowered soil pH leaches away nutrients cations and increases the exposure of heavy toxic metals, which reduces soil chemical properties that enhances soil fertility. When the soil chemistry is compromised, it impacts negatively on growth and productivity of plants and forest trees. Basically, the degree of acidity of water and soil is measured by pH, which is a shorthand version of potential hydrogen. Figure 1 displays the origin of pollutants that



acidifies rain water, cause climate change and other environmental threats.

Figure 1. Cause and Effect Diagram for Environmental Pollutants Which Acidifies Rain Water

2.1 Gas Flaring Proximity to Residential Areas

In Niger-Delta, there are widespread perceptions that due to human habitation in close proximity to flare locations, it has adversely affected the region in terms of human health status, environmental degradation, and social-economic issues (Nriagu et al., 2016; Otache et al., 2021). This is due to daily released amount of the dangerous toxins into the atmosphere, resulting to the pollution of air, water, soil and the ecosystem (Oghenejoboh et al., 2007).

The impact of gas flaring spreads across extensive radius from the point of generation. In Niger-Delta at least Two Million (2,000,000) people lives within Four Kilometres (4KM) (2.5 miles) in flaring locations (NOAA Virtual Night Flare, 2018).



Figure 2. Yellow Spots Showing Population of Residential Homes at less than 2KM from Flare Sites in Niger-Delta

Source: Global Gas Flaring Tracker Report, July, 2020; https://gasflaretracker.ng/

These emissions have caused series of litigation from the host communities to the oil and gas company, government agencies, resulting to claims and counter claims (Nduka et al., 2008). Flaring as a major source of greenhouse gases generates noise and heat leading to health issues and environmental degradation (Emam, 2015; CAPP 2012; Abiodun, 2014; Oseji, 2007; Ejiogu et al., 2019). Scientific studies have identified over 250 toxins released from flaring. They include carcinogens such as benzopyrene, benzene, carbon-disulphide (CS2), carbonyl-sulphide (COS) and toluene. Others are metals such as mercury, arsenic and chromium, sour gas with H_2S and SO_2 , nitrogen oxides (NOx), carbon-dioxide (CO₂), methane (CH₄) etc which contributes to greenhouse gases (EPA 2014; Christiansen et al., 2016; Mobolaji Sunmoni, 2018).

2.2 Specific Effects of Acid Rain

Specifically, acid rain affects human health, damages the soil, plants, trees as wells as buildings and structures (Singh & Agrawal, 2007; Abbasi et al., 2013). Acid rain not only damages the chemistry of soil but also changes the quality of soil (Fiza Fatima et al., 2021). It distorts the enzymes of microbes in the soil, kills them, leaches the soil essential nutrients, decreases soil fertility and causes stunted growth of plants (Singh & Agrawal, 2007; Atuma & Ojeh, 2013).

Acid rain washes heavy metal toxins like Magnesium (Mn), Aluminium (Al), Lead (Pb), Iron (fe), Mercury (Hg) and gets them dissolved in the soil, which permeates down to the ground drinking water and poisons it. While some of these toxins are washed off and flows to the rivers, lakes and streams (Nwankwo & Ogagarue, 2011; Ejiogu et al., 2019; Ebong et al., 2022). The accumulated heavy metals in human bodies through ingestion of the poisoned water, causes headache, irritation of throat and nose, coughs etc. Excess ingestion of these toxins contributes to kidney and heart issues, lung diseases such as Asthma, bronchial problems, etc.

Direct exposure of human body to acidified liquids affects the immune system, which drastically reduces human antibodies (Nagae et al., 2011). The direct droplet of acidic rain water lowers the pH of the water bodies therefore adversely affects the living things in the water. Accumulation of heavy metals in the water bodies affects the breaths of fishes leading to premature deaths. The above phenomenon equally affects the food chain at different levels. When humans eat these poisoned fishes, the heavy metals will be deposited into the human body, also when animals or birds eat the dead fishes; they also become a secondary receiver of the poisoned food.

2.3 Chemistry of CO₂ Release from Combustion Process

Flared gases are composed of various forms of gases (methane, ethane, propane, butane, pentane, hexane, etc.), water vapour, hydrogen sulphide, nitrogen, volatile organic matters, etc. (Peterson, 2007; Putriastuti, et al., 2021). During gas flaring, the combusted gases generate mainly Carbon-dioxide (CO_2) , water vapor and heat (Gzar & Kseer, 2009). This is evident in equations (2.1-2.5).

$$CH_{4(g)} + 2O_{2(g)} \to CO_{2(g)} + 2H_2O_{(g)} + Heat$$
 (2.1)

$$2C_2H_{6(g)} + 7O_{2(g)} \to 4CO_{2(g)} + 6H_2O_{(g)} + Heat$$
(2.2)

$$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(g)} + Heat$$
 (2.3)

$$C_4 H_{10(g)} + 6.5 O_{2(g)} \to 4 C O_{2(g)} + 5 H_2 O_{(g)} + Heat$$
(2.4)

$$C_5H_{12(g)} + 8O_{2(g)} \rightarrow 5CO_{2(g)} + 6H_2O_{(g)} + Heat$$
 (2.5)

The presence of CO_2 in the atmosphere causes acidity of rain water according to the chemical reactions blow.

$$CO_2 + H_2O \to H_2CO_3 \tag{2.6}$$

$$H_2 CO_3 \to H^+ + H CO_3^- \tag{2.7}$$

In equation (2.6), carbon dioxide (CO₂) reacts with rainwater (H₂O) to form carbonic acid. The presence of hydrogen ion molecules "H⁺" in the water renders it acidic by lowering the pH as shown in equation (2.7). Accumulation of H⁺ due to higher concentration of CO₂ from combustion process further acidifies the rain water.

3. Materials and Methods

In this research, a field work around a flare location in a community in Kwale area of Delta state was carried out. The sole purpose was to measure the pH of rain water harvested in the format describe in Figure 3 and in three stages as described in Figures 4, 5 & 6. A measurement tape, machete, labeled white plastic bowls, labeled retrieval bottles, Beaker and a digital pH meter were the key apparatus used for the field sampling and experimental evaluation.



Figure 3. Model for Rain Water

Sampling Points: F=Farm Area; R=Residential Area; X1,X2,X3=Sampling Axis with Sampling Points.

3.1 Research Method

The sampling stages and experimental scenarios follow the sequence defined in Figures 4, 5 & 6 of this report.

3.1.1 Stage 1: Chart for Rain Water Harvesting and pH Experimentation along Axis X1

Total of thirty three (33) rain water samples were harvest from axis X1, X2, X3 for the three (3) stages of field work as describe below. Figure 4 is the first stage done which involves sampling points clearing, positioning of bowl for rainwater collection and pH experimentation. Four points cleared in Day 1, seven points in Day 2 while the bowls were positioned on the eleven cleared points in Day 3, followed by pH evaluation in Day 4.



Figure 4. Sampling and pH Evaluation Timeline along X1 Axis

Stage 2: Chart for Rain water harvesting and pH experimentation along Axis X2

Figures 5 & 6 is the second stage of the sampling and experimentation process along axis X2 and X3. The process includes sampling points clearing, bowls positioning and pH evaluation in the laboratory for the harvested water samples.



Figure 5. Sampling and pH Evaluation Timeline along X2 Axis

Stage 3: Chart for Rain water harvesting and pH experimentation along Axis X3

Figures 3 & 4, is the last stage of the sampling and experimentation process along axis X3 done in the third year of this research. The process is in similar fashion with stages X1 and X2.



Figure 6. Sampling and pH Evaluation Timeline along X2 axis

Where;

X1, X2, X3=Axis of measurement

P1, P2, P3 ... P11=Sampling points;

B1, B2, B3 ... B11=Sampling Bowls

pH.S1, pH.S2, pH.S3......pH.S11=Evaluated pH of each retrieved water samples

3.1.2 Assessment of Flared Gases and CO₂ in Niger-Delta Using Quantification Approach

The amount of flared gases and emitted CO_2 over 11 years (2012-2022) as monitored by Nigeria Gas Flare Tracker, an online software was use to quantify the volume of flared gases (MSCF) released on daily basis in Niger-Delta states and its environ. Earth Observation Group (EOG) at the Colorado School of mines in 2011 developed this satellite software that tracts and records flaring data with locations, temperature, source, sizes and radiant heats from infrared emitters worldwide.

In Nigeria, this software is monitored via (<u>https://gasflaretracker.ng</u>) and managed by National Oil Spill Detection and Response Agency (NOSDRA). Table 1 displays volume of flared gas vis-a-vis the amount of CO_2 respectively emitted in Edo, Delta, Rivers, Bayelsa, Akwa-Ibom, Imo and Abia state. These are the states that comprise Niger-Delta.

 Table 1. 11 Years Profile of Emitted Carbon-dioxide (x10³ Tonnes) from Flared Gases (x10³

 MSCF) in Niger-Delta States

									AKWA	AI-IBO				
	EDO		DELTA		RIVER	S	BAYE	LSA	М		IMO		ABIA	
	F.Gas	E.CO ₂												
Yr.	x10 ³	x10 ³												
2012	12200	648.9	49000	2600	55400	2900	30400	1600	3700	197.3	15100	800.1	45.9	2.4
2013	19100	1000	67600	3600	57500	3100	34500	1800	6800	359.9	16400	869.5	1300	71.3
2014	21200	1100	62200	3300	68100	3600	36200	1900	5500	294.1	9400	500	1000	54.1
2015	21600	1100	65900	3500	56800	3000	26500	1400	6100	322.2	7500	397.9	458.8	24.4
2016	9900	527.6	52400	2800	68000	3600	37000	2000	5700	304.8	8400	444.5	132.9	7.1
2017	14100	746.9	69600	3700	70000	3700	36200	1900	6000	316.8	7600	404.9	451	24
2018	24800	1300	113200	6000	65700	3500	45500	2400	5900	312.7	6600	353.8	1200	64.5
2019	24800	1300	105200	5600	68900	3700	47000	2500	4600	246.5	8200	435.2	1100	56.8
2020	17800	947.8	99700	5300	57900	3100	42400	2300	3100	164.8	10300	545	603.1	32
2021	16900	897.8	66300	3500	38600	2100	23500	1200	2500	130.3	6900	366.3	385.5	20.5
2022	12900	684.1	58200	3100	31800	1700	18100	1000	2500	130.9	4600	241.8	0	0

Note. Where: F.Gas=Flared Gas; E.CO₂=Emitted CO₂.

3.1.3 Experimental Procedure

Thirty three (33) samples were collected at intervals of 200 meters (0.2KM) from the bunk wall of a typical flare site to a distance of 2KM along axis X1, X2 and X3. The task includes clearing of sampling points, positioning of water collection bowl and laboratory investigation.

Upon retrieval of the harvested rain water in labeled receptacles, standard quantity of 100ml of the sample was measured and poured into a calibrated beaker, and the digital pH meter was switched ON

for 30 minutes to warm up, next was calibration of the unit in a buffer solution. The sample was stirred for 2 minutes, the electrode rinsed, the meter set in pH mode and the electrode inserted into the beaker followed by activating the pH measurement button. A stable pH reading was achieved within 60 seconds. After each reading the electrode was rinsed with distilled water and second and third reading done on same sample for result comparison. By implication, all harvested rain waters were tested thrice for data validation using same procedure.

3.1.4 Rain Water pH Analytical Procedure

The evaluated pH data was analyzed by Risk Matrix Approach using percentage standard deviation method. Risk is a function of probability of occurrence of an undesired event in addition with a measure of its adverse consequence. The procedure involves identification of the hazards, quantification of likelihood and consequence of those hazards on health and environment. Standard deviation is a measure of amount of dispersion or variation from the data set. It specifically gives a clue on how far each value lies from the average or mean. A high standard deviation indicates that the values are far from the mean and vise verse. This approach was used in this research to analyze the rain water pH along X1, X2 and X3 axis and compared with the standard mean (x) value of 5.6.

The Standard Percentage Deviation (SPD) for the harvested rain water pH data was computed in Excel spreadsheet using equation (3.1).

$$SD = \sqrt{\left(\frac{X1 - \bar{X}}{N}\right)^2} x \frac{100}{1}$$
(3.1)

Presented in Table 2 and 3 are the Flared Gas Risk Assessment Matrix and Risk Factor respectively employed as tools for the Risk Evaluator based on the magnitude of the flare pollutants effects on the people, community or environment. The Risk Factor (R.F) is a product of probability of occurrence (Likelihood) and severity. Mathematically,

$$R. F = f(Pr * Sev.)$$

$$Where;$$

$$P_r = Probability (Likelihood);$$

$$Sev. = Severity$$
(3.2)

Table 2. Risk Assessment Matrix

	RISK ASSESSMENT MATRIX									
ev.		Increasing Likelihood								
Ś	Consequences	Α	В	С	D	Е				
0	Zero	Deviation, Action: Ne	D: ≤ 5.0% gligible							
1	Zero-Slight Effect		Deviation Action: Re	, D: 5.01 – 10% eview Activity						
2	Slight-Minor Effect			Deviation, D: Action: Contin	10.01– 20% 1uous Improv	ement				
3	Minor-Moderate Effect				Deviation, D: 2 Action: Critic	0.01– 50% al Control				
4	Moderate-High Effect									
5	High-Critical Effect				Deviation, Action: Sto	D: >50% p Activity				

		RANKIN	IG CODE	IMPACT RATING CODES		
0A	1A	2A	3A	4A	5A	Negligible - Low Risk Zone (NLRZ)
0B	1B	2B	3B	4B	5B	Low-Medium Risk Zone (LMRZ)
0C	1C	2C	3C	4C	5C	Medium-High Risk Zone (MHRZ)
0D	1D	2D	3D	4D	5D	High - Critical Risk Zone (HCRZ)
0E	1E	2E	3E	4E	5E	Critical-Intolerable Risk Zone (CIRZ)

Table 3. Risk Factor

3.1.5 Impact Rating and Description

Negligible-Low Risk Zone (NLRZ): It is characterized with negligible effects from flaring activities but mitigation measures may be desirable. The flare impact may not result to significant effects on the people, community or environment even if ignored.

Low-Medium Risk Zone (LMRZ): It is characterized with significant impact, requiring mitigation to curb the effects. The flare impacts may results to negative Short-to-Medium Term effects on the people, community or environment.

Medium-High Risk Zone (MHRZ): It is characterized with serious impact requiring immediate mitigation plan to drastically curb the menace. The flare impacts may result to a Medium-to-Long Term effects on the people, community or environment.

High-Critical Risk Zone (HCRZ): It is characterized with severe impact on the people, community and the environment if adequate steps are not employed to stem it. The flare impact may have already resulted to a Long Term adverse effect on the people, community or environment around that zone.

Critical-Intolerable Risk Zone (CIRZ): It is characterized with very severe impact on the people, community and environment. These effects are usually immitigable if the practice continues. The only panacea is to stop the practice generating the effects.

3.2 Model for Determining Safe Habitation Quarter in Sensitive Areas

In order to predict the safe human habitation zone from flare locations, R-Squared was used to study the variance of the independent variable (Distance) to the dependent variable (pH), using the mean regression equation. R-Squared is a coefficient of determination in statistical regression model for evaluating the proportion of variance of the variables (dependent from independent) which defines the goodness of fit from their relationship. Based on the generated R-Squared value, which is more than 80% for the mean pH as shown in figure (12), a regression model was developed.

The regression equation along the path of investigation is defined by:

(3.7)

$pH = \beta_0 + X_i \beta_1$	(3.3)
$\Sigma(\mathrm{pH}) = \beta_o N + \beta_1 \Sigma(\mathrm{Xi})$	(3.4)
$\Sigma(\text{pH}.X_i) = \beta_0 \Sigma(X_i) + \beta_1 \Sigma(Xi^2)$ $\binom{N}{\Sigma Xi} \sum_{Xi^2} \binom{\beta_0}{\beta_1} = \binom{\Sigma \text{pH}}{\Sigma \text{pH}.Xi}$ $\binom{11.00}{11.10} \frac{11.10}{15.41} \binom{\beta_0}{\beta_1} = \binom{53.78}{55.05}$ By Gaussian elimination Method $\binom{1}{2} \binom{\beta_0}{\beta_0} = \binom{4.7018}{2}$	(3.5)
	(3.6)

 $pH_p = Predicted Rain water pH$

Xi = Distance for flare stack

 $\beta o; \beta i = Constant of proportionality$

3.3 Risk Evaluation Model

Generic Risk Model at varied distance, xi $R = f(R.F)_x + (\Delta R.F)_{xi}$ $f(R.F)_x = The Risk Factor at reference point, X$

 $(\Delta R.F)_{xi} = Change in the Risk Factor at varying points$

4. Results and Discussion

This research was done by quantifying the amount of released carbon-dioxide vis-à-vis emitted flared gases for 11 years in seven states of Niger-Delta. This is followed by determination and analyzation of the pH value of 33 samples collected at 200 meters interval and finally evaluating the safe zone for human habitation from flare locations. All data were calculated via Excel worksheet, graphical figures developed analyzed using Origin 2023(10.0) software.



Figure 7. Emitted Flared Gas Profile for 11 Years in Niger-Delta State

4.1 Volume of Emitted Gases Vis-a-vis of CO₂ Released for 10 Years in Niger-Delta States



Figure 8. Area Profile of Emitted CO₂ per State in Niger-Delta

The basic function of the satellite flaring data software is to detect the amount of gas flared on daily basis. Which includes the amount of carbon-dioxide (CO_2) emitted from the flared gases, economic value of the flared gases as well as the potential power generation from the flared gases.

Table 1 shows the amount of CO_2 respectively emitted in Edo, Delta, Rivers, Bayelsa, Akwa-Ibom, Imo and Abia state. Within these periods under study (2012 - 2022), Niger-Delta region has cumulatively flared 2,180,677,000 MSCF of natural gas with the release of 115,749,500 Tonnes of CO_2 in the air space within the study period. The trend revealed Delta state taking the lead on the amount of emitted CO_2 from flared gases within the period of 2018 till 2022. This is closely followed by Rivers state and Bayelsa state at the second and third place.

Apparently, (195,300,000 MSCF; 10,253,100 Tones), (809,300,000 MSCF; 43,000,000 Tones), (638,700,000 MSCF; 34,000,000 Tones), (377,300,000 MSCF; 20,000,000 Tones), (52,400,000 MSCF; 2,780,300 Tones), (101,000,000 MSCF; 5,359,000 Tones) and (6,677,200 MSCF;357,100 Tones) were the flared volume and emitted CO_2 volume respectively emitted from Edo State, Delta State, Rivers State, Bayelsa state, Akwa-Ibom state, Imo state and Abia state. The result showed 809,300,000 MSCF of natural gas has been flared for the 11 year period with a release of 43,000,000 tonnes of CO_2 in Delta state alone where the investigation was carried out. The study area is a community in Kwale area located in Delta state where flaring activity is done on daily basis and at different locations, which poses great concerns on human's lives at close proximity to these flaring sites.

4.2 pH of 33 Harvested Rain Water Samples along X1, X2, X3 and Mean (\ddot{x})

The lower the pH of a substance the stronger its acidity, and the higher the pH the higher the alkalinity of that substance. In this work, a pH value of 5.6 is the mean used to analyze the measured pH of the 33 water samples harvested at axis X1, X2 and X3 as shown in figure (3). Clean Rain water has a pH of 5.6 (Singh & Agrawal, 2007; Abbasi, et al., 2013; Xuan et al., 2021; Al Hameli et al., 2022). pH evaluated on the harvested rain water samples ranges between 4.56±0.06 to 5.10±0.06, which are indisputably below clean rain water pH of 5.6 and are all acidic.

Figures 9, 10, 11 & 12 are four graphical representation of the measured pH along the three axis of evaluation, X1,X2,X3 and the mean pH

 $\{\ddot{x}=(X1,X2,X3)/3\}.$

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Figure 10. pH Measurement along X2 Axis



Figure 11. pH Measurement along X3 Axis Figure 12. Mean pH Estimate for X1.X2 and X3 Axis

Figures 9, 10, 11 & 12 disclose stronger acidity near the flare location, which eases slowly away from it. This could be attributed to the phenomenon known as dry and wet deposition as well as pollutant plume dispersion. In dry deposition process, the pollutants settles/fall under gravitational influence usually close to the point of origin (source of generation), where it reacts and acidify water body or soil in contact. In wet deposition, the pollutant got scavenged in the cloud, travels by dispersion and falls wet at some distance from the generated location due to the influence of wind.



Figure 13. Overview pH Measurement along the Three Axis

4.3 Risk Matrix Evaluation Results

The calculated standard deviation of the 33 rain water samples and the Risk Rating results using the evaluation tools (Risk Assessment Matrix, Risk Factor) are displayed as shown in Table 4.

#	Deviation	Deviation	Deviation	% Mean Ď:	Severity	Prob. Of	Risk	Risk	Remark/Panacea
	D:@X1	D:@X2	D:@X3	@X1,X2,X3	(S)	Impact	Factor	Rating	
						(Pf)	(RF)	RIR)	
1	29.8496	31.3572	28.9451	30.0506	3	Е	3E	High	Stop Gas Flaring/
									Capture & Sequester CO ₂
2	22.3118	28.9451	23.8194	25.0254	3	D	3D	High	Stop Gas Flaring/
									Capture & Sequester CO ₂
3	20.5028	22.0103	22.9149	21.8093	3	D	3D	High	Stop Gas Flaring/
									Capture & Sequester CO2
4	23.8194	20.8043	27.4375	24.0204	3	D	3D	High	Stop Gas Flaring/
									Capture & Sequester CO2
5	23.8194	22.3118	20.8043	22.3118	3	D	3D	High	Stop Gas Flaring/
									Capture & Sequester CO ₂
6	19.2967	20.8043	19.8998	20.0003	3	D	3D	High	Stop Gas Flaring/
									Capture & Sequester CO ₂
7	25.9299	19.5982	20.5028	22.0103	3	D	3D	High	Stop Gas Flaring/
									Capture & Sequester CO ₂

Ta	abl	e 4	. Risk	Rating	and	Control	Measure
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8	18.6937	21.7088	17.1862	19.1962	5	В	5B	Medium	Stop Gas Flaring/	
									Capture & Sequester CO ₂	
9	15.3771	20.5028	17.1862	17.6887	4	В	4B	Medium	Stop Gas Flaring/	
									Capture & Sequester CO ₂	
10	18.9952	17.4877	15.0756	17.1862	4	В	4B	Medium	Stop Gas Flaring/	
									Capture & Sequester CO ₂	
11	15.3771	17.4877	16.2816	16.3821	3	С	3C	Medium	Stop Gas Flaring/	
									Capture & Sequester CO ₂	



Figure 14. pH Standard Deviation along the Sampling Points

The main objectives of Risk Assessment Matrix is to identify potential vulnerability to environment and health followed by defining situations management, compare alternatives, provide knowledge on patterns of events and to identify critical parts of the operations. Risk Assessment Matrix evaluated the magnitude of the deviation of the experimental results from instituted standards. It weighs the severity of potential risk against the probability or likelihood the risk might occur. In Table 2, a scale of consequences of 0, 1, 2, 3, 4 & 5 were used to designate increasing severity at the vertical axis, and likelihood scale of A,B,C,D & E at the horizontal axis that designated the probability of the adverse effects on the people, environment and ecosystem.

The Risk Matrix Evaluator was utilized to generate the Risk Factor (RF) from the evaluated Standard Percentage Deviation (SPD) of the rain water pH along axis X1, X2 and X3 as shown in Table 3. This is considered reliable tool for analyzing and standardizing quantitative risk by categorizing all threats to safety, health, and environment based on their deviation from the acceptable limit. The Risk Factor (RF)

was estimated from equation (3.2) by multiplying the "Severity in the vertical column to the Likelihood in the horizontal row" and consistently noting the corresponding color codes in the Risk Matrix Evaluator. For example, the ranking codes 2A, 3A and 4A are same as 2xA, 3xA and 4xA respectively. Equation (3.1) was used to calculate the Standard Percentage Deviation (SPD) with 5.6 as the mean rain water pH. The evaluated SPD along X1, X2 and X3 axis ranges from 15.3770% - 29.8496%, 17.4877% - 31.3572% and 15.0756% -30.0506% respectively. From the results, the calculated Mean Standard Deviation ranges from 16.39% - 30.05%, which falls within the BLUE and YELLOW color coded zones.

The deviation at the BLUE zone is designated (10.01-20%), which covers 2C, 2D, 2E, 3B, 3C, 4B and 5B color coded background as shown in Table 2. For analytical purpose, the deviation is distributed amongst the RF which is seven in number within the BLUE zone. This is done by first calculating the deviation difference and dividing it by the total number of RF in that zone, followed by apportioning the common factor to each of the risk factors, i.e.,{(20-10.01)/7=1.43%}. The value "1.43" is added successively to each of the RF's. The range of application of 2C, in the BLUE code zone is: 2C=(10.01%-11.44%) which means 2C lies within 10.01% to 11.44%. Others 2D, 2E, 3B, 3C, 4B and 5B are designated 2D=(11.45%-12.87%), 2E=(12.88%-14.3%), 3B=(14.44%-15.87%), 3C=(15.88%-17.31%), 4B=(17.32%-18.75) and 5B=(18.76%-20%).

In the same vein, at the YELLOW coded zone, the deviation ranges from (20.1-50%), with the risk factors (3D, 3E, 4C, 4D & 5C) and having {(50-20.01)/5=5.98%} as the common factor. The range of application of 3D, 3E, 4C, 4D, & 5C in the YELLOW coded zone are {3D=(20.1%-26.08%), 3E=(26.09%-32.07%), 4C=(32.08%-38.06), 4D=(38.07%-44.05) and 5C=(44.06%-50%)}. The mean deviation (Ď) value "30.0506% and 25.8194%" in roll 1 and 2 of Table 4 falls within the RF "3E and 3D" respectively. Hence the Risk Factors (RF) for the calculated mean deviation in table 4 all falls within 3C, 3D, 3E, 4B and 5B.

4.4 Model Validation and Sensitivity Analysis

The pH profile from the experimental evaluation was compared with those predicted by the model at same spacing, resulting to close match as shown in Figure 15. A sensitivity analysis carried out on the developed model predicted save residential area to be from 4.81 KM from the flare location (Figure 15). The model was tested at intervals of 0.1KM starting from the flare site. The predicted distance for clean rain water (where pH is 5.6) is from 4.81KM as shown in Appendix 1 of this report.

The results are in tandem with the assertion by (Abassi et al., 2013; Larssen et al., 2006), "Acid rains and the pollutant that creates them are often transported far away by wind from their points of origin and the adverse effect of the pollutant reduces at some distance apart". Again, dispersion plays a vital role in which the plume of the emitted pollutant travels far from the point of generation to points they undergoes some form of chemical reactions. The extent they travel is a function of the pollutants dispersion coefficient.



Figure15. Model Validation



Figure 16. Boundary between Polluted and Unpolluted Zones for Human Habitation from Flare Areas

5. Conclusion

Environmental risk of emitted CO_2 from flared associated petroleum gases was investigated in this research by harvesting 33 samples of rain water within 2KM radius from the bund wall of flares. The evaluated pH was analysed by Standard Percentage Deviation (SPD) and Quantitative Risk Matrix (QRM) evaluation methods. The present work was borne out of concern for more than two million (2,000,000) people residing at close proximity to flaring locations as reported in Figure 2. Flared gases in sensitive zones such as human residential and farm areas requires improved risk management by intensified monitoring, evaluation and designed mitigation plan.

First, the study shows accumulation of CO_2 in the air space of the study area as disclosed by the flare tracker. This is evident in Figures 2 and Table 1 of this report. It revealed 809,300,000 MSCF of flared gases for the 11 year period with a release of 43,000,000 tonnes of CO_2 in Delta state alone. Secondly,

it revealed decreasing acidification of acid rain away from the flare location as shown by the experimental data evaluations. Finally, the model predicted 4.81KM radius from flare locations for human habitation.

It is worthy to note that carbon-dioxide, nitrogen oxide and sulphur oxide are the three main trans-atmospheric gases that precipitates rain water and making it acidic by increasing the concentration of hydrogen ion (H+). This work only addresses carbon-dioxide due to its deleterious and trans-boundary environmental concerns as a greenhouse gas. The research does not in any way undermine the effects of NOx and SOx as regards rain water acidification.

The developed and validated risk model is a framework suitable for evaluation of safe residential zones in sensitive areas. The Physicochemical parameters should be assessed based on the criticality of the Risk Factor (RF). The response of the risk screening model may presumably differ in other Niger-Delta states due to differences in the volume of emitted flare gases as shown in Table 1. The study area was chosen because of high flaring volume on daily basis as compared to other areas.

The remedy/panacea is to stop gas flaring and/or put control measures in place. One of the control measures is by initiating Carbon Capture and Sequestration (CCS) projects in Niger-Delta region of Nigeria, so as to meet the 2050 Net-Zero Goals. Hydrocarbon exploration, production and processing in Niger-Delta region of Nigeria started since 1957, which has led to reservoir depletion and abandonment. Some of the depleted reservoirs in Niger-Delta brown fields are presently termed Marginal Fields. Nigeria has not less than 251 Marginal fields (Mobolaji & Okoro, 2020), some of which are suitable for Carbon Capture and Geological Storage (CCGS), to reduce CO_2 emissions and to achieve 2050 Carbon Neutrality goal.

Besides Saline Aquifers, the depleted gas or oil reservoirs are proven to be suitable for implementation of CO_2 geo-sequestration in Enhanced Gas Recovery or Enhanced Oil Recovery. Umar et al. (2020), Davis et al. (2022), assessed the potential for CO_2 geo-sequestration in Niger-Delta Basin, using seismic and well information data from wells in Agbada formation. The results were compared to formation basin screening criteria reported by (Bachu, 2003; CO2CRC, 2008). The assessments rated Niger-Delta formation "Very Good" and "Excellent" depending on the screened criteria and parameter. Hence Niger-Delta formations are safe for geological storage of CO_2 .

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The author(s) declared no conflicts of interest with respect to the research and publication of this article.

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Appendix 1

Results of sensitivity analysis on model									
DISTANCE, XI RAIN WATE									
B0	BI	(KM)	ACIDITY, p.H						
0.1856	4.7018	2.0	5.0730						
0.1856	4.7018	2.1	5.0916						
0.1856	4.7018	2.2	5.1101						
0.1856	4.7018	2.3	5.1287						
0.1856	4.7018	2.4	5.1472						
0.1856	4.7018	2.5	5.1658						
0.1856	4.7018	2.6	5.1844						
0.1856	4.7018	2.7	5.2029						
0.1856	4.7018	2.8	5.2215						
0.1856	4.7018	2.9	5.2400						
0.1856	4.7018	3.0	5.2586						
0.1856	4.7018	3.1	5.2772						
0.1856	4.7018	3.2	5.2957						
0.1856	4.7018	3.3	5.3143						
0.1856	4.7018	3.4	5.3328						
0.1856	4.7018	3.5	5.3514						
0.1856	4.7018	3.6	5.3700						
0.1856	4.7018	3.7	5.3885						
0.1856	4.7018	3.8	5.4071						
0.1856	4.7018	3.9	5.4256						
0.1856	4.7018	4.0	5.4442						
0.1856	4.7018	4.1	5.4628						
0.1856	4.7018	4.2	5.4813						
0.1856	4.7018	4.3	5.4999						
0.1856	4.7018	4.4	5.5184						
0.1856	4.7018	4.5	5.5370						
0.1856	4.7018	4.6	5.5556						
0.1856	4.7018	4.7	5.5741						
0.1856	4.7018	4.8	5.5927						
0.1856	4.7018	4.9	5.6112						
0.1856	4.7018	5.0	5.6298						
0.1856	4.7018	5.1	5.6484						
		25							

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	0.1856	4.7018	5.2	5.6669
	0.1856	4.7018	5.3	5.6855
	0.1856	4.7018	5.4	5.7040
	0.1856	4.7018	5.5	5.7226
	0.1856	4.7018	5.6	5.7412
	0.1856	4.7018	5.7	5.7597
	0.1856	4.7018	5.8	5.7783
	0.1856	4.7018	5.9	5.7968
_	0.1856	4.7018	6	5.8154