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Towards Sustainable Development in Air Quality: Using Basic Chemistry Models in Quantifying Photochemical Ozone Formed in the Niger-Delta Area of Nigeria

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Abstract *Over the past 40 years, crude petroleum from the Niger-Delta area of Nigeria has become the main engine of Nigeria's economic development and industrialization, and also a significant source of petroleum-crude supply to the world. The exploration and exploitation of crude petroleum in the Niger-Delta oil/gas fields releases significant levels of methane (CH_4) and other volatile hydrocarbons into the troposphere, which photochemically react with nitrogen dioxide and water vapor to form ozone and smog in the troposphere. Handicapped by unavailability of ultraviolet (UV) absorption ozone analyzer for the experimental monitoring of the concentrations and trends of ozone, and possibly other air pollutants from photolysis (photochemical reaction) in the Niger-Delta troposphere, a theoretical attempt involving the use of basic chemistry stoichiometry was applied in estimating the magnitude of ozone and smoggy chemical. Therefore, this article examines the formation in the troposphere of photochemical smog from petroleum-methane and hydrocarbon emissions, and estimates the quantities of photochemical ozone and smog formed from the hydrocarbon emissions. To this end, the chemistry of photochemical smog formation was formulated on the basis of literature review, and the stoichiometric functions were developed using basic chemistry methods of calculating masses from balanced chemical equations. These were applied in estimating the quantities of tropospheric ozone and smog formed from the hydrocarbon emissions in the Niger-Delta oil fields as this article will show. Consequently, the annual trend of photochemical smog quantities and ozone magnitudes are presented and discussed.*

Keywords basic chemistry stoichiometry, hydrocarbon emissions, photochemical ozone, photochemical smog, photolysis, volatile hydrocarbons

1. Introduction

The Niger-Delta area of Nigeria is one of the largest wetlands in the world. It is the heart of Nigeria's oil/gas fields. It lies within the equatorial and tropical climatic zones. The south of the Niger-Delta area is the coast of the Atlantic Ocean about the Gulf of Guinea (see Appendix), while the north of the Niger-Delta area is forests of sorts. According to Shell Petroleum Development Company (SPDC) of Nigeria (1999), the Niger-Delta area covers an area of 70,000 square kilometers and consists of a number of characteristic

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ecological zones: sandy costal ridge barriers, brackish or saline mangroves, freshwater permanent and seasonal swamp forests, and lowland rain forest.

The Niger-Delta area is populated by 7 million people who make up 1,600 communities, according to a 1999 estimate, and it is also a habitat to bio-diversities of sorts. Also, it harbors assets and facilities of (a) downstream oil/gas production companies, (b) upstream oil/gas processing corporations, and (c) upstream natural gas utilization plants (e.g., power plants).

Nigeria produces almost two million barrels of oil a day from its oil fields in the Niger-Delta area, and most of the oil comes from reservoirs containing gas, which is produced with the oil (SPDC, 1996). The associated gas is separated from the oil at the flow station, and it is either flared or vented. This work will focus on the hydrocarbon emission from oil/gas production in the Niger-Delta area of Nigeria.

To this end, this study is broken up into the following objects:

1. review of relevant literature about photochemical smog constituents, formation conditions, and effects, and also stoichiometry of chemical reactions;
2. representation of chemical model for smog formation and the determination of stoichiometric function in preparation for the estimations of smog/ozone quantities in the Niger-Delta area of Nigeria; and
3. estimations and presentation of the data.

2. Review of Relevant Literature

2.1. Photochemical Smog Constituents

Photochemical smog is a complex air pollutant known to consist of a mixture of ozone, aldehydes, peroxyacyl nitrates, and nitric acid.

Photochemical smog, according to Miller (1998) is a mixture of pollutants formed when some primary pollutants (mostly nitrogen oxides from motor vehicles and volatile hydrocarbons from various human and natural sources) interact under the influence of sunlight to produce a mixture of more than 100 secondary air pollutants, including ozone (O_3), aldehydes (such as formaldehydes, CH_2O), tear-producing chemicals called peroxacyl nitrates or PANS, and nitric acid (HNO_3).

2.2. Smog and Ozone Formation Conditions

Tropospheric ozone is used as a measure of photochemical smog. According to Miller (1998), the severity of smog is generally associated with atmospheric concentrations of ozone at ground level.

Photochemical smog tends to be most intense in the early afternoon, when the sunlight intensity is greatest (Porteous, 1991). The hotter the day, the higher the levels of ozone and other components of photochemical smog (Miller, 1998).

In photochemical smog phenomenon, Porteous (1991) writes that some 80 separate reactions have been identified or postulated, but two stages have been identified:

Stage 1: smog concentration is linked to both the amount of sunlight and hydrocarbon, respectively; and

Stage 2: the amount is dependent on the initial concentration of nitrogen oxides.

2.2.1. Relevance of the Niger-Delta Circumstance. Given the forgone, the Niger-Delta area has abundant supplies of the following reactants required for the photochemical smog formation: (1) the equatorial and tropical climates where intense sunshine is made available by nature; (2) significant quantities of hydrocarbons vented/emitted from oil/gas production/processing, and other un-quantified natural sources like anaerobic reactions in Niger-Delta wetlands, landfills, paddies, animal breeding, termites, and bush burning; (3) considerable amounts of nitrogen oxides produced by fuel combustions in power plants, refineries, petrochemical plants, gas-flare stations, motor vehicles, and other mobile plants situated in the Niger-Delta troposphere; (4) an inexhaustible supply of atmospheric/tropospheric oxygen; and (5) an appreciable supply of tropospheric water vapor supplied by the troposphere bothering the Atlantic Ocean, the Niger River, and other rivers and seas situated in the Niger-Delta area.

2.3. Effects of Photochemical Ozone and Smog

Manahan (1979) reports that the harmful effects of smog occur mainly in the areas of (a) human health and comfort, (b) effects on material, (c) effects on the atmosphere, and (d) effects on plants. Ozone is known to be damaging to health, and it has a pungent odor. Peroxyacyl nitrates and aldehydes found in smog are eye irritants. Godish (1991) writes that apparently, oxidant levels are indicators of eye irritant potential of photochemical air pollutants, such as PAN, acrolein, aldehydes, and other photochemically derived compounds. The threshold for eye irritation by oxidants is approximately 0.10–0.15 ppm (Godish, 1991). Ozone cracks and ages rubber, which has a strong affinity for ozone. Indeed, the cracking of rubber is one test for ozone (Manahan, 1979). According to Miller (1998), mere traces of these photochemical oxidants (ozone, peroxyacyl nitrates) and aldehydes in photochemical smog can irritate the respiratory tract and damage crops and trees. Also, ozone has proved to be a cause of fatality in animals. For example, Godish (1991) reports that laboratory studies indicate that combined exposures of animals to ozone and influenza infections increases influenza-related mortality; the increased mortality is related to ozone doze.

Therefore, to ensure sustainable development in Nigeria's Niger-Delta oil/gas producing zone, there is a need to put air quality under serious consideration. Thus, this work will attempt to apply the stoichiometry of chemical reaction, a basic chemistry tool, in quantifying the magnitude and trend of ozone and photochemical smog in Nigeria's oil/gas fields.

2.4. Stoichiometry of Chemical Reaction

Ebbing (1993) defined stoichiometry as the calculation of the quantities of reactants and products involved in a chemical reaction. It is based on the chemical equation and on the relationship between mass and moles. Metcalfe et al. (1982) defined a chemical equation as a concise, symbolized statement of a chemical reaction. Useful quantitative information about a reaction is provided by a balanced formula equation.

Stoichiometric interpretation of a chemical equation is based on molecular basis, molar basis, and mass basis (Ebbing, 1993). For this work, stoichiometric interpretations and calculations will be based on reacting masses. Accurate stoichiometric calculations are based on balanced chemical equations. Metcalfe et al. (1982) stated three conditions that must be met in a balanced equation, namely: (1) the equation must represent the facts of the reaction, the substances that react, and the products formed; (2) the symbols or formulae for all reactants and products must be written correctly; and (3) the law of conservation of atoms must be satisfied.

This means that a balanced stoichiometric equation must keep track of the atoms in the formula masses (molecular weights) of both the reactants and products of the chemical reaction. Also, keeping track of the atoms in a stoichiometric equation means obeying the law of conversation of mass. Holderness and Lambert (1981) defined the law of conservation of mass (or indestructibility of matter) as matter that is neither created nor destroyed in the course of chemical action.

3. Representation of Chemical Equation for Smog and Ozone Formation

3.1. Some Assumptions

a) Miller (1998) showed that the constituents of volatile organic compounds are methane (CH_4), propane (C_3H_8), benzene (C_6H_6), and chlorofluorocarbons (CFC_s). To this end, the first assumption is that the reactive hydrocarbons are CH_4, C_3H_8, and C_6H_6.
b) The dispersion/diffusion of reactants of the photochemical reaction is assumed to be very slow.
c) The photochemical reaction goes to completion and the reactants are entirely consumed; that is, there are neither excess reactants nor limiting reactants. The relentless gas flaring in the Niger-Delta oil/gas fields produces huge quantities of NO_x, hence NO_x may not pose a limiting reactant. Oguejiofor (2000) estimates annual emissions of NO_x from gas flaring in the Niger-Delta oil/gas fields, and the excerpts are shown in Table 1.
d) There are no competing reactions that occur simultaneously with the reactants, thereby resulting in scarcity of reactants; that is, there are no parallel reactions that deplete the stocks or supplies of the reactants.
e) The products of the photochemical reaction are fairly stable; that is, the reaction chain terminates with products formation, namely O_3, CH_2O, HNO_3, and PANs.

3.2. Model Representation

A simplified model of the numerous complex photochemical reactions involved in the formation of photochemical smog may be represented as:

$$\text{Nitrogen dioxide} + \text{Oxygen} + \text{Volatile hydrocarbons} + \text{Water vapor} \xrightarrow[\text{activated}]{\text{Sunlight}} \text{Ozone} + \text{Peroxyacyl nitrate} + \text{Formaldehyde} + \text{Nitric acid}. \tag{1}$$

Table 1
Annual levels and trends of NO_x from gas flaring in Nigeria

Year	NO_x quantities, tonnes	NO_x growth rate, %
1995	42,859.8	+3.0
1996	42,596.4	−0.6
1997	42,971.0	+0.9
1998	42,349.5	+0.9
1999	42,092.3	−2.9

Source: Extracted from Oguejiofor (2000).

By representing this, using the empirical chemical formula, the following equation is obtained:

$$NO_2 + O_2 + CH_4 + C_3H_8 + C_6H_6 + H_2O \xrightarrow[\text{Radiation}]{\text{Solar}} O_3 + CH_3CO_2NO_3 + CH_2O + HNO_3. \quad (2)$$

The balanced chemical equation becomes

$$10NO_2 + 12O_2 + 2H_2O + CH_4 + C_3H_8 + C_6H_6 \xrightarrow[\text{Radiation}]{\text{Solar}} 2O_3 + 4CH_3CO_2NO_3 + 2CH_2O + 6HNO_3. \quad (3)$$

The coefficients on the molecular formula of the reactants and products made the chemical equation balance. The balanced equation provides the basis for calculations involving masses.

3.3. *Stoichiometric Function*

The stoichiometric function is determined from the formula masses of the reactants and products of the balanced equation. When ($H = 1$; $C = 12$; $N = 14$; $O = 16$), then the formula masses of the reactants and products become what is shown in Table 2.

From the formula masses in Table 1, the stoichiometric function becomes:

$$\begin{aligned} &460 \text{ g of } NO_2 + 384 \text{ g of } O_2 + 36 \text{ g of } H_2O + 16 \text{ g of } CH_4 + 44 \text{ g of } C_3H_8 \\ &+ 78 \text{ g of } C_6H_6 \xrightarrow[\text{radiation}]{\text{Solar}} 96 \text{ g of } O_3 + 484 \text{ g of } CH_3CO_2NO_3 \\ &+ 60 \text{ g of } CH_2O + 378 \text{ g of } HNO_3. \end{aligned} \quad (4)$$

Table 2
Calculations of the formula masses of the reactants and products from Eq. (3)

S/No	Molecular formula of reactants/products	Calculation details	Formulae masses, g
a)	$10NO_2$	$10(14 + (16 \times 2))$	460
b)	$12O_2$	$12(16 \times 2)$	384
c)	$2H_2O$	$2((1 \times 2) + 16)$	36
d)	CH_4	$12 + (1 \times 4)$	16
e)	C_3H_8	$(12 \times 3) + (1 \times 8)$	44
f)	C_6H_6	$(12 \times 6) + (1 \times 6)$	78
g)	$2O_3$	$2(16 \times 3)$	96
h)	$4CH_3CO_2NO_3$	$4(12 + (1 \times 3) + 12 + (16 \times 2) + 14 + (16 \times 3))$	484
i)	$2CH_2O$	$2(12 + (1 \times 2) + 16)$	60
j)	$6HNO_3$	$6(1 + 14 + (16 \times 3))$	378

By consolidating some components the stoichiometric function may be rewritten as:

$$460 \text{ g of } NO_2 + 384 \text{ g of } O_2 + 36 \text{ g of } H_2O + 138 \text{ g of VOCs} \xrightarrow[\text{radiation}]{\text{Solar}} 1{,}018 \text{ g of Smog}, \tag{5}$$

or

$$460 \text{ g of } NO_2 + 384 \text{ g of } O_2 + 36 \text{ g of } H_2O + 138 \text{ g of VOCs} \xrightarrow[\text{radiation}]{\text{Solar}} 96 \text{ g of } O_3 + 922 \text{ g of smoggy components}, \tag{6}$$

where VOC_s mean volatile organic compounds plus CH_4.

4. Estimations and Data Presentation

Basis: Oil/gas statistics show that SPDC emits about half of the total quantities of hydrocarbon emissions. According to SPDC (1996), about half of the gas flared in Nigeria is produced by SPDC in the course of providing half the country's oil exports. Also, SPDC (1999) reports that gas produced in association with, and as a by-product of, oil is called associated gas; Nigeria currently flares 95% of all such gas, about half of which is produced by SPDC operations. Therefore, the total hydrocarbon emission is twice the amounts produced by SPDC.

Using available annual data on emissions of hydrocarbons (VOCs + CH_4) from oil/gas production, provided by SPDC (2001, 2003), the estimates of smog and ozone quantities in the Niger-Delta area of Nigeria are made using the stoichiometric functions noted by Eqs. (5) and (6). The results are given in Table 3.

Table 3
Estimates of annual magnitudes of smog and ozone in Niger-Delta area of Nigeria

Year	Hydrocarbons emission by SPDC, thousand tonnes	Hydrocarbons emission by SPDC & other oil/gas operators, thousand tonnes	Smog, thousand tonnes	Ozone, thousand tonnes
1998	150.0	300.0	2,213.04	208.70
1999	135.3	270.6	1,996.17	188.24
2000	160.2	320.4	2,363.53	222.89
2001	183.3	366.6	2,704.34	255.03
2002	148.6	297.2	2,193.40	206.75

Source: Computed from annual data compiled from SPDC (2001) and SPDC (2003).

5. Discussion

5.1. Discussion about the Results of Ozone and Smog Formation

Figure 1 and Table 3 show the profile of smog and ozone quantities formed in the Niger-Delta area of Nigeria over the years 1998–2002. It is based on theoretical estimations using basic chemistry tools and methods. On observation, one would notice variations in smog and ozone quantities over the years (see Table 3 and Figure 1). For example, 1999 estimates are the least on magnitudes showing 1,996,170 tonnes of smog and 188,240 tonnes of ozone, respectively. Estimates for 2001 show the highest quantities, with 2,704,340 tonnes of smog and a corresponding 255,030 tonnes of ozone (Table 3 and Figure 1). However, these pollutants are not static as they are usually dispersed by wind.

The variations observed in the smog and ozone quantities may be as a result of the following:

a) increase in oil production resulting in more associated gas production and vice versa;
b) host communities' sabotage and disturbances leading to greater amounts of emissions of volatile hydrocarbons;
c) technical defects and equipment/facilities' failures resulting in increased emissions of hydrocarbon volatiles (examples are fugitive emissions from production, transmission, and storage facilities and vessels);
d) more gas venting than gas flaring done by oil companies, thereby resulting in growth of emission levels and vice versa; and
e) trade union strike actions and ethnic clashes.

These are the apparent causes of the rise and fall observed in the smog and ozone quantities, demonstrated by Table 4 and Figure 2.

5.2. Discussion about Ensuring Sustainable Development

This discussion focuses on safeguarding human well being and abating harmful consequences on other biodiversities against photochemical ozone and smog impacts, while at

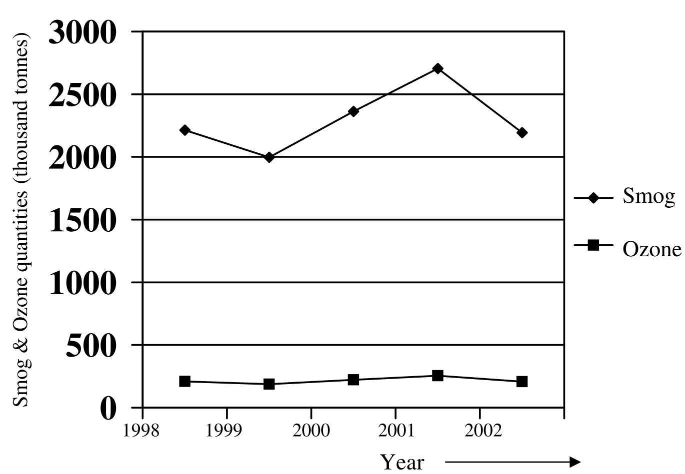

Figure 1. Profile of smog and ozone magnitudes over the years (thousand tonnes).

Table 4
Annual growth/reduction rates in smog and ozone quantities

Year	Smog, thousand tonnes	Ozone, thousand tones	Smog growth/reduction rate, %	Ozone growth/reduction rate, %
1998	2,213.04	208.70		
1999	1,996.17	188.24	−10.86	−10.87
2000	2,363.53	222.89	15.54	15.55
2001	2,704.34	255.03	12.60	12.60
2002	2,193.40	206.75	−23.30	−23.35

the same time ensuring economic progress and industrial development in the Niger-Delta oil/gas region.

By recalling from the literature review section, the harmful effects of photochemical ozone and smog on the health of humans, animals, and vegetation, as reported by Manahan (1979), Miller (1998), and Godish (1991), the plausible way of inhibiting the supply of volatile hydrocarbons (chiefly methane), which are the key reactants in the formation of photochemical ozone and smog, could be discussed.

In this regard, to avoid the harmful impacts, which the estimated levels of photochemical ozone and smog (see Table 3) could likely pose to 7 million inhabitants and the biodiversities in the Niger-Delta, it is suggested that volatile hydrocarbons should be trapped/harnessed at sources/flowstations and buried underground in depleted oil/gas wells, or alternatively re-injected into operational oil/gas wells. The Associated Gas Re-injection Act (Cap 26 Laws of the Federation of Nigeria, 1990) provides for the re-injection of gas associated with oil extraction. However, this act needs serious enforcement about compliance by oil/gas operators so as to ensure the safeguard of 7 million inhabitants (according to 1998 estimate) made up 1,600 communities and other biodiversities.

The smog and ozone quantities (Table 3 and Figure 1) are modest estimates, as they exclude hydrocarbons (CH4) from other anthropogenic sources like wet rice agriculture, livestock, solid waste, and coal mining. For example, The World Bank (1996) showed the data displayed in Table 5 as Nigeria's methane emissions for 1993.

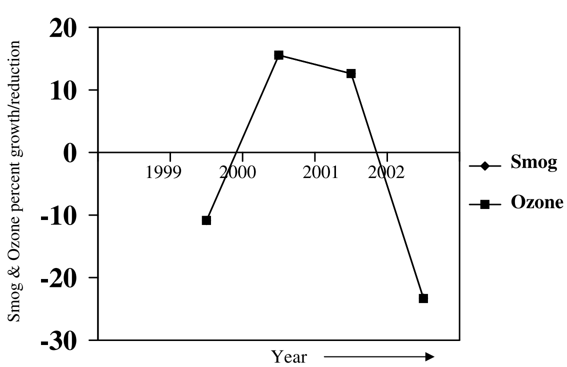

Figure 2. Trend of percentage rise/fall in smog/ozone formation levels over the years

Table 5
Nigeria's 1993 methane emissions from various sources

CH_4 source	Quantities, thousand tonnes
Oil/gas	3,600
Wet rice agriculture	220
Livestock	760
Coal mining	1
Solid waste	3
Total	4,584

Evidently, from Table 5, the quantity of methane from oil/gas production ranked the highest and grossly overwhelmed the methane quantities from other sources, namely, wet rice, livestock, coal mine, and solid waste.

5.3. A Way to Advance the Study

This study focused on theoretical quantification of photochemical ozone and smog from hydrocarbon emissions from oil/gas production only. Providing for a comparative investigation could enhance this study. It is therefore recommended that a UV absorption ozone analyzer be obtained from any manufacturer/vendor (such as OPSIS, Sweden) and deployed for the practical monitoring of ozone and smoggy concentrations and trends in Nigeria's oil/gas fields.

6. Conclusion

Significant levels of theoretical smog and ozone formation from hydrocarbon emissions in oil/gas production in Nigeria have been established by this study. The estimates of smog and ozone magnitudes established by this study used basic chemistry tools and methods that are very simple in approach. Obviously, the basic chemistry method applied in the counting of photochemical ozone and smog quantities circumvented the handicap by the lack of ozone monitoring and measuring equipment. Based on chemistry principles, the results obtained are indicative of (a) the silent photochemical reactions taking place in the Niger-Delta troposphere of Nigeria; (b) their resultant formation of smoggy pollutants (smog/ozone); and (c) their attendant adverse effects on human health, vegetation, and ecosystems in the Niger-Delta region and other areas where the pollutants are dispersed. It is hoped that this study will sensitize and create awareness about photochemical ozone and smoggy pollutants formation in Nigeria's oil/gas fields.

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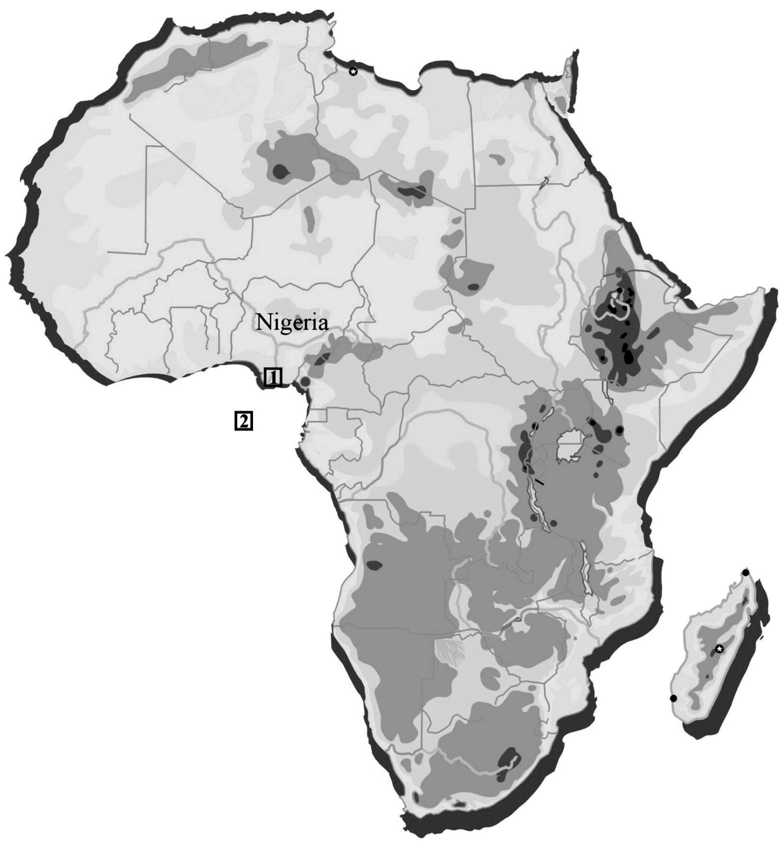
Appendix

Map of Africa Showing Niger-Delta Area of Nigeria



1. Niger-Delta Area oil Oil Region 2. Gulf of Guinea