Ozone Formation Potential and Toxicity Potential of VOCs emissions from a Nigerian petroleum products depot

Muhibbudin Eniola Ismail*
Chemical Engineering Department, University of Ilorin
*Correspondence author: muhibbudin.ei@unilorin.edu.ng

Received: 8 February 2020/ Accepted: 12 August 2020/ Published: 31 September 2020

Abstract: Emissions of volatile organic compounds (VOCs) are major causes of tropospheric ozone and aerosol pollutions. This research provided information on ozone formation potential (OFP) and toxicity potential (TP) resulting from VOCs emission from a Nigeria petroleum depot. In this work, speciated VOCs were provided on basis of updated emissions within and around the depot. The observed concentration of individual VOCs and maximum incremental reactivity (MIR) coefficient were applied to assess the OFP of individual VOC in the ambient atmosphere. Major aromatic VOCs species were considered at various locations. The total OFP in the atmosphere of the depot is 1522.42 μg O\textsubscript{3}/m\textsuperscript{3}. Toluene specie was revealed to be major contributor to OFP with 71.47% while others species were in descending order of benzene (9.16%), m-xylene (8.41%), ethyl benzene (3.98%), p-xylene (3.51%) and o-xylene (3.46%). The TP levels of aerosols pollutions were also reported with respect to locations. The Slop tank area had the highest OFP and TP level. An assessment of TP level and OFP suggests that occupants of some location within the depot are exposed to unhealthy air conditions. The study established that OFP and TP have a relationship within the atmosphere of the depot with respect to location. It is recommended that aggressive controlled measures of VOCs sources should be adopted within the petroleum depot as a way of curtailing the impact of tropospheric ozone and aerosol pollutions.

Keywords: source contribution; OFD; TP; MIR; tropospheric ozone; ambient air; industrial area.

1. Introduction
Volatile organic compounds (VOCs) are most crucial hydrocarbon air pollutants found in petroleum depot facility and refinery and major participants in atmospheric photochemical processes. The air pollutions caused by VOCs most especially aromatic VOCs are known to have direct and indirect impact on climate change, photochemical smog, the ecosystem and human health. Aromatic VOCs play important roles in the increase formation of ozone, secondary organic aerosol (SOA) and other secondary pollutants (Liu et al., 2008) through their reaction with atmospheric radicals like hydroxyl (OH), nitrate (NO\textsubscript{3}) and chlorine (CL) in presence of sunlight. Studies on the relationship of VOCs profiles and emission sources in ozone incidence in regions have shown that ozone formation potential is dependent on VOCs emissions (Lee et al., 2002). Ozone and other oxidized products (atmospheric aerosols) in photochemical smog are formed from the particle- gas phase reaction of oxides of nitrogen (NO\textsubscript{x}) and VOCs. VOCs differ in their setup on ozone formation. Therefore better understanding of distribution characteristics of VOCs is fundamental to analyzing and estimating of photochemical ozone formation potential and variation of toxicity potential of fine particulate matter.
Aromatic VOCs exist as gas phase pollutant (chemical composition) at the same time particle phase pollutant (physical composition) which are atmospheric aerosol. Aromatic VOCs are source of PM \textsubscript{2.5} that is particulate matter with an aerodynamic diameter <2.5 μm (Han Meng et al., 2015) which contributes to low visibility incident.
The major gas phase aromatic VOCs species are benzene, toluene, ethyl benzene and xylene and its isomers. Their photochemical ozone formation potential is of concern because each aromatic VOCs species have different tendencies for ozone formation. These tendencies varies because different inherent chemical behavior (Carter and Atkinson, 1989). The contribution of each aromatic VOCs species to photochemical ozone formation varies from one compound to another and region to region (Zhang, 2008). Each aromatic VOC has a different impact in the ozone levels, which is related with the rate, reaction mechanisms, and conditions of the VOCs emission and how these reactions promote or
inhibit ozone formation (Carter and Atkinson, 1989). Ozone as the oxidized products of photochemical reactions is major environmental concern because its impact on human health, crops and ecosystem. Exposure to ozone has been linked to a number of respiratory health effect, inflammation of airways and caused several cough/pain symptoms when breathing deeply (USEPA, 2012).

Carter in 1994 reported that ethyl benzene has highest ozone forming potential. The toluene, ethyl benzene, xylene and benzene in the formation SOA has been subject to several investigations (Odum et al., 1997; Cocker et al., 2001). According to Kwangsmam Naa et al (2005) toluene and ethyl benzene contain less than two methyl substituent have a higher SOA yield than xylene (Odum et al., 1997). The SOA formed can also affect lung function (Seaton et al., 1995) and contribute to visibility degradation (Appel et al., 1985).

The reaction of aromatic VOCs with OH and NO3 serves as dominant degradation processes for aromatic VOCs in the atmosphere. These oxidations of VOCs by these radicals are sources of SOA which is called atmospheric aerosol. The condensed portion of the aerosol is the ultra fine particulate matter (PM2.5). The chemical and physical properties of PM depend on the geographical location, time of year and meteorological conditions at the time of formation (US EPA, 2013), as well as the nature of the source. Exposure to particulate pollution has been linked with premature death, difficult breathing, aggravated asthma and increased respiratory symptoms (US EPA, 2013). Particulate matter can also discolor buildings and other structures. Environmental effects of increased particulate matter include reduced visibility and decreased growth as well as productivity of vegetation, due to interference with photosynthesis.

Aromatic VOCs may account for as much as 50% of total fine particle mass on average (Health Canada, 1998). Few studies have examined the contribution of VOCs toward secondary particulate matter formation. According to the Ontario Ministry of the Environment (MOE), alkenes and aromatics are the most important of the many VOC species with respect to fine particle formation (MOE, 1999). Each VOC species in the atmosphere may produce other VOC species during reaction; therefore, the contribution of a compound to PM formation may be highly complex.

The purpose of this study is to (1) study the behavior of aromatic VOCs emission in gas and particle phase. (2) To estimate ozone forming potential and toxicity potential of aromatic VOCs emitted from a Nigeria petroleum products depot.

2.0 Method and data
2.1 General information on Mosimi petroleum depot. Mosimi depot is one of the depots under PPMC which is a subsidiary of Nigeria National Petroleum Corporation (NNPC), located at Sagamu, Ogun state, Nigeria. The basic activities in Mosimi Depot are; reception of petroleum products such as, PMS, DPK, and AGO from Atlas Cove and local refineries. The Petroleum products are pumped to both Ibadan and Ore depots. Others activities that often take place include: quality control analysis of products (laboratory analysis), inter -tank transfer, tank dipping and sampling, blending of an off-spec with on-spec products, fiscalization, calibration and stock-taking activities.

The depot operates with a total number of 21 storage tanks as at the time of this study designated with numbers of specifications. Tank 21, 22, 16, 41, 42 and 43 are made for Premium Motor Spirits (PMS) with a total capacity of 19,200m³ each, for tank 44, 45, 46, 47 and 14 are for Dual Purpose Kerosene (DPK) with a total capacity of 19,000m³ each. Tank 51, 52, 53, 54, 55 and 56 are made for Automotive Gas Oil (AGO) with a total capacity of 23, 074m³ each. Tank 71, 72, 73 and 74 are called “Slop tank” with a total capacity of 200m³. The Depot pumped and received products via pipelines.

2.2 Emission inventory and area profile
The latest emission air inventory provided by Muhibbu-din Ismail (2020) on atmospheric VOCs emissions from a Nigerian petroleum product was used in this study as a basis for the speciation of VOCs emission as indicated in Table 1. The data were collated and compiled into different categories. Air samples were collected over activated charcoal using a low volume air sampler at different sampling locations within and around the depot. Aromatic VOCs species were identified and quantified by flame ionization detector in a gas chromatography (GC-FID) (Model: HP6890). The mean diurnal temperature of the depot varies from 29.71°C to 33.92°C with sampling time starting from 9.00 am end by 5.00 pm. Aromatic VOCs measurement was established on the basis of area profile which is consistent with ANSI/ASTM procedure and used in this study for aromatic VOCs species inventory as indicated in Table 1.

2.3 Calculation of Ozone Formation Potential
Aromatic VOCs play key roles in formation of photochemical smog (atmospheric aerosol) and ozone formation. The ozone formation potential is generally used to assess the photochemical activity of VOCs
the ambient air. Ozone formation potential (OFP) of VOCs depend on the concentrations and reactivity of the species in the atmosphere (Atkinson and Arey, 2003). Different mechanism can be used to determine OFP. Chemical mechanism modeling such as second generation Regional Acid Deposition Model (RADM2), the Statewide Air Pollution Research Center 07 (SAPRC07) and Carbon Bond 05(CB05) have been widely used in chemical transport models (CTMs). These models can accurately estimate OFP but requires heavy computation. There is maximum incremental reactivity (MIR) method for OFP estimation developed by Carter, 1994. This simply involve multiplication of concentration each VOCs species and maximum incremental reactivity (MIR) of a VOC. MIR is derived from chamber experiments and thus confined to specific atmospheric conditions, therefore it is more suitable for OFD estimation. It is use to evaluate the contribution of individual VOCs to ozone production. OFD estimation can be mathematically expressed as follows:

\[ \text{OFP} = C_i \times \text{MIR}_i \]  

where OFP is the ozone formation potential of a VOC specie, mg/m^3, \( C_i \) the actual measured mass concentration of a VOC, \( \text{MIR}_i \) is the maximum incremental reactivity of a VOC (Carter. 2010). The ratings of the VOCs species are done with respect to OFP using Carter’s MIR. The MIR scale has been used in California, to quantify the reactivity of alternatively fueled vehicles, scaled to reactivity of exhaust emissions from a vehicle using standard gasoline (Russell et al, 1995). Grosjean et al (1998) F is the factor to convert from averaging period \( t_1 \) to \( t_2 \) at averaging period

\[ F = \left( \frac{t_2}{t_1} \right)^{n} \]  

\( N = 0.28 \), the stability dependent exponent.

3.0 Result:

The reactivity with respect to ozone formation potential of aromatic VOCs species within and around Mosimi petroleum products depot, Sagamu, Nigeria is presented in Table 4. The 8-hour measured and 24-hour extrapolated concentrations of atmospheric aerosol resulting from condensed VOCs emission from Mosimi petroleum products depot were presented in Table 3. The 8-hour concentration also utilized the MIR to assess the VOCs reactivity in the urban area of Porto Allegre city, Brazil.

2.4 Toxicity Potential of particle phase VOCs atmospheric aerosol.

Toxicity Potential (TP) is a quantitative toxic equivalency which expresses the potential physical harm of a unit pollutant emitted into the environment (Fakunle et al., 2019; Muhhibbu-din 2017). It indicates ecotoxicological effect of condensed VOCs emitted on human and atmosphere above certain dose. It is mathematically expressed as ratio of measured ambient PM concentration to the statutory limit of ambient concentration as follows:

\[ TP = \frac{C_i(t) / SL_i(t)}{F} \]  

where TP represent the toxicity potential of pollutant \( i \), \( C_i(t) \) is the measured/ extrapolated concentration of pollutant \( i \) at time \( t \) in \( \mu g/m^3 \); \( SL_i(t) \) is the statutory concentration limits of pollutants \( i \) at time \( t \) in \( \mu g/m^3 \). The statutory limits used in computing the toxicity potential of VOCs atmospheric aerosols emitted and retained for 24 hrs are that of United States Environmental Protection (USEPA) and World Health Organization air quality standards (Table 4). Basher et al in 2009 proposed atmospheric stability formula for extrapolated values of pollutant \( i \) at time \( t \) in \( \mu g/m^3 \) expressed in equation below:

\[ C_2 = C_1 \times F \]  

where \( C_2 \) is the concentration at the averaging period \( t_2 \)

\[ C_1 \] is the concentration at the averaging period \( t_1 \)

dose ranged between 18.82µg/m^3 and 182.09µg/m^3 which on extrapolation 24 hour (daily dose) became 13.74 µg/m^3 and 132.92 µg/m^3. Table 4 gives comparative air quality standards by USEPA, WHO and Canada. Table 5 give accounts of computed daily toxicity potential of atmospheric VOCs aerosol from the depot. Table 1 give report of latest inventory data of VOCs emission from Mosimi depot and Table 2 also give account of Ozone Formation Potential (OFP) with respect to MIR coefficient.
Table 1: Sum and average measured concentrations (µg/m³) of VOCs species at Mosimi PPMC depot

<table>
<thead>
<tr>
<th>Location</th>
<th>Coordinate</th>
<th>Benzene (µg/m³)</th>
<th>Toluene (µg/m³)</th>
<th>Ethyl benzene (µg/m³)</th>
<th>p-Xylene (µg/m³)</th>
<th>m-Xylene (µg/m³)</th>
<th>o-Xylene (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/S</td>
<td>6°45’14”N 3°33’05”E</td>
<td>59.54</td>
<td>78.53</td>
<td>3.55</td>
<td>1.59</td>
<td>2.56</td>
<td>1.34</td>
</tr>
<tr>
<td>S/T</td>
<td>6°45’11”N 3°33’04”E</td>
<td>71.12</td>
<td>99.75</td>
<td>4.49</td>
<td>2.18</td>
<td>2.64</td>
<td>1.91</td>
</tr>
<tr>
<td>G1</td>
<td>6°45’18”N 3°33’05”E</td>
<td>16.6</td>
<td>23.16</td>
<td>3.2</td>
<td>1.38</td>
<td>1.99</td>
<td>1.01</td>
</tr>
<tr>
<td>T/F</td>
<td>6°45’09”N 3°33’01”E</td>
<td>18.08</td>
<td>27.06</td>
<td>3.9</td>
<td>1.78</td>
<td>2.64</td>
<td>1.52</td>
</tr>
<tr>
<td>G2</td>
<td>6°45’04”N 3°32’57”E</td>
<td>10.22</td>
<td>16.3</td>
<td>1.79</td>
<td>0.79</td>
<td>1.23</td>
<td>0.42</td>
</tr>
<tr>
<td>O/V</td>
<td>6°45’24”N 3°33’20”E</td>
<td>7.73</td>
<td>8.88</td>
<td>1.01</td>
<td>0.4</td>
<td>0.69</td>
<td>0.11</td>
</tr>
<tr>
<td>M/B</td>
<td>6°45’19”N 3°33’04”E</td>
<td>10.37</td>
<td>18.34</td>
<td>2.01</td>
<td>1.04</td>
<td>1.39</td>
<td>0.58</td>
</tr>
</tbody>
</table>

|          | Summation          | 193.66         | 272.02         | 19.95                | 9.16            | 13.14           | 6.89            |
|          | Average             | 27.67          | 38.86          | 2.85                 | 1.31            | 1.88            | 0.98            |
|          | Standard deviation  | 26.20          | 35.35          | 1.27                 | 0.61            | 0.79            | 0.65            |

W/S-Workshop, S/T- Slop tanks, G1- Gate 1, T/F- Tank Farm, G2- Gate 2, O/V- Otiyelu Village, M/B- Marketer’s Block

Table 2: Ozone Formation Potential (OFP) with respect to MIR coefficient

<table>
<thead>
<tr>
<th>VOCs species</th>
<th>MIR a (gO₃/gVOCs)</th>
<th>W.S.</th>
<th>S.T.</th>
<th>G1</th>
<th>T.F</th>
<th>G2</th>
<th>O.V</th>
<th>M.B</th>
<th>Summation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.72</td>
<td>51.21</td>
<td>11.95</td>
<td>13.02</td>
<td>7.36</td>
<td>5.57</td>
<td>7.47</td>
<td>139.45</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>4.00</td>
<td>314.12</td>
<td>92.64</td>
<td>108.24</td>
<td>65.20</td>
<td>35.52</td>
<td>73.36</td>
<td>1088.08</td>
<td></td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>3.04</td>
<td>10.79</td>
<td>13.65</td>
<td>11.86</td>
<td>5.44</td>
<td>3.07</td>
<td>6.11</td>
<td>60.65</td>
<td></td>
</tr>
<tr>
<td>p-Xylene</td>
<td>5.84</td>
<td>9.29</td>
<td>12.73</td>
<td>8.06</td>
<td>10.40</td>
<td>4.61</td>
<td>2.34</td>
<td>6.07</td>
<td></td>
</tr>
<tr>
<td>o-Xylene</td>
<td>7.64</td>
<td>10.23</td>
<td>14.59</td>
<td>7.72</td>
<td>11.61</td>
<td>3.21</td>
<td>0.84</td>
<td>4.43</td>
<td></td>
</tr>
<tr>
<td>Summation</td>
<td>412.26</td>
<td>516.92</td>
<td>149.50</td>
<td>180.87</td>
<td>97.81</td>
<td>54.07</td>
<td>44.3</td>
<td>1522.42</td>
<td></td>
</tr>
</tbody>
</table>

Notes: *a*Maximum incremental reactivity in gO₃/gVOCs, *b*Ozone formation potential (µg O₃/m³).

Table 3: Measured and Extrapolated concentration particle phase VOCs atmospheric aerosol from Mosimi petroleum depot

<table>
<thead>
<tr>
<th>Sampling Location</th>
<th>Measured concentration (µg/m³) 8 hours</th>
<th>Extrapolated concentration (µg/m³) 24 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Workshop</td>
<td>147.11</td>
<td>107.40</td>
</tr>
<tr>
<td>Slop Tanks</td>
<td>182.09</td>
<td>132.92</td>
</tr>
<tr>
<td>Gate 1</td>
<td>47.34</td>
<td>34.56</td>
</tr>
<tr>
<td>Tank Farm</td>
<td>54.98</td>
<td>40.14</td>
</tr>
<tr>
<td>Gate 2</td>
<td>30.76</td>
<td>22.45</td>
</tr>
<tr>
<td>Otiyelu Village</td>
<td>18.82</td>
<td>13.74</td>
</tr>
<tr>
<td>Marketer’s Block</td>
<td>33.73</td>
<td>24.62</td>
</tr>
</tbody>
</table>

Table 4: Air quality standard for PM 2.5 (statutory limit for atmospheric aerosol)

<table>
<thead>
<tr>
<th>Authority</th>
<th>24-hr concentration (µg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>USEPA</td>
<td>35</td>
</tr>
<tr>
<td>WHO</td>
<td>25</td>
</tr>
<tr>
<td>CANADA</td>
<td>30</td>
</tr>
</tbody>
</table>

Notes: USEPA- United State Environmental Protection Agency; WHO- World Health Organization; CANADA- Canada-Wide Standards issued by the Canadian Council of Ministers of the Environment.
4.0 Discussion:
The total possible OFP for the seven locations is 1522.42 μg O₃/m³. The largest contributor specie to ozone production in the depot is toluene with (35.52 – 399) μg O₃/m³ while the least contributor among the aromatic VOCs considered is o-xylene with 0.84-14.59 (μg O₃/m³). The toluene is responsible for 71.47% of total OFP. This can attributed to the reactivity and abundance to toluene emissions within and around the depot. The ranking order of aromatic VOCs species with respect to OFP were in descending order of toluene (71.47%), benzene (9.16%), m-xylene (8.41%), ethylbenzene (3.98%), p-xylene (3.51%) and o-xylene (3.46%). The majority of OFP within and around the depot was at Slop Tank area with 516.92 μg O₃/m³. This can be ascribed to evaporative and fugitive emissions from many pipelines within the area. Openness and low height of four Slop Tanks in that area and closeness to Tank Farm. Slop Tank contributed 33.95% to OFP formation. Workshop area is 27.08% to OFP with 412.26 μg O₃/m³. This area is the beehive of activities within the depot. OFP is largely influence due closeness to loading gantry, decanting point, slop pit, pumping pit and bolster pump pit. Second to Slop Tank area in OFP. Tank Farm area is third with OFP with 180.87μgO₃/m³. This is the area used to stored petroleum products in large tanks. OFP here are influence by good height of Tank Farm. Gate 1 area, OFP is 149.50 μgO₃/m³ with 9.82%. Gate 1 area is largely influence by VOCs emissions from loading gantry and vehicular emission. At Gate 2 area, OFP here is 97.81μgO₃/m³ with 6.42%. The contributing sources are from separator pit, waste water from the depot and tank farm at the rear of the depot. OFP outside the depot include the one at Market’s block and that of Otiyelu village are 7.29% and 3.55% with 110.99 μg O₃/m³ and 54.07 μg O₃/m³ respectively. OFP at Marketer’s block are ascribed to vehicular emission and emissions from haulage; place where petroleum products are drawn from loading truck. OFP at Otiyelu village are influence by her distance (geographical location) from contributing sources from the depot. The low value is as a result of atmospheric dispersion and dilution of VOCs species. The ranking order OFP with respect to locations were in descending order of Slop Tank area (33.95%), Workshop area (27.08%), Tank Farm area (11.88%), Gate 1area (9.82%), Gate 2 area (6.42%), Marketer’s block (7.29%) and Otiyelu village (3.55%).

The statutory limits for PM₂.₅ were exceed in the USEPA, CANADA 24-hr (daily) guidelines for workshop area, slop tank area and tank farm area. For WHO daily limit of 25 μg/m³ were breached Workshop area, Slop Tank area, Tank Farm area and Gate 1. This be could attributed high number of contributing sources of aromatic VOCs emissions in the identified areas. Elevated concentrations of PM₂.₅ were observed in these areas because of continuous suspension of fine particle in the atmosphere of the depot.

As summarized in Table 5, the computed toxicity potential (TP) obtained when the statutory limit in Table 4 were used. The TP ranges are 0.39- 3.80, 0.55- 5.32, 0.46- 3.58 and 0.46- 4.43 when the statutory limits of USEPA, WHO and CANADA were proportion to 24-hr atmospheric VOCs aerosol concentration for PM₂.₅.

Toxicity potential values in Table 5 greater than unity indicate that concentration of atmospheric aerosol has great tendency of causing harm to occupants (workers, business men and visitors) and therefore should be controlled. The least breached limit areas beyond the depot include Otiyelu village, Marketer’s block area, Gate 2 which are safe from harmful effect of VOCs atmospheric aerosol while other locations are not safe. The descending order of TP of VOCs atmospheric aerosol was: Slop Tank > Workshop > Tank Farm> Gate 1> Gate 2> Marketer’s block> Otiyelu Village.

5.0 Conclusion:
This study has shown that VOCs emissions from a Nigerian petroleum products depot contribute to elevation in concentration of atmospheric aerosols (PM) and photochemical production of tropospheric
ozone. This research also established that individual VOCs species have different ozone formation potential. Toluene specie contributes more to OFP more any other aromatic VOCs species considered within and around Mosimi depot. People are exposed to significant concentration levels of aerosols from VOCs emission in the depot as toxicity potential were above 1 in some locations within the depot. Where toxicity potential values are greater than unity, a more aggressive control measures should be adopted for VOCs emission. Air quality standards for PM$_{2.5}$ had been set by various countries like USA, Canada and Australia (WHO) by respectable authorities. The result obtained from this research for both OFP and TP with respect to locations suggest that aromatic VOCs are evidential contributor, therefore must be curtailed and controlled. No air quality limits have yet been published in Africa for this particulate size. Inhabitants, workers and general public around the depot should be educated and enlighten about impact of atmospheric aerosol and ozone from VOCs emission and proper regulating monitoring should be continued to assess the change in VOCs level from source profiling.

ACKNOWLEDGMENT

Our profound gratitude goes to my wife, my best friend and sweet companion, Mrs. Nusirat Muhibbudin for her unquantifiable love, support and encouragement throughout the rough and good time during the course of this study.

CONFLICT OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this manuscript.

Reference


Zhang YH, Su H, Zhong LJ (2008) “Regional ozone pollution and observation-based approach for analyzing ozone precursor relationship during the PRIDE-