Analysis of Concentration Levels of Atmospheric Pollutants in Warri, Nigeria

Ifeanyi Innocent Onwosi1,2*, Emmanuel Iruka Njoku1, Emmanuel Fartiyahcha Nymphas1

1Department of Physics, University of Ibadan, Ibadan, Nigeria
2Department of Physics and Engineering, Delaware State University, Dover, DE, USA

Email: *innocentonwosi@gmail.com

Abstract

A critical environmental problem facing the Niger Delta region is Air Pollution. This study therefore analyses concentration levels of atmospheric pollutants in the region. Statistical analysis of CH4 and O3 concentrations for the period of 2003 to 2012 and NO2 and CO2 concentrations for the period of 2011 to 2014 were carried out. The results showed that concentration levels of the pollutants were lower during the rainy season than during the dry year time. This is due to higher occurrences of atmospheric instability during the rainy season. On the other hand, ozone (O3) concentration reached its peak value during the peak period of the rainy season unlike the other pollutants. In all likelihood, some of the ozone-depleting substances such as aerosols and atmospheric hydrogen chloride become soluble in water and are being washed off by precipitation during rainy season, thereby leading to increased tropospheric ozone concentration during the rainy season. The study also revealed a steady increase in the concentration of CO2 within the period of investigation. This steady increase in CO2 can be traced to the alarming increase in anthropogenic activities which appreciably increases the amount of CO2 in the atmosphere. Methane (CH4) had higher standard deviation values than carbon dioxide (CO2), meaning that on a per molecule basis, a proportional rise in CH4 is much more effective as a greenhouse gas than a similar increase in CO2. However, CO2 has a greater effect than CH4 on climate change owing to its higher atmospheric concentration. The Mann-Kendall rank statistics of the atmospheric pollutants revealed that the standardization variables U(t) and U'(t) have a sequential fluctuating behavior around a zero level.

Keywords

Air Pollution, Atmospheric Pollutants, Mann-Kendall Rank Statistics
1. Introduction

Air pollution is the addition of harmful substances known as air pollutants to the atmosphere, resulting in damage to the natural or built environment, human health, and quality of life. The major sources of air pollution in the Niger Delta area are gas flaring, traffic emissions and industrial emissions [1].

Since Nigeria’s discovery of oil in the 1950’s, the country (especially the Niger Delta region) has been suffering the undesirable environmental repercussions of oil development [2]. Nigeria is accountable for about 46% of Africa’s total gas flared per tonne of oil produced and has the highest record (19.79%) of natural gas flaring globally [3]. [4] carried out a comparison of concentrations of ambient air pollutants in Lagos and in the Niger Delta region. He concluded that concentration levels of the pollutants were highest in the Niger Delta region. [5] undertook an air quality assessment of the Niger Delta. The study revealed that the levels of volatile oxides of carbon, sulphur and nitrogen exceed existing Federal Environmental Protection Agency (FEPA) limits for CO: 10 ppm, SO₂: 0.01 ppm and NO₂: 0.04 - 0.06 ppm. Also, [6] examined air samples obtained from 16 communities in the Niger Delta region for their suspended particulate matter (SPM) composition. The study showed that the particulate load was above the World Health Organization (WHO) specification for both PM_{2.5} and PM_{10} annual mean and 24-h mean (PM_{2.5}: 10 μg/m³ annual mean, 25 μg/m³ 24-h mean; PM_{10}: 20 μg/m³ annual mean, 50 μg/m³ 24-h mean). Furthermore, [7] undertook an assessment of the atmospheric levels of PM_{10} in Port Harcourt. The study revealed that the trend in the seasonal PM_{10} concentration levels was dry > transition > wet. Even though some amount of work has been done on the air quality assessment of some other parts of the Niger Delta area, not much work has been undertaken on the analysis of emission levels of atmospheric pollutants in Warri which is one of the major hubs of petrochemical activities in the Niger Delta region. Understanding the extent of the emission of atmospheric pollutants in Warri could assist in the mitigation of air pollution in the Niger Delta area.

2. Study Station, Materials and Method

2.1. Study Station

The city of Warri (5.52°N, 5.75°E) is a major center of petroleum activities in southern Nigeria. It has a population of over 311,970 (2006 census) [8]. The climate is marked by two different seasons: the rainy season (May to October) and the dry season (November to April). Figure 1 is the map of Delta state showing gas flaring sites and highlighting study station (Warri). The area is characterized with annual rainfall amount of about 2768.8 mm with rainfall periods varying from January to December. Over the course of the year, temperature typically varies from 20.56°C to 31.11°C and is rarely below 16.11°C or above 33.33°C.

2.2. Materials

Data description
The daily methane (CH\textsubscript{4}), carbon dioxide (CO\textsubscript{2}), nitrogen dioxide (NO\textsubscript{2}) and tropospheric ozone (O\textsubscript{3}) concentrations data used in this study were obtained from the National Aeronautics and Space Administration (NASA).

2.3. Method

Monthly and annual averaging of the daily pollutant concentrations (NASA data) within the period of investigation were carried out. Statistical analysis of CH\textsubscript{4} and O\textsubscript{3} concentrations for the period of 2003 to 2012 and NO\textsubscript{2} and CO\textsubscript{2} concentrations for the period of 2011 to 2014 were carried out. The sequential version of the Mann-Kendall rank statistics was then used to analyze the atmospheric pollutants data in order to identify long-term trends. The effective application involves the following steps in sequence:

- The values \(x_i\) of the initial series are substituted by their ranks \(y_i\), set up in ascending order.
- The magnitudes of \(y_i\) (\(i = 1, ..., N\)) are compared with \(y_j\) (\(j = 1, ..., i - 1\)). At each comparison, the number of cases \(y_i > y_j\) is counted and represented by \(n_i\).
- A statistic \(t_i\) is given as follows
  \[
  t_i = \sum n_i
  \]
  \[
  \text{(1)}
  \]
- The distribution of the test statistic \(t_i\) has a variance and a mean as follows
  \[
  \text{var } t_i = \frac{i(i-1)(2i+5)}{72}
  \]
  \[
  \text{(2)}
  \]
\[ E(t_i) = \frac{i(i-1)}{4} \]  

- The values of the statistic \( u(t_i) \) in sequence are then calculated as
\[ u(t_i) = \frac{t_i - E(t_i)}{\sqrt{\text{var} \ t_i}} \]

- Likewise, the values of \( u(t) \) are calculated backward starting from the end of the series.

3. Results and Discussion

3.1. Average Monthly Concentration of the Atmospheric Pollutants

Table 1, Table 2 show the values of average monthly concentration of CH\(_4\) (ppmv) and O\(_3\) (ppmv) respectively for the period of 2003 to 2012, while Table 3, Table 4 show the values of average monthly concentration of NO\(_2\) (ppmv) and CO\(_2\) (ppmv) respectively for the period of 2011 to 2014.

Table 1. Values of average monthly concentration of CH\(_4\) (ppmv) for the period of 2003 to 2012.

|         | 2003  | 2004  | 2005  | 2006  | 2007  | 2008  | 2009  | 2010  | 2011  | 2012  |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| January | 1775.0| 1745.4| 1741.1| 1727.7| 1739.3| 1748.1| 1759.8| 1741.9| 1751.4| 1780.9|
| February| 1745.0| 1740.2| 1738.3| 1727.5| 1730.9| 1746.5| 1747.2| 1740.8| 1746.9| 1787.8|
| March   | 1748.1| 1737.6| 1745.0| 1730.5| 1743.3| 1739.9| 1749.6| 1741.6| 1746.8| 1777.3|
| April   | 1735.6| 1732.4| 1737.5| 1731.4| 1735.0| 1746.0| 1750.4| 1747.0| 1749.4| 1785.0|
| May     | 1735.1| 1743.9| 1733.4| 1722.5| 1738.7| 1746.2| 1751.7| 1747.9| 1745.6| 1775.8|
| June    | 1724.2| 1721.0| 1731.9| 1733.2| 1737.1| 1745.5| 1744.4| 1746.9| 1732.5| 1766.9|
| July    | 1714.3| 1717.0| 1727.9| 1719.9| 1724.0| 1737.1| 1740.1| 1740.9| 1748.3| 1754.9|
| August  | 1711.1| 1726.7| 1729.0| 1718.6| 1718.1| 1710.1| 1735.6| 1736.0| 1758.2| 1757.7|
| September| 1732.6| 1748.2| 1738.1| 1725.0| 1740.5| 1735.8| 1746.8| 1744.8| 1771.9| 1761.4|
| October | 1757.4| 1750.9| 1750.8| 1739.4| 1759.0| 1749.7| 1754.8| 1757.5| 1784.7| 1769.2|
| November| 1761.3| 1754.7| 1739.9| 1755.6| 1768.9| 1760.4| 1769.2| 1755.1| 1796.1| 1777.9|
| December| 1752.1| 1739.3| 1735.0| 1739.9| 1753.9| 1758.2| 1752.8| 1755.5| 1786.5| 1788.5|

Table 2. Values of average monthly concentration of O\(_3\) (ppmv) for the period of 2003 to 2012.

|         | 2003  | 2004  | 2005  | 2006  | 2007  | 2008  | 2009  | 2010  | 2011  | 2012  |
|---------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| January | 53.083| 54.087| 53.102| 51.841| 52.296| 54.010| 55.492| 53.562| 57.025| 53.947|
| February| 53.020| 54.610| 53.378| 52.988| 52.977| 54.592| 53.956| 52.588| 57.328| 55.076|
| March   | 54.475| 57.048| 53.807| 54.723| 54.523| 56.948| 55.433| 54.360| 58.274| 55.733|
| April   | 57.050| 57.351| 54.234| 57.257| 56.299| 59.102| 57.521| 56.053| 58.216| 56.920|
| May     | 56.903| 57.944| 54.311| 58.751| 56.352| 60.760| 57.939| 56.856| 58.588| 57.495|
| June    | 57.453| 59.799| 54.931| 60.413| 55.851| 61.497| 58.897| 57.872| 59.459| 58.238|
| July    | 58.435| 60.004| 56.209| 61.434| 56.572| 61.865| 60.130| 60.783| 60.032| 58.957|
| August  | 59.857| 60.014| 56.808| 61.170| 57.225| 61.961| 60.363| 61.713| 60.609| 59.552|
| September| 58.779| 59.561| 56.176| 60.357| 56.329| 61.958| 59.632| 62.794| 60.485| 59.249|
| October | 56.736| 56.904| 55.092| 58.134| 55.752| 58.921| 58.306| 61.593| 58.873| 57.000|
| November| 54.428| 55.315| 53.042| 55.519| 54.990| 56.241| 55.710| 59.955| 56.316| 55.523|
| December| 54.918| 54.402| 52.921| 53.095| 54.133| 54.814| 53.729| 58.268| 54.621| 53.915|

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Table 3. Values of average monthly concentration of NO$_2$ (ppmv) for the period of 2011 to 2014.

|       | 2011     | 2012     | 2013     | 2014     |
|-------|----------|----------|----------|----------|
| January | 176.4286 | 143.0500 | 178.4762 | 172.6957 |
| February | 143.4444 | 129.9615 | 115.2105 | 144.6875 |
| March   | 121.8750 | 110.0556 | 127.9500 | 124.3529 |
| April   | 100.9412 | 99.4286  | 121.3500 | 86.1111  |
| May     | 98.7500  | 93.6429  | 99.8333  | 89.8462  |
| June    | 101.2857 | 93.2857  | 86.0000  | 119.1429 |
| July    | 127.8333 | 61.3333  | 127.8333 | 86.4286  |
| August  | 76.0000  | 102.4000 | 79.5000  | 82.1250  |
| September | 68.4444 | 89.5833  | 92.9375  | 81.5882  |
| October | 123.4118 | 107.9444 | 127.5000 | 150.1176 |
| November | 228.1905 | 251.7391 | 197.9048 | 204.5789 |
| December | 261.7308 | 247.7727 | 252.7083 | 251.2857 |

Table 4. Values of average monthly concentration of CO$_2$ (ppmv) for the period of 2011 to 2014.

|       | 2011     | 2012     | 2013     | 2014     |
|-------|----------|----------|----------|----------|
| January | 388.2671 | 386.9302 | 384.7967 | 382.8482 |
| February | 384.7967 | 384.8546 | 391.1232 | 391.8489 |
| March   | 382.8482 | 387.1007 | 390.5237 | 390.1177 |
| April   | 384.6600 | 385.4377 | 387.5442 | 389.6226 |
| May     | 376.1521 | 385.2328 | 382.4967 | 392.9677 |
| June    | 380.1761 | 379.6688 | 384.8706 | 391.7415 |
| July    | 378.7995 | 381.1844 | 380.6630 | 389.4396 |
| August  | 377.4204 | 379.7802 | 384.0695 | 391.4127 |
| September | 383.4106 | 387.5586 | 389.4768 | 393.5066 |
| October | 388.8309 | 391.1420 | 393.5256 | 396.0969 |

3.2. Average Annual Concentration of the Atmospheric Pollutants

Table 5 shows the values of average annual concentration of CH$_4$ (ppmv) and O$_3$ (ppmv) for the period of 2003 to 2012 while Table 6 shows the values of average annual concentration of NO$_2$ (ppmv) and CO$_2$ (ppmv) for the period of 2011 to 2014.

3.3. Descriptive Statistics of the Atmospheric Pollutants

Table 7 shows the descriptive statistics (Minimum and Maximum values, Mean and Standard Deviation) of annual averages of CH$_4$, O$_3$, NO$_2$ and CO$_2$ concentrations within the period of investigation.

3.4. Time Series Plot of the Atmospheric Pollutants Concentration

Figures 2(a)-(d) show the graph of average monthly concentration levels of the atmospheric pollutants within the period of investigation, while Figures 3(a)-(d)
Table 5. Values of average annual concentration of CH$_4$ and O$_3$ for the period of 2003 to 2012.

| Year | Mean CH$_4$ (ppmv) | Mean O$_3$ (ppmv) |
|------|--------------------|-------------------|
| 2003 | 1740.994           | 56.262            |
| 2004 | 1738.120           | 57.253            |
| 2005 | 1737.331           | 54.501            |
| 2006 | 1730.918           | 57.139            |
| 2007 | 1740.740           | 55.272            |
| 2008 | 1743.628           | 58.556            |
| 2009 | 1750.178           | 57.259            |
| 2010 | 1746.312           | 58.033            |
| 2011 | 1759.923           | 58.319            |
| 2012 | 1773.787           | 56.800            |

Table 6. Values of average annual concentration of NO$_2$ (ppmv) and CO$_2$ (ppmv) for the period of 2011 to 2014.

| Year | Mean NO$_2$ (ppmv) | Mean CO$_2$ (ppmv) |
|------|--------------------|--------------------|
| 2011 | 135.695            | 382.370            |
| 2012 | 127.516            | 385.108            |
| 2013 | 133.934            | 388.111            |
| 2014 | 132.747            | 392.186            |

Table 7. Descriptive statistics of annual averages of CH$_4$, O$_3$, NO$_2$ and CO$_2$ concentrations within the period of investigation.

|                  | Minimum | Maximum | Mean   | Standard Deviation |
|------------------|---------|---------|--------|--------------------|
| CH$_4$ (ppmv)    | 1730.918| 1773.787| 1746.193| 12.500             |
| O$_3$ (ppmv)     | 54.501  | 58.556  | 56.939  | 1.300              |
| NO$_2$ (ppmv)    | 127.516 | 135.695 | 132.473 | 3.519              |
| CO$_2$ (ppmv)    | 380.139 | 392.186 | 386.944 | 4.208              |

show the graph of average annual concentration levels of the atmospheric pollutants within the period of investigation.

3.5. Mann-Kendall Trend Validation

Table 8 shows the Mann-Kendall rank statistics for CH$_4$ and O$_3$ for the period of 2003 to 2012, while Table 9 shows the Mann-Kendall rank statistics for NO$_2$ and CO$_2$ for the period of 2011 to 2014.

Figures 4(a)-(d) show the graph of Mann-Kendall trend validation for CH$_4$, O$_3$, NO$_2$ and CO$_2$ respectively within the period of investigation. The results of the Mann-Kendall trend validation for the atmospheric pollutants showed that the standardization variables $U(t)$ and $U'(t)$ have a sequential fluctuating behavior around a zero level.

3.6. Discussion

The results of the descriptive statistics of the annual averages of CH$_4$, O$_3$, NO$_2$
Figure 2. (a)-(d) Graph of average monthly concentration of CH$_4$, O$_3$, NO$_2$ and CO$_2$ respectively within the period of investigation.

Table 8. Mann-Kendall rank statistics for CH$_4$ and O$_3$ for the period of 2003 to 2012.

| Year | CH$_4$ (ppmv) | $U(t_i)$ | $U'(t_i)$ | O$_3$ (ppmv) | $U(t_i)$ | $U'(t_i)$ |
|------|---------------|----------|-----------|-------------|----------|-----------|
| 2003 | 1740.994      | 0.000    | -1.920    | 56.262      | 4.114    | -2.469    |
| 2004 | 1738.120      | 3.977    | -2.880    | 57.253      | 3.291    | -3.017    |
| 2005 | 1737.331      | 1.920    | -0.274    | 54.501      | 4.526    | -2.880    |
| 2006 | 1730.918      | 1.920    | -1.646    | 57.139      | 2.469    | -2.469    |
| 2007 | 1740.740      | 2.057    | -0.960    | 55.272      | 2.606    | -2.606    |
| 2008 | 1743.628      | 1.783    | -1.509    | 58.556      | 3.977    | -2.743    |
| 2009 | 1750.178      | 2.194    | -1.920    | 57.259      | 3.566    | -2.606    |
| 2010 | 1746.312      | 1.646    | -0.274    | 58.033      | 0.137    | -2.331    |
| 2011 | 1759.923      | -0.549   | -1.920    | 58.319      | 4.663    | -3.017    |
| 2012 | 1773.787      | 1.371    | -1.371    | 56.800      | 4.526    | -2.880    |
Figure 3. (a)-(d) Graph of average annual concentration of CH₄, O₃, NO₂ and CO₂ respectively within the period of investigation.

Table 9. Mann-Kendall rank statistics for NO₂ and CO₂ for the period of 2011 to 2014.

| Year | NO₂ (ppmv) | U(t) | U'(t) | CO₂ (ppmv) | U(t) | U'(t) |
|------|------------|------|-------|------------|------|-------|
| 2011 | 135.695    | 0.000| −2.057| 382.370    | 1.509| −1.509|
| 2012 | 127.516    | 1.509| 0.137 | 385.108    | 0.960| −0.960|
| 2013 | 133.934    | 0.686| −2.194| 388.111    | 1.783| −0.137|
| 2014 | 132.747    | −1.097| −1.920| 392.186    | 0.411| −0.411|

and CO₂ concentrations within the period of investigation revealed that CH₄ had the highest standard deviation value of 12.500 ppmv while O₃ had the lowest standard deviation value of 1.300 ppmv. NO₂ and CO₂ had standard deviation values of 3.519 ppmv and 4.208 ppmv respectively. Therefore CH₄ concentration values were the most dispersed or spread out around the mean of 1746.193 ppmv,
while $O_3$ concentration values were the least dispersed around the mean of 56.939 ppmv. Methane ($CH_4$) had higher standard deviation values than carbon dioxide ($CO_2$), meaning that on a per molecule basis, a proportional rise in $CH_4$ is much more effective as a greenhouse gas than a similar increase in $CO_2$ [9]. However, $CO_2$ has a greater effect than $CH_4$ on climate change owing to its higher atmospheric concentration.

The results from the analysis of the average monthly concentration of the atmospheric pollutants within the period of investigation indicated that methane ($CH_4$) concentration had the lowest value of 1710.1 ppmv in August, 2008 and the highest value of 1796.9 ppmv in November, 2011. Tropospheric ozone ($O_3$) concentration had the lowest value of 51.841 ppmv in January, 2006 and the highest value of 62.794 ppmv in September, 2010. Nitrogen dioxide ($NO_2$) concentration had the lowest value of 61.333 ppmv in July, 2012 and the highest value of 261.7308 ppmv in December, 2011. Carbon dioxide ($CO_2$) concentra-

Figure 4. (a)-(d) Graph of Mann-Kendall trend validation for $CH_4$, $O_3$, $NO_2$ and $CO_2$ respectively within the period of investigation.
tion had the lowest value of 376.1516 ppmv in June, 2011 and the highest value of 396.0969 ppmv in December, 2014. Hence, concentration of CH$_4$, NO$_2$ and CO$_2$ has minimum values during the peak of the rainy season between June and September and begins to increase as the dry season sets in. Therefore, concentration levels of the atmospheric pollutants were lower during the rainy season than during the dry yeartime. This is due to higher occurrences of atmospheric instability during the rainy season. This finding is in agreement with the result of [7]. On the other hand, ozone (O$_3$) concentration reached its peak value during the peak period of the rainy season unlike the other pollutants. In all likelihood, some of the ozone-depleting substances such as aerosols and atmospheric hydrogen chloride become soluble in water and are being washed off by precipitation during rainy season, thereby leading to an increase in tropospheric ozone (O$_3$) concentration during the rainy season. This finding is also in concurrence with the result of [10].

The results from the analysis of the average annual concentration of the atmospheric pollutants within the period of investigation showed that Methane (CH$_4$) concentration had the lowest value of 1730.918 ppmv in 2006 and the highest value of 1773.787 ppmv in 2012. Tropospheric ozone (O$_3$) concentration had the lowest value of 54.501 ppmv in 2005 and the highest value of 58.556 ppmv in 2008. Nitrogen dioxide (NO$_2$) concentration had the lowest value of 127.516 ppmv in 2012 and the highest value of 135.695 ppmv in 2011. Carbon dioxide (CO$_2$) concentration experienced a steady increase with time, having its lowest value of 380.139 ppmv in 2011 and its highest value of 392.186 ppmv in 2014. This steady increase in CO$_2$ can be traced to the alarming increase in anthropogenic activities (such as combustion of fossil fuels, industrial emissions, gas flaring and deforestation) which appreciably increases the amount of CO$_2$ in the atmosphere. The lifespan of a CO$_2$ molecule in the atmosphere is of the order of a century or more. This is more than enough time for the billions of tons of anthropogenic CO$_2$ to uniformly envelop the planet like a blanket [11].

The results of the Mann-Kendall trend validation for CH$_4$, O$_3$, NO$_2$ and CO$_2$ revealed that the standardization variables $U(t)$ and $U'(t)$ have a sequential fluctuating behavior around a zero level as shown in Figures 4(a)-(d), this therefore confirms the validity of the trends [12] [13].

4. Conclusions

The results of the analysis of concentration levels of the air pollutants showed that concentration levels were lower during the rainy season than during the dry yeartime. This is due to higher occurrences of atmospheric instability during the rainy season. On the other hand, ozone (O$_3$) concentration reached its peak value during the peak period of the rainy season unlike the other pollutants. In all likelihood, some of the ozone-depleting substances such as aerosols and atmospheric hydrogen chloride become soluble in water and are being washed off by precipitation during the rainy season, thereby leading to increased tropospheric
ozone concentration during the rainy season.

The study also revealed a steady increase in the concentration of CO$_2$ within the period of investigation. This steady increase in CO$_2$ can be traced to the alarming increase in anthropogenic activities (such as combustion of fossil fuels, industrial emissions, gas flaring and deforestation) which appreciably increases the amount of CO$_2$ in the atmosphere. Methane (CH$_4$) had higher standard deviation values than carbon dioxide (CO$_2$), meaning that on a per molecule basis, a proportional rise in CH$_4$ is much more effective as a greenhouse gas than a similar increase in CO$_2$. However, CO$_2$ has a greater effect than CH$_4$ on climate change owing to its higher atmospheric concentration. The Mann-Kendall rank statistics of the pollutants showed that the standardization variables $U(t_i)$ and $U'(t_i)$ have a sequential fluctuating behavior around a zero level.

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**Conflicts of Interest**

The authors declare no conflicts of interest regarding the publication of this paper.

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