

# Analysis of Concentration Levels of Atmospheric Pollutants in Warri, Nigeria

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## 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 CH<sub>4</sub> and O<sub>3</sub> concentrations for the period of 2003 to 2012 and NO<sub>2</sub> and CO<sub>2</sub> 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 (O<sub>3</sub>) 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 CO<sub>2</sub> within the period of investigation. This steady increase in CO<sub>2</sub> can be traced to the alarming increase in anthropogenic activities which appreciably increases the amount of CO<sub>2</sub> in the atmosphere. Methane (CH<sub>4</sub>) had higher standard deviation values than carbon dioxide (CO<sub>2</sub>), meaning that on a per molecule basis, a proportional rise in CH<sub>4</sub> is much more effective as a greenhouse gas than a similar increase in CO<sub>2</sub>. However, CO<sub>2</sub> has a greater effect than CH<sub>4</sub> on climate change owing to its higher atmospheric concentration. The Mann-Kendall rank statistics of the atmospheric pollutants revealed that the standardization variables  $U(t_i)$  and  $U'(t_i)$  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, SO<sub>2</sub>: 0.01 ppm and NO<sub>2</sub>: 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<sub>2.5</sub> and PM<sub>10</sub> annual mean and 24-h mean (PM<sub>2.5</sub>: 10 µg/m<sup>3</sup> annual mean, 25 µg/m<sup>3</sup> 24-h mean; PM<sub>10</sub>: 20 µg/m<sup>3</sup> annual mean, 50 µg/m<sup>3</sup> 24-h mean). Furthermore, [7] undertook an assessment of the atmospheric levels of PM<sub>10</sub> in Port Harcourt. The study revealed that the trend in the seasonal PM<sub>10</sub> 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 petroleum 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.

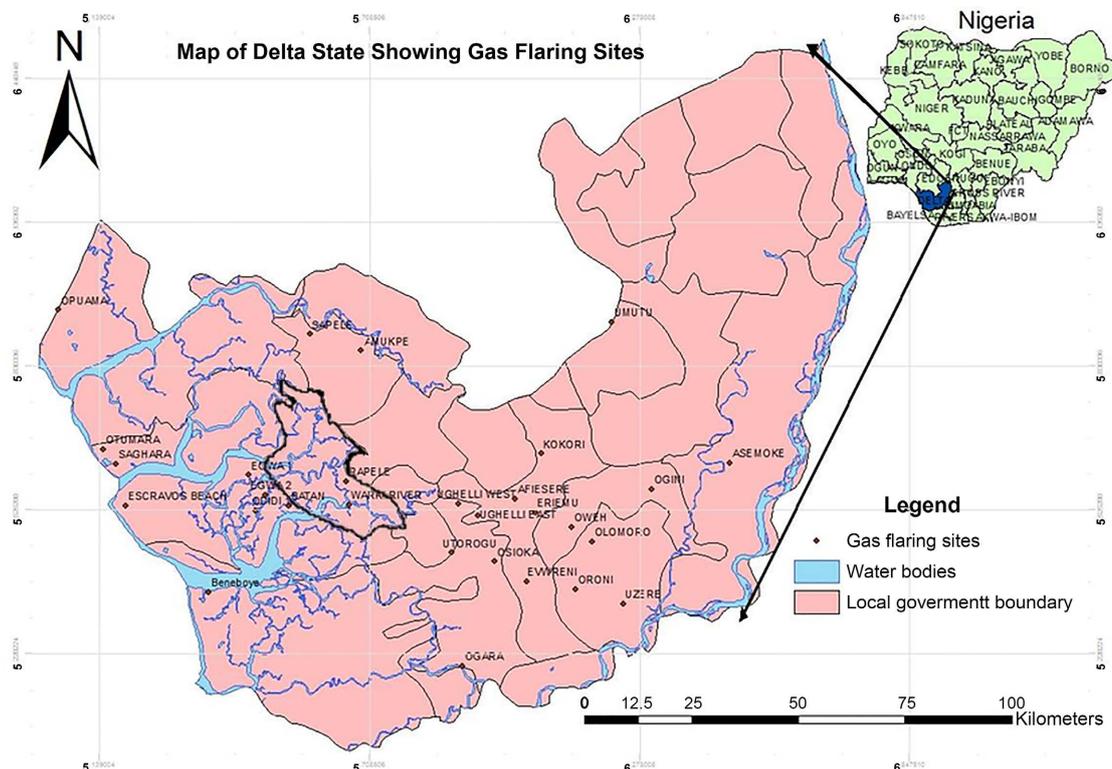
## 2. Study Station, Materials and Method

### 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



**Figure 1.** Map of Delta State showing gas flaring sites and highlighting study station: Warri. Source: NASRDA.

The daily methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), nitrogen dioxide ( $\text{NO}_2$ ) and tropospheric ozone ( $\text{O}_3$ ) 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  $\text{CH}_4$  and  $\text{O}_3$  concentrations for the period of 2003 to 2012 and  $\text{NO}_2$  and  $\text{CO}_2$  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  $x_j$  of the initial series are substituted by their ranks  $y_j$ , set up in ascending order.
- The magnitudes of  $y_p$  ( $i = 1, \dots, N$ ) are compared with  $y_j$  ( $j = 1, \dots, i - 1$ ). 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

$$t_i = \sum_1^i n_i \quad (1)$$

- The distribution of the test statistic  $t_i$  has a variance and a mean as follows

$$\text{var } t_i = \frac{i(i-1)(2i+5)}{72} \quad (2)$$

$$E(t_i) = \frac{i(i-1)}{4} \tag{3}$$

- The values of the statistic  $u(t_i)$  in sequence are then calculated as

$$u(t_i) = \frac{[t_i - E(t_i)]}{\sqrt{\text{var } t_i}} \tag{4}$$

- Likewise, the values of  $u(t_i)$  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<sub>4</sub> (ppmv) and O<sub>3</sub> (ppmv) respectively for the period of 2003 to 2012, while **Table 3, Table 4** show the values of average monthly concentration of NO<sub>2</sub> (ppmv) and CO<sub>2</sub> (ppmv) respectively for the period of 2011 to 2014.

**Table 1.** Values of average monthly concentration of CH<sub>4</sub> (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	1796.9	1779.9
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<sub>3</sub> (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	56.259	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

**Table 3.** Values of average monthly concentration of NO<sub>2</sub> (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<sub>2</sub> (ppmv) for the period of 2011 to 2014.

	2011	2012	2013	2014
January	388.2671	389.7453	394.1395	393.8462
February	386.9302	386.7494	393.6935	394.1328
March	384.7967	384.8546	391.1232	391.8489
April	382.8482	387.1007	390.5237	390.1177
May	384.6600	385.4377	387.5442	389.6226
June	376.1516	382.8430	385.2102	391.4982
July	376.1521	385.2328	382.4967	392.9677
August	380.1761	379.6688	384.8706	391.7415
September	378.7995	381.1844	380.6630	389.4396
October	377.4204	379.7802	384.0695	391.4127
November	383.4106	387.5586	389.4768	393.5066
December	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<sub>4</sub> (ppmv) and O<sub>3</sub> (ppmv) for the period of 2003 to 2012 while **Table 6** shows the values of average annual concentration of NO<sub>2</sub> (ppmv) and CO<sub>2</sub> (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<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub> 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<sub>4</sub> and O<sub>3</sub> for the period of 2003 to 2012.

Year	Mean CH <sub>4</sub> (ppmv)	Mean O <sub>3</sub> (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<sub>2</sub> (ppmv) and CO<sub>2</sub> (ppmv) for the period of 2011 to 2014.

Year	Mean NO <sub>2</sub> (ppmv)	Mean CO <sub>2</sub> (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<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub> concentrations within the period of investigation.

	Minimum	Maximum	Mean	Standard Deviation
CH <sub>4</sub> (ppmv)	1730.918	1773.787	1746.193	12.500
O <sub>3</sub> (ppmv)	54.501	58.556	56.939	1.300
NO <sub>2</sub> (ppmv)	127.516	135.695	132.473	3.519
CO <sub>2</sub> (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.

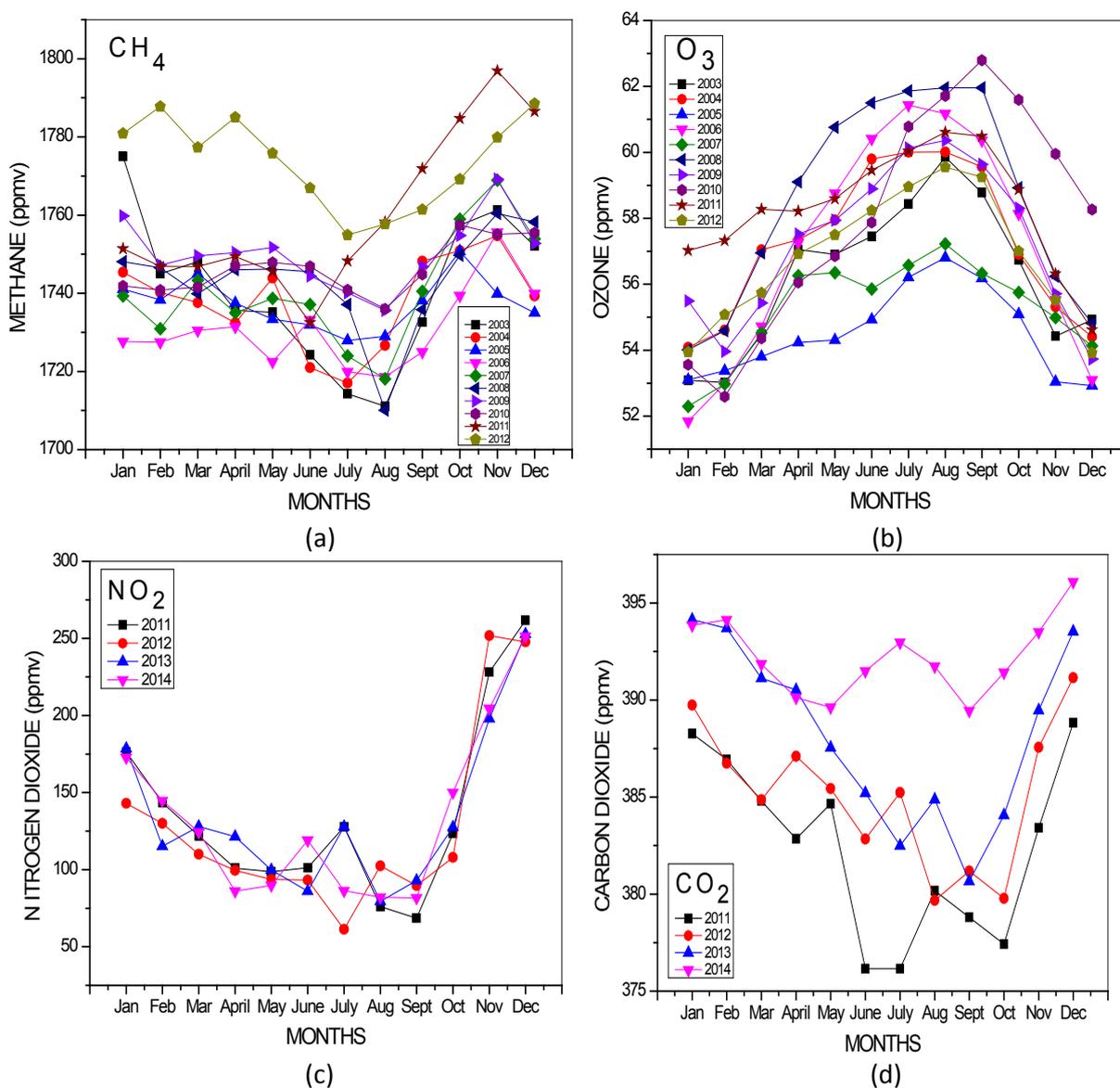
### 3.5. Mann-Kendall Trend Validation

**Table 8** shows the Mann-Kendall rank statistics for CH<sub>4</sub> and O<sub>3</sub> for the period of 2003 to 2012, while **Table 9** shows the Mann-Kendall rank statistics for NO<sub>2</sub> and CO<sub>2</sub> for the period of 2011 to 2014.

**Figures 4(a)-(d)** show the graph of Mann-Kendall trend validation for CH<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub> respectively within the period of investigation. The results of the Mann-Kendall trend validation for the atmospheric pollutants showed that the standardization variables  $U(t_i)$  and  $U(t)$  have a sequential fluctuating behavior around a zero level.

### 3.6. Discussion

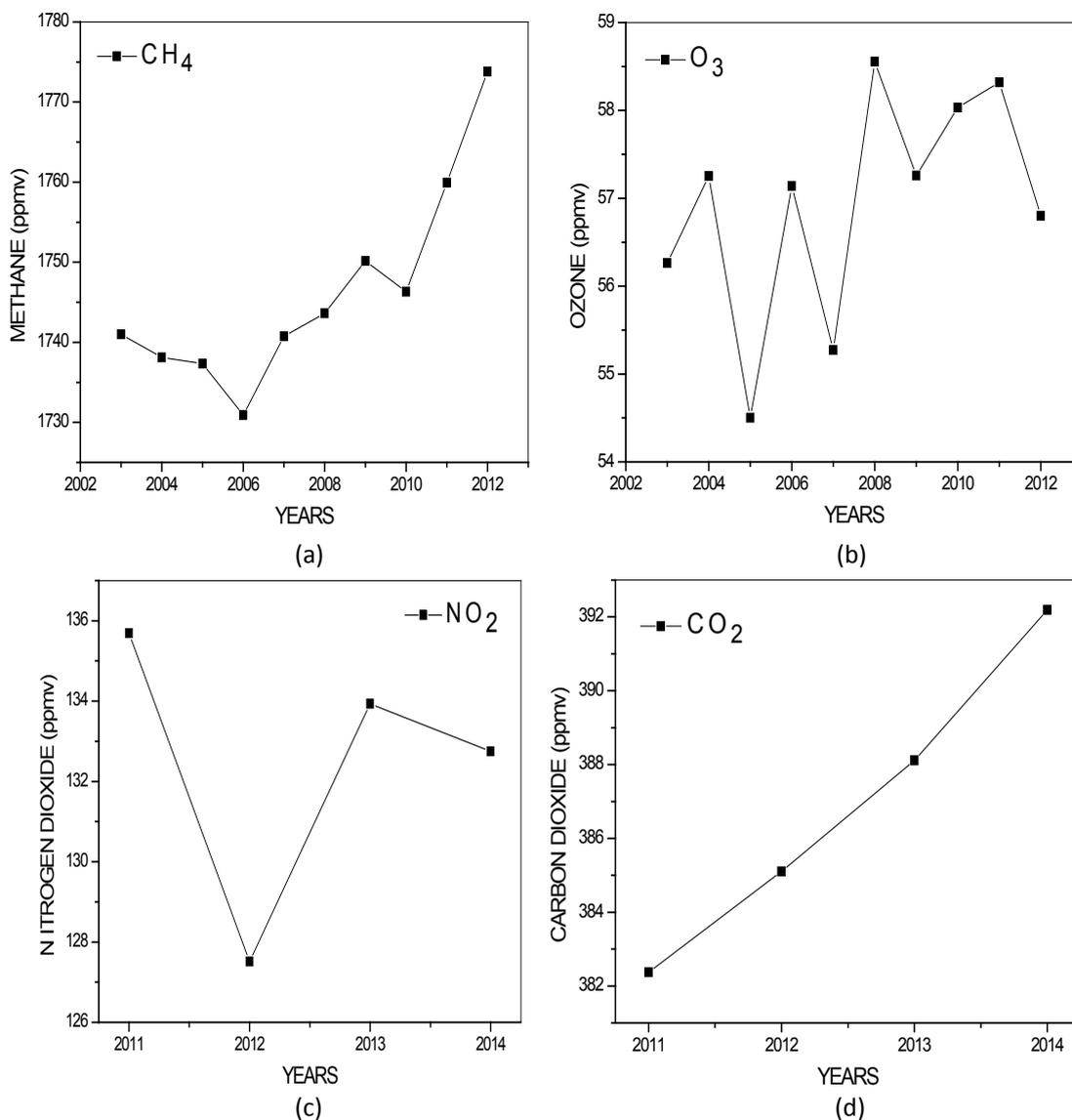
The results of the descriptive statistics of the annual averages of CH<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub>



**Figure 2.** (a)-(d) Graph of average monthly concentration of CH<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub> respectively within the period of investigation.

**Table 8.** Mann-Kendall rank statistics for CH<sub>4</sub> and O<sub>3</sub> for the period of 2003 to 2012.

Year	CH <sub>4</sub> (ppmv)	$U(t_i)$	$U(t_j)$	O <sub>3</sub> (ppmv)	$U(t_i)$	$U(t_j)$
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

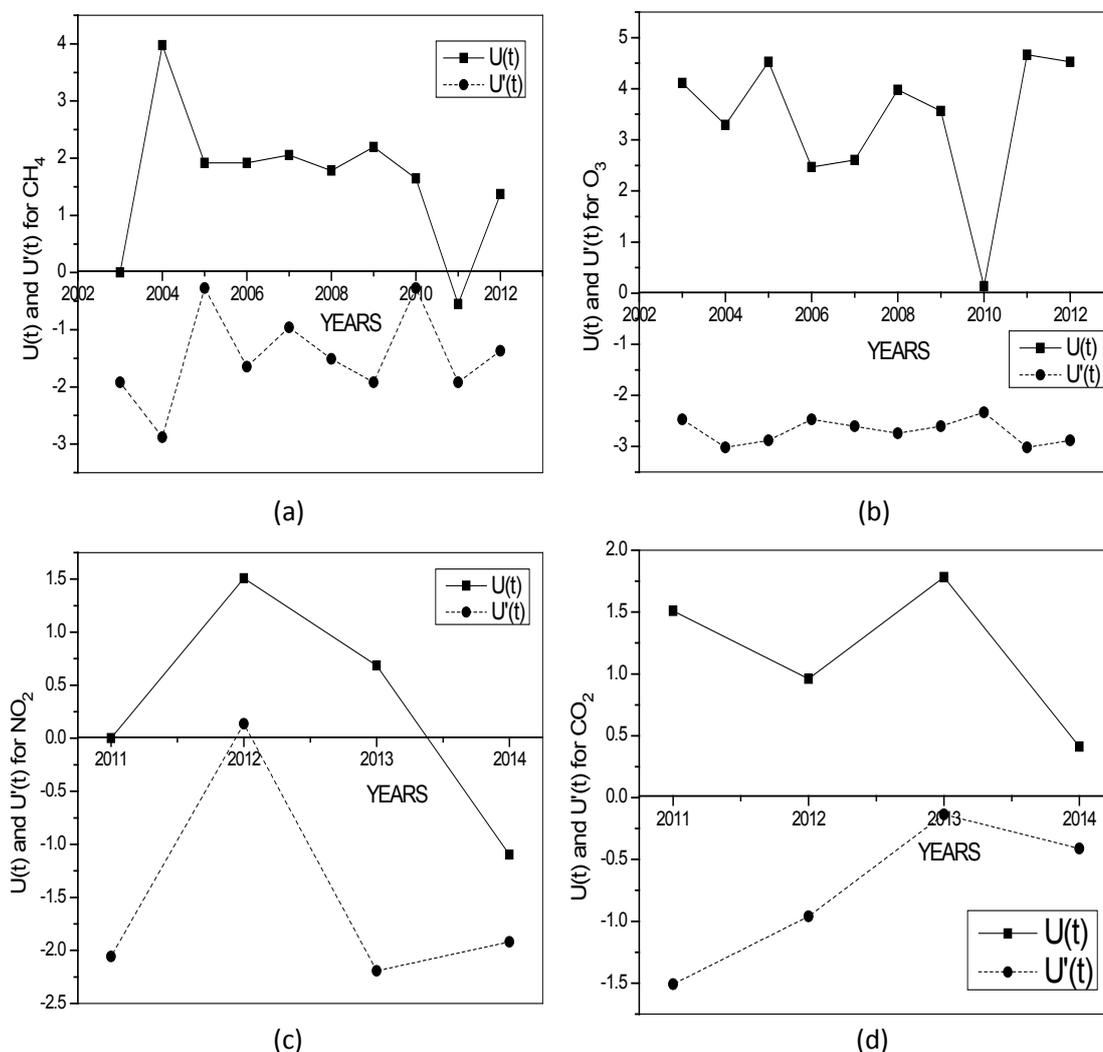


**Figure 3.** (a)-(d) Graph of average annual concentration of  $\text{CH}_4$ ,  $\text{O}_3$ ,  $\text{NO}_2$  and  $\text{CO}_2$  respectively within the period of investigation.

**Table 9.** Mann-Kendall rank statistics for  $\text{NO}_2$  and  $\text{CO}_2$  for the period of 2011 to 2014.

Year	$\text{NO}_2$ (ppmv)	$U(t_i)$	$U'(t_i)$	$\text{CO}_2$ (ppmv)	$U(t_i)$	$U'(t_i)$
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  $\text{CO}_2$  concentrations within the period of investigation revealed that  $\text{CH}_4$  had the highest standard deviation value of 12.500 ppmv while  $\text{O}_3$  had the lowest standard deviation value of 1.300 ppmv.  $\text{NO}_2$  and  $\text{CO}_2$  had standard deviation values of 3.519 ppmv and 4.208 ppmv respectively. Therefore  $\text{CH}_4$  concentration values were the most dispersed or spread out around the mean of 1746.193 ppmv,



**Figure 4.** (a)-(d) Graph of Mann-Kendall trend validation for CH<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub> respectively within the period of investigation.

while O<sub>3</sub> concentration values were the least dispersed around the mean of 56.939 ppmv. Methane (CH<sub>4</sub>) had higher standard deviation values than carbon dioxide (CO<sub>2</sub>), meaning that on a per molecule basis, a proportional rise in CH<sub>4</sub> is much more effective as a greenhouse gas than a similar increase in CO<sub>2</sub> [9]. However, CO<sub>2</sub> has a greater effect than CH<sub>4</sub> 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<sub>4</sub>) 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<sub>3</sub>) 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<sub>2</sub>) concentration had the lowest value of 61.3333 ppmv in July, 2012 and the highest value of 261.7308 ppmv in December, 2011. Carbon dioxide (CO<sub>2</sub>) concentra-

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<sub>4</sub>, NO<sub>2</sub> and CO<sub>2</sub> 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<sub>3</sub>) 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<sub>3</sub>) 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<sub>4</sub>) concentration had the lowest value of 1730.918 ppmv in 2006 and the highest value of 1773.787 ppmv in 2012. Tropospheric ozone (O<sub>3</sub>) concentration had the lowest value of 54.501 ppmv in 2005 and the highest value of 58.556 ppmv in 2008. Nitrogen dioxide (NO<sub>2</sub>) concentration had the lowest value of 127.516 ppmv in 2012 and the highest value of 135.695 ppmv in 2011. Carbon dioxide (CO<sub>2</sub>) 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<sub>2</sub> 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<sub>2</sub> in the atmosphere. The lifespan of a CO<sub>2</sub> 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<sub>2</sub> to uniformly envelop the planet like a blanket [11].

The results of the Mann-Kendall trend validation for CH<sub>4</sub>, O<sub>3</sub>, NO<sub>2</sub> and CO<sub>2</sub> revealed that the standardization variables  $U(t_i)$  and  $U'(t_i)$  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<sub>3</sub>) 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<sub>2</sub> within the period of investigation. This steady increase in CO<sub>2</sub> 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<sub>2</sub> in the atmosphere. Methane (CH<sub>4</sub>) had higher standard deviation values than carbon dioxide (CO<sub>2</sub>), meaning that on a per molecule basis, a proportional rise in CH<sub>4</sub> is much more effective as a greenhouse gas than a similar increase in CO<sub>2</sub>. However, CO<sub>2</sub> has a greater effect than CH<sub>4</sub> 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  $U(t_j)$  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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