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Spatial and Diurnal Assessment of Methane(CH_4) in Port Harcourt, Rivers State, Nigeria

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ABSTRACT
This study monitored the levels of methane, CH_4 in the different periods of the day in three sites in Port Harcourt urban city using on-site digital portable monitor for 21 days .The results showed that the levels of methane in the sites during the monitoring campaign ranged between 0.01-0.07ppm. Site 2 had highest levels of methane relative to sites 1 and 3. ANOVA statistics showed that the difference in mean concentration of methane between the sites were not statistically significant ($p< 0.05$) and differences were observed perhaps by random chance in the sampling process..The spatial variation had the trend : morning methane concentrations > evening concentrations > afternoon concentrations. There is no international/ national guideline limit for methane. However, the levels of methane found by this study are lower compared to literature values reported for studies in industrialized cities in Europe and Asia.

Keywords: Diurnal, Methane, Minitab, PGM50, Port Harcourt, Spatial, Urban

INTRODUCTION

Methane is a colourless, odourless neutral gas. It is one of the Volatile Organic Compounds,(VOCs) and the first member of the alkanes series. It is slightly soluble in water and less dense than air (Ohia et al, 2005) .The concentrations of CH_4, the most abundant organic trace- gas in the atmosphere has increased dramatically over the last few centuries, more than doubling its concentration. The increasing concentration is of special concern because of its effects on climate and atmospheric chemistry. On a per molecule basis, additional CH_4 is much more effective as a green house gas than additional CO_2 (Sodhi, 2005). At present the atmospheric concentration of CH_4 is about 1.7ppm by volume (Sodhi, 2005). It has been estimated that the concentration of CH_4 is increasing at a rate of 1.5% per year and that CH_4 contributes to the green house effect to an extent of 19 percent (Sodhi, 2005). For instance, data on atmospheric CH_4 concentrations from the Law Dome (East side) Ice core from 1841-1978 was published by the Common Wealth Scientific and Industrial Research Organization, Aspendale, Victoria, Australia (Khali, Rasmussen and Morae, 1993).. The atmospheric CH_4 at Cape Meares Oregon, U. S. A for the period 1979-1992 were collected using continuous automated sampling and measurement system based on gas chromatography and flame ionization detection **(**Chappellaz,et al,1990**).** Also Carbon Cycle Greenhouse Gases Group of the National Oceanic and Atmospheric Administration Earth System Research Laboratory reported the atmospheric CH_4 concentrations between 1984 and 2008 in Marine Boundary layer. The above datasets all showed a steady climb in atmospheric CH_4 level**.**

From the 1990 onwards, atmospheric CH_4 concentration tends to be declining (Khali and Rasmussen, 1983, Khali and Rasmussen, 1990, Rasmussen and Khali, 1981). This has been attributed, in part, to the reduced tropical biomass burning. Again it is believed that with the large depletion of stratospheric ozone, the stratosphere is exposed to a large dose of ultraviolet radiation, which in turn has increased the concentration of hydroxyl radicals (by photo dissociation of water). Hydroxyl radicals reacts with atmospheric methane and eventually coverts it to CO_2. (Sze, 1977).

CH_4 is not among the criteria pollutants (SO_2, NO_2, CO, O_3, Pb, and suspended particulate matter) that are regulated by the National Ambient Air Quality Standards(NAAQS) in USA and some other countries . However its impact as a green house gas that causes climate change through atmospheric warming (Dickison and Cicerone, 1986) has made its level to be routinely monitored in several quarters using different methods (Khali

and Rasmussen 1983; Khali and Rasmussen 1990; Rasmussen and Khali 1981; Sodhi, 2005).

The sources of CH_4 include action of anaerobic bacteria on rice paddies, leakage from coal mine and natural gas pipeline, decomposition of organic matter in landfills, and incomplete combustion of forest or range fires **(**Khali and Rasmussen, 1983**).** CH_4 sinks include photochemical sink, consumption by soil and sediment (Whalen and Reeburgh 1990),

This work aimed at measuring the concentrations and variations of CH_4 in three sites in Port Harcourt, Nigeria.

MATERIALS AND METHOD

Study Area

The study covered three selected sites in Port Harcourt urban, Rivers State. The city of Port Harcourt and environs is densely populated. It harbours many industries and service companies that deal with crude oil exploration and exploitation activities including petroleum and natural gas processing.

The phenomena and activities in the city that have potential for impacting on the environment (air pollution) include the sea spray, salt volatilization from the Ocean, emission of gases(especially CH_4) from the decaying of organic substances in swampy environment, emissions from the agglomerations of industries (large, medium and small scale) in the city, emissions from oil exploration, exploitation activities including refinery and gas flaring operations (Argo,2001) and emissions from the heavy vehicular traffic in the city.

The climatic condition of the city is tropical, characterized by wet and dry seasons. The wet season sets in between April and October while the dry season is usually between November and March (Strachler and Strahler, 1977)

Sampling Site Selection.

Each of the sites was chosen in the 'heart' of the city based on visible human activities, high population density and traffic volume. The coordinates of each site was measured with Garmin global position system, model etrex H (Taiwan).

Monitoring Protocol

A multirae plus CH_4 gas monitor PGM 50 equipped with a photo – ionization detector device was used to monitor the CH_4 levels in the sites. The measurement was typically done by hand holding the portable monitor at a height of two metres from the ground in the direction of the prevailing wind. Each reading was recorded at stability of the instrument. Each reading was replicated three times and averaged.

Data analysis

The data collected from the 21 days monitoring campaign was computed for descriptive statistics, variance as well as box plot comparisons of mean values of morning, afternoon and evening CH_4 levels in the sites using version-15 Minitab statistical soft ware

RESULTS AND DISCUSSION

Table 1 shows the sampling sites description while Tables 2, 3 and 4 show the average daily concentrations in ppmv in sites 1, 2 and 3 respectively.. Tables 5a and 5b show the descriptive statistics and analysis of variance (ANOVA) of the methane levels in the three sites depicted as M1, M2, M3; A1, A2, A3; E1, E2 and E3 where M, A and E stand for morning, afternoon and evening measurements respectively. The associated numbers 1, 2 and 3 represent the site number. For the 21 days study period, the morning, afternoon and evening mean values were 0.014048 ± 0.005723, 0.013905 ±.0.005847 and 0 .018048 ± 0.006895 respectively. The daily mean had a minimum of 0.01 and maximum of 0.026667ppmv with a mean value of 0.015333± 0.006155 in site 1 as shown in Table 2 .The corresponding values for site 2 were 0.032381± 0.018949, 0.019762 ± 0.011454 and 0.035238±0.017498 with daily mean value of 0.029127 ± 0.015967 ppmv and a range of 0.013333 -0.05 ppmv (Table 3). In addition, site 3 had the 21 days' morning, afternoon and evening mean values of 0.023333±0.011547, 0.014762±0.006796 and 0.027143±0.040018ppm respectively. The daily mean and range were 0.021746± 0.019454 and 0.013333 - 0.086667 ppmv respectively (Table 4).

Table 1: Sampling site Number, Name, GPS Coordinates and Description.

Site No.	Site Name	Site GPS	Site Description
1	Mile 3 Junction	N04º 48.148′ ,E006º 59.227	A road junction with dense vehicular traffic with an adjacent market for diverse commercial activities
2	Eleme junction	N04º 51.344′ , E007º 04.015′	A 4-way road junction with dense vehicular traffic,surrounding residential and commercial houses
3	Ajip junction	N04º 48.503′ , E006º 59.019′	Busy road junction with high vehicular traffic volume/residential and commercial buildings.

Table 2: Average morning, afternoon ,evening and daily concentrations of CH_4 (ppm) in site 1

Day	Date	8-9am	1-2pm	5-6pm	Daily mean
Mon	3/2/2014	0.023	0.01	0.015	0.016
Tue	4/2/2014	0.012	0.01	0.014	0.012
Wed	5/2/2014	0.012	0.012	0.015	0.013
Thur	6/2/2014	0.01	0.02	0.02	0.016667
Fri	7/4/2014	0.03	0.02	0.02	0.023333
Sat	8/2/2014	0.01	0.01	0.01	0.01
Sun	9/2/2014	0.01	0.01	0.02	0.013333
Mon	10/2/2014	0.02	0.02	0.04	0.026667
Tue	11/2/2014	0.02	0.01	0.02	0.016667
Wed	12/2/2014	0.01	0.01	0.02	0.013333
Thur	13/2/2014	0.01	0.01	0.01	0.01
Fri	14/2/2014	0.016	0.02	0.018	0.018
Sat	15/2/2014	0.01	0.01	0.016	0.012
Sun	16/2/2014	0.01	0.01	0.02	0.013333
Mon	17/2/2014	0.019	0.03	0.02	0.023
Tue	18/2/2014	0.01	0.01	0.014	0.011333
Wed	19/2/2014	0.01	0.01	0.01	0.01
Thur	20/2/2014	0.01	0.02	0.02	0.016667
Fri	21/2/2014	0.02	0.02	0.03	0.023333
Sat	22/2/2014	0.011	0.01	0.015	0.012
Sun	23/2/2014	0.012	0.01	0.012	0.011333
21Days'mean		**0.014048**	**0.013905**	**0.018048**	**0.015333**
Std.dev.		0.005723	0.005847	0.006895	0.006155

Table 3: Average morning, afternoon, evening and daily concentrations of CH_4 (ppm) in site 2

Day	Date	8-9am	1-2pm	5-6pm	Daily mean
Mon	3/2/2014	0.04	0.03	0.07	0.046667
Tue	4/2/2014	0.02	0.01	0.05	0.026667
Wed	5/2/2014	0.01	0.01	0.02	0.013333
Thur	6/2/2014	0.02	0.03	0.03	0.026667
Fri	7/4/2014	0.07	0.04	0.05	0.053333
Sat	8/2/2014	0.03	0.02	0.03	0.026667
Sun	9/2/2014	0.02	0.01	0.02	0.016667
Mon	10/2/2014	0.05	0.03	0.06	0.046667
Tue	11/2/2014	0.03	0.01	0.02	0.02
Wed	12/2/2014	0.02	0.01	0.02	0.016667
Thur	13/2/2014	0.02	0.015	0.03	0.021667
Fri	14/2/2014	0.06	0.04	0.05	0.05
Sat	15/2/2014	0.04	0.02	0.06	0.04
Sun	16/2/2014	0.02	0.01	0.02	0.016667
Mon	17/2/2014	0.07	0.04	0.06	0.056667
Tue	18/2/2014	0.03	0.02	0.03	0.026667
Wed	19/2/2014	0.02	0.01	0.02	0.016667
Thur	20/2/2014	0.01	0.01	0.02	0.013333
Fri	21/2/2014	0.06	0.03	0.04	0.043333
Sat	22/2/2014	0.02	0.01	0.03	0.02
Sun	23/2/2014	0.02	0.01	0.01	0.013333
21Days' mean	**0.032381**	**0.019762**	**0.035238**	**0.029127**	
Std.dev.		0.018949	0.011454	0.017498	0.015967

Table 4: Average morning, afternoon and evening concentration of CH_4 (ppm) in site 3

Day	Date	8-9am	1-2pm	5-6pm	Daily mean
Mon	3/2/2014	0.04	0.02	0.2	0.086667
Tue	4/2/2014	0.02	0.01	0.02	0.016667
Wed	5/2/2014	0.02	0.02	0.02	0.02
Thur	6/2/2014	0.01	0.01	0.02	0.013333
Fri	7/4/2014	0.04	0.02	0.03	0.03
Sat	8/2/2014	0.02	0.02	0.01	0.016667
Sun	9/2/2014	0.02	0.01	0.02	0.016667
Mon	10/2/2014	0.05	0.03	0.03	0.036667
Tue	11/2/2014	0.03	0.02	0.02	0.023333
Wed	12/2/2014	0.02	0.01	0.02	0.016667
Thur	13/2/2014	0.02	0.01	0.01	0.013333
Fri	14/2/2014	0.03	0.01	0.02	0.02
Sat	15/2/2014	0.01	0.01	0.02	0.013333
Sun	16/2/2014	0.01	0.01	0.01	0.01
Mon	17/2/2014	0.04	0.02	0.02	0.026667
Tue	18/2/2014	0.02	0.01	0.01	0.013333
Wed	19/2/2014	0.02	0.01	0.02	0.016667
Thur	20/2/2014	0.01	0.01	0.01	0.01
Fri	21/2/2014	0.03	0.01	0.02	0.02
Sat	22/2/2014	0.02	0.03	0.02	0.023333
Sun	23/2/2014	0.01	0.01	0.02	0.013333
21 Days'mean		**0.023333**	**0.014762**	**0.027143**	**0.021746**
Std Dev.		0.011547	0.006796	0.040018	0.019454

The highest mean concentration of CH_4 in the study was 0.03524±0.01750 ppmv and was recorded in site 2 in the evening period while the lowest mean level of 0.01390±0.00585 ppmv was measured in site 1 in the afternoon period of the day. This result points to the possibility of CH_4 concentration in the sites being dominated by contributions of vehicular traffic. Site 2 which showed the maximum mean daily CH_4 concentration is a popular 4-way road junction and is among the junctions that record the highest volume of vehicular and human traffic in Port-Harcourt. This site also leads to the Eleme Petrochemical plant. Site1 on the other hand is a 2-way road junction (Table 1) with relatively less vehicular and other anthropogenic activities. In 2008, Para *et al* studied the ambient air level of VOCs (including CH_4) using passive sampling technique and had their samples analyzed by thermal adsorption followed by chromatography/mass-selective detection in Northern Spain. They found that traffic emission was the main source of VOCs compounds in the studied sites. The minimum level of CH_4 in the afternoon period may be due to photochemical excavation action of atmospheric –OH radical on CH_4 which peaks in the sunlight (afternoon)(Sze,1977)..

CH_4 mean levels within the study period in the sites ranged from a minimum value of 0.01000 to a maximum value of 0.0700 ppmv (Table 5a). Site-wise comparison reveals that site 2 had the highest mean concentrations of CH_4 relative to sites 1 and 2 (fig 1d). However, one-way analysis of variance (ANOVA) for the differences in the mean levels of CH_4 in the three sites showed that although there is variation in the mean levels of CH_4 in the sites such variations were not statistically significant($p<0.05$). Also the regression analysis of the data showed that levels of CH_4 in the sites were poorly correlated with R-square value of 16.67%. (Table5b).This may probably be due to dissimilarity in the CH_4 sources and intensities in the sites.

The diurnal variation of CH_4 in the three sites showed a trend of morning concentration > afternoon concentration> evening concentration (Table 5a, Fig.1a, b, c and d).

The level of CH_4 in this study is lower than that obtained in similar studies in some

European and Asian cities. There is no national / International guideline limit for CH_4 yet.

Table 5a: **Descriptive Statistics of Methane Level (ppm) in Sites 1, 2 and 3 in the Morning, Afternoon and Evening Periods (M1, M2, M3, A1, A2, A3, E1, E2, E3)**

Variable	N	Mean	StDev	Minimum	Median	Q3	Maximum
M1	21	0.01405	0.00572	0.01000	0.01100	0.01950	0.03000
M2	21	0.03238	0.01895	0.01000	0.02000	0.04500	0.07000
M3	21	0.02333	0.01155	0.01000	0.02000	0.03000	0.05000
A1	21	0.01390	0.00585	0.01000	0.01000	0.02000	0.03000
A2	21	0.01976	0.01145	0.01000	0.01500	0.03000	0.04000
A3	21	0.01476	0.00680	0.01000	0.01000	0.02000	0.03000
E1	21	0.01805	0.00690	0.01000	0.01800	0.02000	0.04000
E2	21	0.03524	0.01750	0.01000	0.03000	0.05000	0.07000
E3	21	0.02714	0.04002	0.01000	0.02000	0.02000	0.20000

Table 5b: **One-way ANOVA in Sites 1,2 and 3 in the Morning, Afternoon and Evening Periods (M1, M2, M3, A1, A2, A3, E1, E2, E3)**

Source	DF	SS	MS	F	P
Factor	8	0.010773	0.001347	4.50	0.000
Error	180	0.053837	0.000299		
Total	188	0.064610			

S = 0.01729 R-Sq = 16.67% R-Sq(adj) = 12.97%

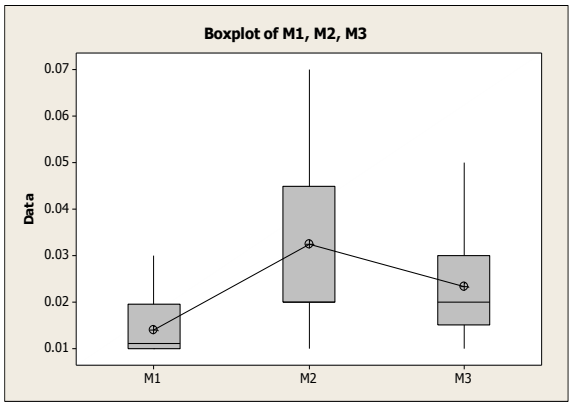

Figure 1a: **:** Boxplot of CH_4 level in the morning Period in site 1,2 and 3

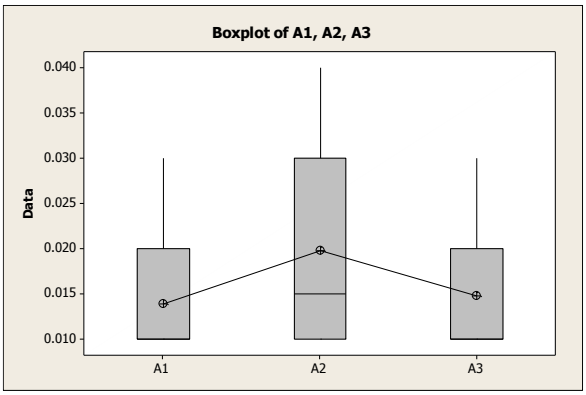

Figure1b: Boxplot of CH_4 level in the afternoon Period in site 1,2 and 3

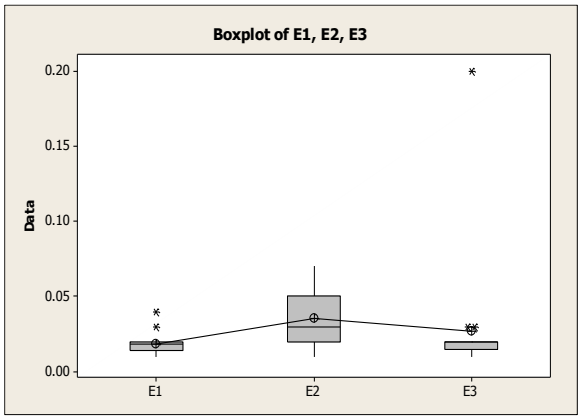

Figure 1c: Boxplot of CH_4 level in the evening different Period in site 1,2 and 3

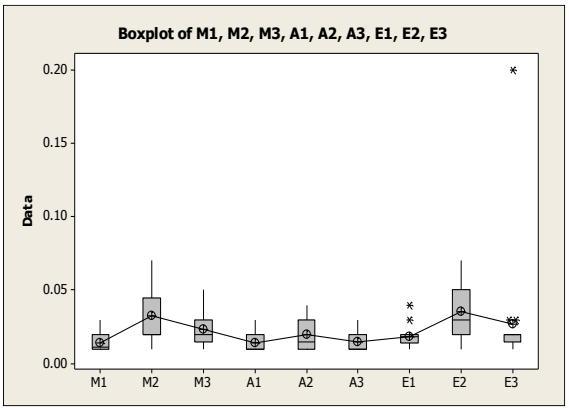

Figure 1d: Boxplot of CH_4 level for the day Periods in site

CONCLUSION

This study revealed that the concentration of CH_4 in the ambient air of the study area within the period of the study had a minimum value of 0.01000 and a maximum value of 0.0700 ppmv. The level of CH_4 obtained in this study is below those observed in literature for some European cities. Furthermore, the variation of $_{CH4}$ during the day period followed the pattern morning concentration > evening concentration > afternoon concentration

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