



Correlating Methane Gas Emission and Physiochemical Properties of Soil along River Nworie, Imo State, Nigeria

Nwokeforo Churchill Ugochukwu¹, Verla Andrew Wirnkor^{2*}, Ibe Maduabuchi Valentine² and Verla Evelyn Ngozi³, Excellence Amaibiam Okonkwo⁴ and Muna Stela Ebele⁵

¹Department of Mathematics/ Statistics, Imo State Polytechnic, Omuma, Imo State, Nigeria

² & ⁵Green Researchers in Analytical Chemistry, Environment and Climate Change (GRACE & CC), Department of Chemistry, Imo State University Owerri, P. M. B 2000, Imo State, NIGERIA

³Department of Environmental Technology, FUTO, Owerri, Imo State, P. M. B. 1526, NIGERIA

⁴Department of Industrial Chemistry, King David University of Medical Sciences, PMB 211, Uburu Ohaozara, Ebonyi State, NIGERIA

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*Corresponding author: Verla Andrew Wirnkor

Green Researchers in Analytical Chemistry, Environment and Climate Change (GRACE & CC), Department of Chemistry, Imo State University Owerri, P. M. B 2000, Imo State, NIGERIA

Abstract

Soil and rivers are high ranking most abundant natural resources in our planet and the importance of their health cannot be over emphasized. This study was carried out to determine the concentration of methane gas emissions along the River Nworie of Owerri Imo state and its possible relationship with physiochemical properties of the soil along the same river. This was achieved by measuring the concentrations of the methane gas at strategic points of the river during morning and evening hours daily for a period of six days using the JCB4 New Generation Gas detector. Some physiochemical properties of the soil were also considered such as; Temperature, Electrical Conductivity, pH, Moisture Content and Organic Matter. It is observed that the concentrations of methane along the river, which was an average of 0.15% during the morning hours and 0.16% during evening hours, had very close to zero value of the correlation coefficient (R) to the physiochemical properties of the soil except for Temperature and Organic Matter, where Temperature possesses the strongest positive value of R in the morning hours and Organic Matter possesses the strongest negative value of R in the evening hours. From the results also, we observe an average concentration of 0.155% for methane along the river daily with an average coefficient of variation value of 21.4. Although the values of the concentrations are within safe limits when compared to National Institute for Occupational Safety and Health's maximum recommended safe methane concentrations for workers during an 8-hour period, the results indicate significant influence from anthropogenic activities taking place around the river during daytime. It is highly recommended that policies and precautionary measures be taken to keep the concentrations within safe limits.

Keywords: Anthropogenic, Correlation, Variability, Methane, River Nworie.

INTRODUCTION

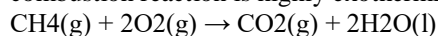
Methane is a gas that is found in small quantities in the atmosphere. It is the simplest hydrocarbon consisting of one carbon atom and four hydrogen atoms. It is also a powerful greenhouse gas.^[1] It is produced under conditions where little to no oxygen is available and about 30% of methane emissions are produced by agricultural processes due to a combination of livestock waste management and rice cultivation.^[2] Some characteristics of methane include but are not limited to; it is an odorless gas and is lighter than air, it tends to rise and accumulate near the higher stagnant parts of enclosed buildings and also tightly closed manure storage pits and is most likely to accumulate during hot, humid weather.

There is also concept of atmospheric methane which describes the methane which is present in earth's atmosphere, this atmospheric methane concentrations are of interest because it is one of the most potent greenhouse gases in the earth's atmosphere.^[3]

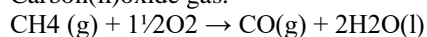
Specific Physical properties of methane are as follows: Molecular weight (g) – 16.04; Critical temperature (0 F) – 116.2; Critical pressure (P_{sia}) – 673.0 Boiling point (0F) – -258.7; Melting point (0 F) – -296.5; Specific gravity – 0.565.

Some well-known Chemical properties of methane gas are briefly discussed here. Chemically methane is very stable and remains unaffected when treated with strong oxidizing agents and acids such KMnO₄, K₂Cr₂O₇ and H₂SO₄ under normal conditions.

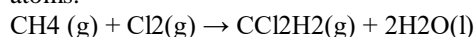
Methane burns in excess air or oxygen with a pale-blue non-luminous flame to give Carbon (iv) oxide and water. The combustion reaction is highly exothermic; therefore, methane is an excellent combustion fuel.



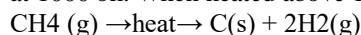
In the presence of insufficient air (or oxygen) methane undergoes incomplete (or partial) combustion producing Carbon(ii)oxide gas.



Methane undergoes substitution reactions with chlorine and bromine (Halogenation) in the presence of sunlight or halogen-carrier to give halo-alkanes, in which one or more hydrogen atoms are replaced by equal number of hydrogen atoms.



Methane gives hydrogen when mixed with steam and the mixture is passed over nickel supported on alumina and heated at 1000 ok. When heated above 1300ok, (Pyrolysis) methane gas decomposed to give carbon black and hydrogen.^[4]



It is general knowledge that healthy soils are essential for healthy plant growth, human nutrition and water filtration amongst other things. Healthy soils support a land scape that is more resilient to the impacts of droughts, floods or fire. Soils also help to regulate the earth's climate and stores more carbon than all of the world forests combined.^[5] hence, the importance of soil health and quality cannot be over emphasized as it is fundamental to our survival.

Apart from being home to many organisms and nutrients, soil acts as sources and sinks of greenhouse gases such as Carbon(iv)oxide (CO₂), Methane (CH₄) and Nitrogen(iv)Oxide (NO₂).^[6] These amongst others are known as soil gases and they are found in airsapces between soil components. The spaces between solid particles of the soil when they do not contain water are filled with air; primarily Nitrogen, Carbon(iv)oxide and Oxygen.^[7] Other natural gases are Nitrogen(ii)oxide (NO), Nitrogen(i)oxide (N₂O), Methane (CH₄) and Ammonia (NH₄).^[8]

Studies have been carried out in which oxidizing agents such as free Iron, amorphous Fe(iii), easily reducible Manganese (Mn), Nitrate (NO₃⁻), Sulphate (SO₄²⁻) were measured as possible decreasing an increasing factor in Methane (CH₄) emissions and no relation was found between the total CH₄ emission and any single factor investigated.^[9] Soil methane is produced as the end product of anaerobic decomposition of organic matter, in the absence of oxygen, methane is very stable but it is mineralized to carbon dioxide by methanotrophic bacteria under aerobic conditions.

Some meta-analysis although, shows that there is a substantial variation in the soil CH₄ flux responses to bio-char amendment, hence interactions of soil properties tend to regulate the soil CH₄ emission/uptake response to bio-char addition.^[10] It has also been observed that response to bio-char applied into soils had a strong impact diverse soil chemical and biological properties and consequently on the fluxes of greenhouse gases. Where we have it that bio-char produced from cow manure decreased emissions of CO₂ and CH₄ fluxes for volcanic and non-volcanic soils probably due to beta-glucosidase activity.^[11]

Hence, it is presumable that the emission of greenhouse gases of which Methane CH₄ is inclusive, has some correlation with the physical and chemical properties of the sampled soil and these relationships are what is aimed to be determined and analyzed in this study of the soil along river Nworie in Imo state, which in this case is an alluvial soil.

Bearing the importance rivers in mind and also the importance of methane, not only as a greenhouse gas but also as a very relevant soil gas for plant and microbial life, and also the possible dangers of its over concentration which can be mostly caused by anthropogenic activities; which can clearly be seen around the river, this study looks to strategically and critically analyze the current states of all these factors in order to prescribe urgent solutions and recommendation when and where necessary.

Materials & Methods

Description of Study Area

The work of analysis was carried out by first sharing the length of the River into five strategic points where the equipment was taken to the river at these points. The points are characterized by flyover/bridge, the vegetation is made up of grasses and mainly coconut trees, and there is also a garden. There is a hospital located also at one of the points. There are visible in flow channels for water from the town in to the river and there are also waste dump sites around them. There are some areas of stagnant water beside the river with some dilapidating residential buildings. There is also dredging activity taking place at some points.

Procedure for Determination of Temperature, Humidity and Methane Concentration Using; JCB4 New Generation Gas Detector and AZ77532 Air Quality Meter:

The equipment was placed at the strategic points along the bank of the river at positions where uninterrupted air would easily flow to the sensors. Once placed at these points, the equipment is turned on and given a reasonable distance in order to prevent interference of possibly body temperature etc. on the reading of the devices. Turned on, the devices begin to measure. The readings are then allowed to stabilize before taken. This exercise was carried out for six days (day and night) so as to obtain reasonable amount of comparable data.

Procedure for Determination of Soil Temperature, Electrical Conductivity, pH, Moisture content and Organic Matter in soil sample:

The temperature was determined using the Soil Gardener's thermometer by inserting the probe into the sediment by depth of 3-6cm for 6 minutes and readings taken.

The electrical conductivity was measured using HANNA HI8733 EC Meter in μcm . calibrated using KCl. 50 g of the air-dried sediment sample is carefully weighed into a beaker and 100mls of distilled water was added. It was then shaken vigorously to allow separation of the sediment sample and allowed to stand. The EC probe is then introduced into the soil-water suspension for 60 seconds and readings is taken.

The pH was determined using JENWAY 3510 pH Meter which was calibrated using buffer 4 and buffer 7 by dissolving one capsule each in 100ml of distilled water respectively. The pH was determined also with the same method used for the EC measurement.

The moisture content was determined using the gravimetric method. 10g of the soil was weighed into a porcelain dish (which was previously weighed, WD). Then placed in an oven at 105 oC for 2 hours until all the water is driven off (i.e constant weight, Y2). The difference in weight is the amount of moisture in the soil. The moisture in the soil is calculated using the formula;

$$\% \text{moisture content} = \frac{(\text{initial weight} - \text{final weight})}{\text{final weight}} \times 100 \text{-----1}$$

The organic matter content was determined using the weight loss on ignition (LOI) method. From the moisture content determination, the entire oven-dried test soil sample with the porcelain dish was placed in the muffle furnace using the tongs and allowed to cool to room temperature. Then the mass of the dish containing the ash (burned soil) i.e MPA is determined and recorded.

Calculations were done as using equations 2 -5 as follows;

Determine the mass of the dry soil (Md) from the moisture determination:

$$Md = Y2 - Wd \text{.....2}$$

Determine the mass of the ashed soil (MA):

$$MA = MPA - Wd \text{..... 3}$$

Determine the mass of organic matter (MO):

$$MO = Md - MA \text{..... 4}$$

Hence percentage soil organic matter (%SOM):

$$\%SOM = \frac{MO}{Md} \times 100 \text{.....5}$$

RESULTS

Table_1: Results from daily analysis of methane concentrations along the river

		MORNING (9:00-11:00am)					EVENING (4:00-6:00pm)				
DATE	PARAMETERS	A	B	C	D	E	A	B	C	D	E
23 rd Aug, 2017	Temp (°C)	29.8	29.0	30.4	29.4	31.5	26.1	26.3	26.9	26.7	26.5
	RH (%)	99.9	98.2	91.0	92.8	98.0	91.4	92.0	96.9	96.3	92.1
	CH ₄ (%)	0.18	0.17	0.18	0.18	0.17	0.17	0.17	0.16	0.16	0.17
24 th Aug, 2017	Temp (°C)	26.2	25.8	26.6	25.6	25.7	27.2	27.6	27.3	27.6	25.8
	RH (%)	87.7	87.4	85.5	86.3	87.3	77.2	78.1	79.2	77.3	76.8
	CH ₄ (%)	0.16	0.14	0.16	0.17	0.17	0.17	0.16	0.15	0.16	0.15
25 th Aug, 2017	Temp (°C)	25.9	26.1	26.6	28.6	30.0	25.22	24.3	24.9	26.3	26.1
	RH (%)	99.9	99.9	99.9	89.7	83.0	99.9	99.7	99.6	99.9	98.6
	CH ₄ (%)	0.13	0.13	0.13	0.17	0.11	0.16	0.17	0.16	0.17	0.17
26 th Aug, 2017	Temp (°C)	29.6	29.1	30.3	29.8	30.2	26.7	26.6	25.9	26.8	27.1
	RH (%)	89.8	94.1	92.9	96.0	89.4	80.0	84.0	80.3	83.6	80.4
	CH ₄ (%)	0.15	0.16	0.15	0.14	0.16	0.16	0.17	0.15	0.17	0.16
27 th Aug, 2017	Temp (°C)	27.7	28.2	28.1	25.4	26.3	26.0	26.1	26.3	24.1	23.8
	RH (%)	94.9	98.7	93.1	93.4	94.7	77.2	78.6	79.3	77.9	80.0
	CH ₄ (%)	0.15	0.15	0.14	0.13	0.12	0.17	0.16	0.16	0.17	0.17
28 th Aug, 2017	Temp (°C)	27.2	27.9	26.2	27.1	28.9	25.1	25.3	26.3	25.7	25.8
	RH (%)	99.9	99.9	98.6	99.3	99.6	89.4	89.3	76.3	79.4	80.6
	CH ₄ (%)	0.15	0.15	0.14	0.16	0.16	0.16	0.17	0.18	0.16	0.17

Table_2: Mean Values and some Descriptive Statistics of Temperature, RH and Methane Results

		Morning (9:00-11:00am)			Evening (4:00-6:00pm)		
DATE	PARAMETERS	MEAN	S.D	C.V	MEAN	S.D	C.V
23 rd Aug, 2017	Temp (°C)	29.94	0.942	3.146	26.68	0.204	0.765
	RH (%)	95.98	3.443	3.587	93.8	2.316	2.469
	CH ₄ (%)	0.176	4.9x10 ⁻³	2.784	0.164	4.9x10 ⁻³	2.987
24 th Aug, 2017	Temp (°C)	25.98	0.371	1.428	27.12	0.631	2.325
	RH (%)	86.84	0.819	0.943	77.64	0.948	1.221
	CH ₄ (%)	0.16	1.1x10 ⁻²	6.875	0.162	7.5x10 ⁻³	4.619
25 th Aug, 2017	Temp (°C)	27.44	1.598	5.824	26.62	0.398	1.493
	RH (%)	94.48	6.968	7.375	81.58	1.820	2.231
	CH ₄ (%)	0.134	1.95x10 ⁻²	14.548	0.158	1.7x10 ⁻²	7.381
26 th Aug, 2017	Temp (°C)	29.8	0.297	0.996	25.34	0.728	2.872
	RH (%)	92.44	2.524	2.730	99.5	0.562	0.565
	CH ₄ (%)	0.152	7.5x10 ⁻³	4.923	0.162	7.5x10 ⁻³	4.63
27 th Aug, 2017	Temp (°C)	27.14	0.968	3.450	25.92	0.989	3.815
	RH (%)	94.96	1.998	2.104	78.62	1.019	1.296
	CH ₄ (%)	0.138	1.17x10 ⁻²	8.451	0.164	4.9x10 ⁻³	2.987
28 th Aug, 2017	Temp (°C)	27.46	0.900	3.278	25.68	0.44	1.713
	RH (%)	99.46	0.484	0.487	83.00	5.371	6.472
	CH ₄ (%)	0.152	0.140	91.447	0.168	7.5x10 ⁻³	4.454

Table 3: Physiochemical Parameters of Soil at Study points

	A	B	C	D	E	MEAN	S.D	C.V
Temp	27.3	27.5	26.5	27.3	27.5	27.22	0.371	1.36
pH	4.8	5.1	5.4	4.6	4.78	4.94	0.282	5.71
E.C	16.7	15.7	17.8	18.3	15.5	16.8	0.865	5.15

S.M	9.1	8.7	8.5	9.2	9.56	9.01	0.375	4.16
O.M	2.3	2.8	0.2	1.8	1.74	1.76	0.873	49.57

Temp=Temperature, E.C=Electronic Conductivity, S.M=Soil Moisture, O.M=Organic Matter

DISCUSSION

Throughout the course of this analysis, some possible comparison or correlation between the concentrations of the methane in the air around the river and some physiochemical parameters of the soil were seen. From the results obtained, we see that the correlation coefficients are in the range of -1.0 - +1.0, showing that the readings correlate. These parameters all have respective relationships with the methane and are discussed consequently.

In relation to soil pH, soils have been subject to significant long-term acidification by acids originating from fossil fuels combustion and agricultural fertilization, and these are factors that can commonly be seen around the river (with bridges for cars and artificial garden cultivation sited around it). The consequences of these acidifications are numerous and include inhibition of at least some microbial populations and transformations, including methane emitting bacteria.^[12] Like most biological process in soils, atmospheric methane consumption varies as a function of pH. For some forest soil studies, there are indications that pH optima for atmospheric methane consumption ranges between about 4.5-6.5. Although some acids have greater/lesser impacts, causing the pH optima to vary.^[13]

There are steep declines in methanotrophic activity typically accompanying increasing alkalination and acidification of soils beyond the optimal pH range. Although some evidence shows difference in pH optima with soil types; where pH optima of agricultural soils appear more notably alkaline than those for forest soils. With peak activity occurring at pH values completely inhibitory for forest soils. Accordingly, acidic pH values that support methane consumption in forest soils strongly inhibit activity in agricultural soils.^[14]

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Soil parameter-Methane concentrations relationship in the morning			Category effect of X on Y		Soil parameter-Methane concentrations relationship in the evening	
Relation	Equation	R ² value	Morning	Evening	R ² value	Equation
CH ₄ /Temp	y= 0.008x + 0.397	0.379	L	VVL	0.112	y= -0.059x + 1762
CH ₄ /PH	y= -0.000x + 0.177	0.000	VVL	VVL	0.073	y= 0.063x - 0.181
CH ₄ /E.C	y= 0.003x + 0.110	0.779	M	VL	0.285	y= 0.031x - 0.402
CH ₄ /S.M	y= 0.003x + 0.206	0.066	VVL	L	0.525	y= -0.127x + 1.284
CH ₄ /O.M	y= -0.002x + 0.180	0.220	VL	VVL	0.004	y= 0.005x + 0.122
CH ₄ /Temp	y= 0.002x + 0.239	0.009	VVL	M	0.605	y= 0.015x - 0.265
CH ₄ /PH	y= -0.020x + 0.261	0.281	VL	VL	0.513	y= -0.019x + 0.255
CH ₄ /E.C	y= 0.003x + 0.094	0.155	VVL	VL	0.334	y= -0.003x + 0.227
CH ₄ /S.M	y= 0.019x - 0.014	0.438	VL	M	0.669	y= 0.016x + 0.014
CH ₄ /O.M	y= -0.005x + 0.169	0.185	VVL	L	0.402	y= 0.005x + 0.152
CH ₄ /Temp	y= 0.003x + 0.229	0.004	VVL	VVL	0.003	y= 0.001x + 0.130
CH ₄ /PH	y= -0.025x + 0.262	0.139	VVL	VVL	0.000	y= -0.000x + 0.164
CH ₄ /E.C	y= 0.014x + 0.100	0.625	M	VVL	0.167	y= 0.002x + 0.115
CH ₄ /S.M	y= -0.004x + 0.178	0.008	VVL	VL	0.229	y= -0.009x + 0.248
CH ₄ /O.M	y= 0.00x + 0.133	0.000	VVL	VVL	0.111	y= 0.002x + 0.156
CH ₄ /Temp	y= 0.007x - 0.037	0.119	VVL	VVL	0.057	y= 0.008x - 0.047

CH ₄ /PH	y= 0.008x + 0.109	0.106	VVL	VVL	0.038	y= -0.008x + 0.198
CH ₄ /E.C	y= -0.006x + 0.258	0.881	M	VVL	0.095	y= 0.003x + 0.103
CH ₄ /S.M	y= 0.000x + 0.145	0.001	VVL	VVL	0.104	y= -0.010x + 0.248
CH ₄ /O.M	y= 0.002x + 0.147	0.088	VVL	VL	0.279	y= 0.007x + 0.145
CH ₄ /Temp	y= -0.004x + 0.248	0.016	VVL	VVL	0.031	y= 0.002x - 0.100
CH ₄ /PH	y= 0.017x + 0.054	0.168	VVL	L	0.466	y= -0.011 + 0.222
CH ₄ /E.C	y= -0.000x + 0.140	0.000	VVL	VL	0.265	y= 0.002x + 0.125
CH ₄ /S.M	y= -0.021x + 0.331	0.475	L	VVL	0.090	y= 0.003x + 0.128
CH ₄ /O.M	y= 0.004x + 0.130	0.097	VVL	VVL	0.069	y= 0.001x + 0.161
CH ₄ /Temp	y= 0.015x - 0.275	0.605	M	L	0.402	y= -0.012x + 0.516
CH ₄ /PH	y= -0.024x + 0.270	0.820	M	M	0.786	y= 0.023x + 0.051
CH ₄ /E.C	y= -0.001x + 0.173	0.037	VVL	VVL	0.009	y= -0.000x + 0.178
CH ₄ /S.M	y= 0.017x + 0.008	0.791	M	L	0.315	y= -0.011x + 0.269
CH ₄ /O.M	y= 0.004x + 0.144	0.231	VL	L	0.426	y= -0.005x + 0.177

The consequences of these acidifications are numerous and include inhibition of at least some microbial populations and transformations, including methane emitting bacteria.^[12] Like most biological process in soils, atmospheric methane consumption varies as a function of pH. For some forest soil studies, there are indications that pH optima for atmospheric methane consumption ranges between about 4.5-6.5. Although some acids have greater/lesser impacts, causing the pH optima to vary.^[13]

Table 4: Details obtained from graphs showing relationship between soil parameter values and Methane (CH₄) morning concentrations. 0.000-0.099; very very low (V V L); 0.199- 0.299; very low (V L); 0.300- 0.599; low,(L) ; 0.600- 0.899; Moderate (M), 0.900-1.0 ; Strong (S)

There are steep declines in methanotrophic activity typically accompanying increasing alkalination and acidification of soils beyond the optimal pH range. Although some evidence shows difference in pH optima with soil types; where pH optima of agricultural soils appear more notably alkaline than those for forest soils. With peak activity occurring at pH values completely inhibitory for forest soils. Accordingly, acidic pH values that support methane consumption in forest soils strongly inhibit activity in agricultural soils.^[14]

The electronic conductivity (EC) is an indirect measurement that correlates very well with several soil physiochemical properties that could affect crop productivity including activities due to presence of organic matter. But in the case of this study, it possesses a near zero negative R value.

From the analysis of relative humidity around the river, there are high levels of humidity with some readings peaking at 99.9% and even though the direct relationship between the humidity and soil physiochemical properties wasn't considered, it is an established fact that the humidity of methane air mixture has influence on explosion limit of the mixed gas as the lower explosion limit falls with increase in relative humidity. Hence it is of great necessity to ensure the methane levels remain safe and moderate as humidity levels are encouraging for possible explosion if there are high level methane concentrations. From the results it is realize that along the river, there is an average mean of 0.15% of methane in the air during the morning hours (9:00am – 11:00am) and 0.16% during the evening hours (4:00pm-6:00pm) which gives us an average of 0.15% of methane gas along the length of the river daily.

In comparison to the National institute For Occupational Safety and Health (NIOSH) maximum recommended safe methane concentration for workers during an 8-hour period. The concentration can be said to be within safe limits of not being able to cause any direct danger to people exposed to it.^[15] With this good news in mind, there is still room and necessity for care to be taken on most of the anthropogenic activities carried out on a daily basis around the river so as to maintain these current healthy levels both for ourselves, our children, the soils and the earth at large, since it is observed from study that human related sources creates majority of the methane emissions, accounting for 64% of the total methane which has caused a double in methane levels over the past 150 years.^[16] Even as the observed drop in methane carrying “heavy” carbon -13 seems to rule out fossil fuels emissions, wildfires or biomass cook stoves ass the reason for rise in methane levels. Nonetheless, we need to save our planet; and it would be a good idea to start from factors which are more easily influenced by us. In order to ensure that cautious steps are taken, policies should be set up and awareness created. Even as we are in an era where the world is going green, the policies and awareness should be established in

ways that would ensure to cover all the areas of human related sources; fossil fuel production, distribution and use, livestock farming landfills and waste, biomass burning, biofuel etc.

From table 4 we see the correlation coefficients (R) between the different soil physiochemical parameters and the mean concentrations of methane. We observe that although all the parameters possess near zero values of R, temperature possess the strongest positive correlation in the morning hours and organic matter content (OM) possess the strongest negative R value for evening. Meanwhile the other parameters possess very close to zero value of R indicating low correlation. A low R-squared value indicates that methane emission (independent variable) is not explaining much in the variation of Physical parameter (dependent variable) - regardless of the variable significance, this is letting you know that the identified independent variable, even though significant, is not accounting for much of the mean of physical parameters. The r-squared values were divided into five categories depicting their effect on methane emission as follows: 0.000-0.099; very very low (V V L); 0.199- 0.299; very low (V L); 0.300- 0.599; low (L) ; 0.600- 0.899; Moderate (M), 0.900- 1.0 ; Strong (S). Though there was no strong effect of any physical parameters on methane emission, E.C. Soil moisture, and Temperature showed low to moderate effect on methane emissions.

CONCLUSIONS

Generally, most physical parameters showed very low effect on methane emission. There was no strong effect of any physical parameters on methane emission, but few showed low to moderate effect on methane emissions. Methane is a natural resource and an obviously useful one, but its capacity as a greenhouse gas, potential bomb and asphyxiates, there is great need for care and precaution to be taken in the handling of all and any of its sources. This would prevent its loss and wastages which would be both to our health and economic benefits. Rivers and soils are also natural resources, they make relevant provisions for our need; both on domestic and industrial scale. They occupy significant areas of the earth's surface hence their health is of great importance to the world and its climate at large. Through the course of this research study, it is observed that the concentrations of methane along the river are within safe limits and possess very close to zero correlation to the soil physiochemical properties except for temperature and organic matter. Nonetheless, the concentrations are found to be more uniform with less coefficient of variation along the length of the river during the evening hours than those obtained from the reading during the day, indicating alterations/influence from anthropogenic activities taking place around the river, both those from fuel powered vehicles passing by the flyover/bridges located at the site of study and also the dredging machines.

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