PHYSICO-CHEMICAL ANALYSIS OF ATMOSPHERIC AEROSOL FROM TWO STATIONS IN THE MANGROVE FOREST REGION, RIVERS STATE, NIGERIA.

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Abstract

Countries around the globe where there are gas flaring have the common resolve of stopping gas flaring from petroleum exploitation which constitutes pollution unimaginable in the environment. The incidence of air pollution which can result in acid rain and its loss of human and material resources on both the government and the citizens is a thing of serious concern. This work investigated the threshold of dissolved pollutants in rainwater from Omoku (a town surrounded by three gas-flaring communities) and Port Harcourt (a densely populated and highly industrialized city) both in Rivers State Nigeria. Although, heavy metals are natural components of the environment, concentrations of certain metals beyond certain levels could become potentially lethal. The aerosol particles present in the atmosphere are regarded as being both liquid and solid suspended particle. Much of the total mass of the natural aerosol is removed from the atmosphere via water precipitation washout; hence, rainfall has a very strong effect on air quality.Weekly rainwater sample were collected from the two stations for fourteen weeks. Non-metallic ion determinations were carried out using DR 2010 data logging spectrophotometer while metallic ion determination were carried out using the unicam model 919 atomic absorption spectrophotometer (A.A.S).The results of the physico-chemical analysis of rainwater from Omoku revealed the mean values of the following parameters; temperature 26.2OC colour 16ptco, pH 5.6 , electrical conductivity 17.07us/cm, NO_3- 25.59 mg/l, SO42- 8.28mg/l, Fez+ 0.14mg/l, Mn2+0.25mg/l Cu2+0.03mg/l, Zn2+1.3mg/l while those of Port Harcourt are, temperature 25.3OOc colour 5ptco, PH 6.00, electrical conductivity 27.14us/cm NO_3- 21.57mg/l, SO24- 8.21mg/l, Fe2+0.08mg/l Mn2+0.43mg/l, Cu2+0.05mg/l,Zn2+0.24mg/l, concentration of ions and colour generally decreased with increased frequency of rainfall. Higher levels of temperature, acidity (low pH), NO-$_3$, SO42- and colour in Omoku town can be attributed mainly to gas flaring and other anthropogenic activities, the high level of pH brought about by the presence of NO3- and SO24- are responsible for the acid rain in area, while higher levels of heavy metals in Port Harcourt can be attributed to industrial activities fossil fuel combustion and other anthropogenic activities. However, ions detected in these samples are within the W.H.O permissible limits except, for manganese for which value is higher than the acceptable limits in Port Harcourt. By putting to a stop gas flaring and reduction of anthropogenic activities by means of viable polices, there could be reduction in anthropogenic emissions.

Keywords: *Omoku, Port Harcourt, Rainwater, Gas flaring, Anthropogenic activities.*

Background to the Study

Rainwater dissolves the gasses of the atmosphere and contains particulates of dust and smoke. The aerosol particles present in the atmosphere are regarded as being a mixture of soluble and insoluble material. Substances may be removed from the atmosphere by water precipitation in one of the two ways, rainout or washout. Rainout occurs within the clouds where the most important process is condensation of water vapour on the solid aerosol. Washout occurs below the clouds and is very efficient for the removal of large solid aerosol. (Ayodele, J.T. 1996, Abubakar. M.B. 1998)

Various types of pollutants exist and these include the dust particles as a result of harmattan wind, and mist fumes, ash, soluble salt, fungi, sulpur (iv) oxide, nitrogen (iv) oxide, phosphorus (v) oxide, chloro-fluorocarbon (CFC) and ammonia. The above gases are removed from the atmosphere by rainout and washout (Abubakar, M.B 1998). Both carbon (ii) oxide and carbon (iv) oxide which are carbon related compounds are sent into the atmosphere by incomplete and complete combustion respectively. Atmospheric source of this carbon monoxide is from the oxidation of methane (Hutzinger, O.D. 1990). This is of a natural source since all the methane in the atmosphere is produced by the anaerobic decomposition of organic matter. Carbon (iv) oxide which is a green house gas absorbs red radiation emitted from the surface of the earth by trapping some of these radiations and preventing them from escaping into space with the result that our planet is some 33OC warmer than it would otherwise be (Arontz, M.E. 2010, Rosool, S.I. and Schnzider, S.H. 1994). Thought fossil fuels, bush burning and other human activities we are increasing the burden of carbon (iv) oxide.

The atmospheric concentration of carbon (iv) oxide is reported to have increased from a pre-industrial value of 290 ppmv to more than 350 ppmv today at the rate of about 0.5 percent per year. In the use of a refrigerator
green house gases can be recognized as being emitted. These are the refrigeration fluid (CFC -12) and (CFC-11). When carbon (iv) oxide comes in contact with water the following occurs. $CO_2 + H_2O$ H_2CO_3
Sulphur related compounds include, $S0_2$ and $S0_3$ cause acid rain. Rainwater usually has a pH of 4-6. This acid water predominantly contains H_2SO_4. Fossil fuels which contain sulphur and its compounds on combustion releases SO_2 which on oxidation with Ozone in the troposphere forms SO_3. The SO_3 dissolves in rainwater to H_2SO_4 resulting in acid rain.

$S + O_2$ SO_2 ----------- (i)
$SO_2 + O_3$ $SO_3 + O_2$ -------- (ii)
$SO_3 + H_2O$ H_2SO_4 ------- (iii)

Acid rain is one of the devastating forms of pollution; it damages vegetation and kill fishes in water. Laboratory data indicate that SO_2 has the potential of slowing down the ciliary movements in the respiratory tract of man. These irritants when they reach the lungs causes respiratory problem (Woldbott, G.L. 1999). Nitrogen forms oxides corresponding to each of its known oxidation states. Of these oxides, only dinitrogen oxide (N_2O), nitrogen monoxide (NO) and nitrogen (iv) oxide appear at measurable quantities in the atmosphere. The most important reactions involving NO and NO_2 occur in groups of reactions known as photochemical smog. A photochemical smog is characterized by a haze, ozone formation, eye irritation and damage to vegetation.

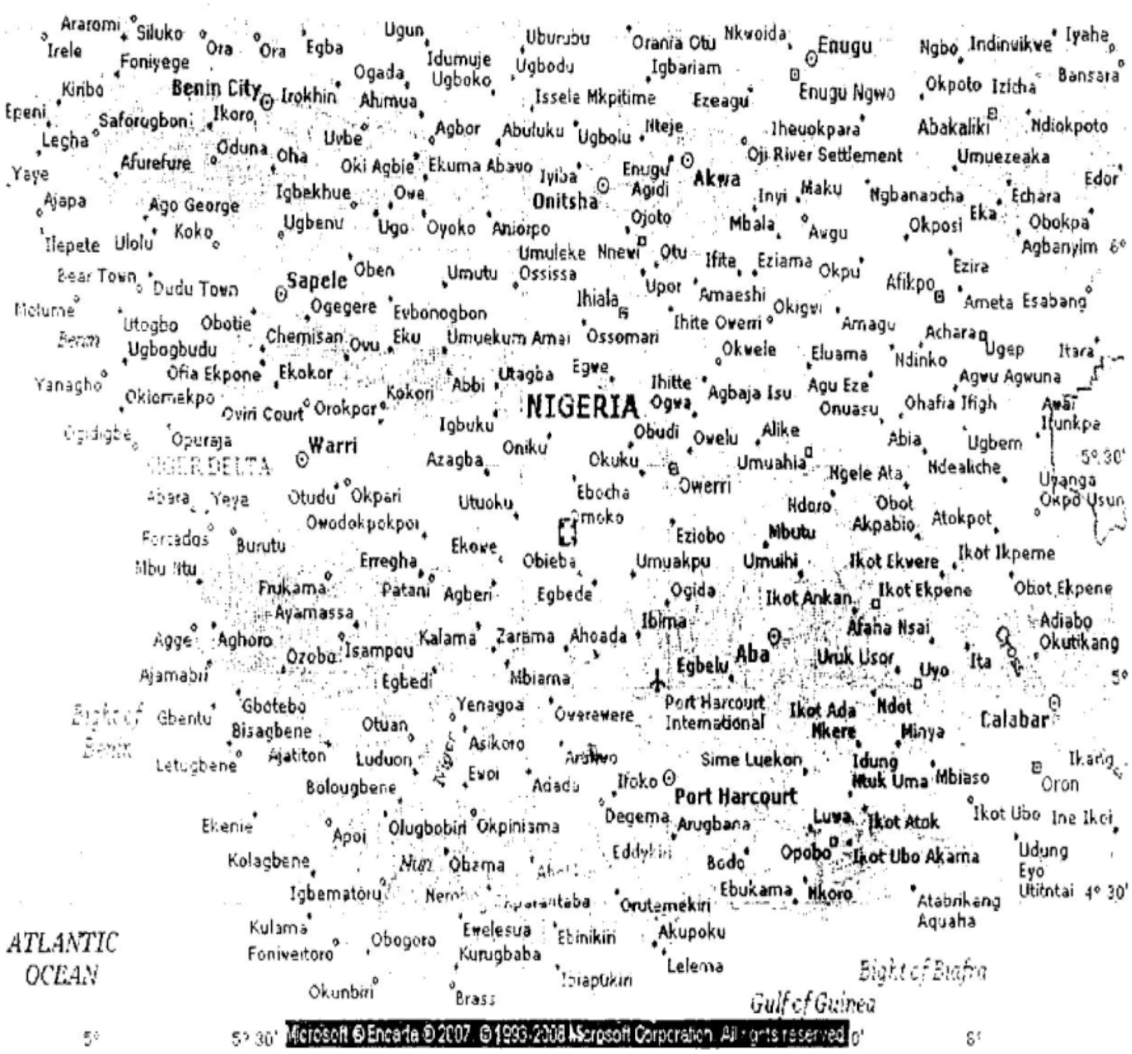
Nitrate is sent into the atmosphere initially as nitrogen (iv) oxide from gas flaring, biomass burning and fossil fuel combustion (Dignon, D. etal 1991). The objective of this work is to investigate the concentration of metallic ions and anions from some aerosols of the environment with a view to highlighting the effects of the consequences and sources of these elemental pollutants.

Description of Study Area

Port Harcourt and Omoku are cities in Rivers State located in the Niger Delta Area of Nigeria. Omoku was chosen owing to numerous gas flaring activities around it. Port Harcourt was chosen because it is a city densely populated by people with numerous industrial activities going on in the area.

Below is map the Niger Delta Area showing the cities of Port Harcorut and Omoku (the research locations)

MAP OF THE NIGER DELTA AREA SHOWING THE CITIES OF PORT HARCOURT AND OMOKU – THE RESEARCH LOCATIONS



╬: OMOKU CITY ON LATITUDE 5⁰ 21N AND LONGITUDE 6⁰ 39E.

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Experimental

Weekly rainwater sample were collected from Omoku (RWSO) and Port Harcourt (RWSP) for fourteen weeks, shaken, flittered, and stored in label bottles for analysis. The samples were collected from the month of June 2001 to the month of November 2011.

pH and Temperature Measurement

The pH and temperature were determined using the SUNTEX pH metre and mercury in glass thermometer respectively.

Colour Measurement

Spectrophotometer with programme number 120 at wave length of 455nm was used to determine the colour. Deionzed water (25ml) was used for zeroing (Willeke, K. et al 1993).

Electrical Conductivity

A conductivity meter was used to determine the conductivity of the samples in us/cm.

Nitrate Determination

This is done using the cadmium reduction method. This used programme number 353 of wavelength 400nm and a DR 2010 was used for spectrophotometer read out.

In one of two sample sells, 25ml of de-ionized water was poured and nitraver 5 reagent added powder pillow added and kept as blank. 25ml of the sample was poured into the second cell bottle and one nitraver 5 reagent powder pillow added. The were swisled to mix thoroughly. The spectrophotometer was switched on, the shift timer was pressed and was timed for 5 minutes. The blank was used for zeroing. The treated sample was later placed into the light shield of the spectrophotometer. The value was digitally displayed after pressing 'READ'

Sulphate Determination

The stored of programme for sulphate (680) was entered into the DR 2010 datalogging spectrophotometer at maximum wavelength of 450nm.

A clean sample was filled with 25cm3 of de-ionized water and one nitraver sulfaver 4 reagent powder pillow added and kept as blank. Another 25cm3 sample cell was filled with one sulfaver 4 sulphater reagents powder pillow. This was swirled for dissolution and was allowed for 5minutes.The blank was used for zeroing. The second sample cell was placed in the spectrophotometer and the value digitally displayed on pressing 'read'.

Metallic Ion Determination

The determination of metallic ions was done using the atomic absorption spectrophotometer (A.A.S) of unicam model 919. The metallic ions determined include; iron, manganese, copper and zinc. Stock solutions from which working standards were prepared as reported in technical bulletin using various cathode tubes specific for each element determined.

Results and Discussion:

Table 1Physico-chemical data of rainwater from Omoku

	Temp. ^{O}C	Colour ptco	pH	Elect Conduct us/cm	NO_3 mg/l	SO_4^{2-} mg/l	Fe^{2+} mg/l	Mn^{2+} mg/l	Cu^{2+} mg/l	Zn^{2+} mg/l
Maximum	26.90	18.00	6.20	35.10	31.01	17.00	0.24	0.50	0.08	3.00
Minimum	24.50	5.00	5.20	5.00	12.00	3.00	0.01	0.02	0.02	0.12
Mean	25.50	8.50	5.70	16.90	21.00	8.10	0.14	0.40	0.05	1.30
Std deviation	0.11	2.49	0.16	0.66	0.00	0.16	0.26	0.20	0.01	0.36
W.H.O std	$25^{O}c$	15.00	6.50-8.50	1,400.00	45.00	400	0.30	0.30	1.50	5.00

Table 2 Physico-chemical data of rainwater from Port Harcourt

	Temp. ^{O}C	Colour ptco	pH	Elect Conduct us/cm	NO_3 mg/l	SO_4^{2-} mg/l	Fe^{2+} mg/l	Mn^{2+} mg/l	Cu^{2+} mg/l	Zn^{2+} mg/l
Maximum	26.00	11.00	6.90	50.00	35.10	14.00	0.20	0.70	0.09	0.50
Minimum	24.50	2.10	5.50	10.00	10.01	3.01	0.01	0.02	0.02	0.50
Mean	25.30	5.90	6.10	27.8	21.60	8.20	0.08	0.42	0.05	0.24
Std deviation	0.14	0.36	0.06	1.33	o.22	0.33	0.44	0.03	0.01	2.77
W.H.O std	$25^{O}c$	15.00	6.50-8.50	50.00	45.00	400.00	0.30	0.30	1.50	5.00

Temperature:

Tables 1 and 2 are the physico-chemical data of rainwater samples from Omoku (RWSO) and Port Harcourt (RWSP) respectively. Water temperature during the study period varied from 24.5OC to 26.9OC with a higher average temperature in Omoku. This can be attributed to heat generated in the area from gas flaring points. Colour: The colour of RWSO is within the range of 5.OOptco – 18.OOptco while that of RWSP is within the range of 2.1Optco – 11.OOptco indicating that RWSO is more coloured than RWSP. This can be attributed to the thick smoke from the flaring pipes around Omoku. The colour in RWSP can be attributed to fossil fuel combustion from various sources as well as dust blown from the ground as a result of pedestrian and automobile activities.

pH

The mean pH value of RWSO is 5.60 which is lower than that of RWSP which is 6.OO and it is on the acidic side (slightly acidic). This indicates that RWSO is slightly more acidic than that of RWSP, thus depicting that rainwater of Omoku can cause corrosion of pipes and other corrodable materials. The lowest pH value of 5.20 was recorded at Omoku. This can be attributed to the presence of large amount of carbon (iv) oxide (CO2) in the atmosphere which is a by product of gas flaring, bush burning and automobile emissions. RWSP had a minimum PH value of 5.5O. The acidity of Port Harcourt rainwater could be attributed to industrial effluent, automobile emissions and other anthropogenic activities.

Electrical Conductivity

The electrical conductivity (EC) in the two study areas range from 5.00-35.10uscm-1 with mean value of 17.07uscm-1 for Omoku and from 10.00-50 uscm-1 for Port Harcourt with mean value of 27.14 uscm-1. Electrical conductivity depends on the amount of dissolved ions and is the ability of a substance to conduct an electric current at a specified temperature usually 20oC or 25oC.

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Nitrate

The nitrate content of RWSO and RWSP lied from 10.00-35.10mg/l-1 RWSO has a slight higher mean value of 21.59mgl-1 than RWSP which has a mean value of 21.57mgl-1. This can be attributed to the high temperature flame which facilitates formation of reactive oxygen and nitrogen atoms from their molecules to produce NO which enters into the atmosphere and slowly turns into NO2 through a series of reactions in the photochemical smog (Narayanan 2009).

The net result is

$NO + ½02 \quad NO2$

NO2 reacts with hydroxyl radicals in the gas phase to form nitric acid, which easily enters aerosols, finally leading to acid rain. NO2 is known to cause pulmonary Oedma an accumulation of excessive fluid in the lungs. It can exacerbate asthma and increase susceptibility to infection (Narayanan 2009). The major sources of NO2 in RWSP are industrial effluents.

Sulphate

Tables 1 and 2 show that mean sulphate concentrate (8.28mgl-1), of RWSO is higher than that of RWSP (8.21mgl-1). Sulphur (iv) oxide is a primary pollutant whose principal source is the combustion of sulphur – containing fossil fuels. It is estimated that 25-30% of global emission of this pollutant is from oil burning (Narayanan 2009). This can happen during biomass burning after oil spillages in the area, which is a recurring decimal in the oil-reach communities around Omoku.

Sulphur (iv) oxide in the atmosphere is oxidized to sulfuric acid by hydroxyl/radicals (OH) produced by photodecomposition of ozone (03)

$HO + SO2 + M \quad HSO3 + M$

$HSO3 + O2 \quad SO3 + HO2$

$SO3 + H2O \quad H2SO4$

Both wet and dry depositions are responsible for damage to building materials, destructions of vegetation and soil degradation.

Observation has shown that nitrate and sulphate ion concentrations were low within the first five weeks when the rain were more frequent but increased as the frequency of the rain decreased within the first five weeks.

Iron

Concentration of iron ranged from 0.01 – 0.24mgl-1 with a mean value of 0.07mgl-1 in RWSO while in RWSP it ranged from 0.01 –0.2mgl-1 with a mean value of 0.14mgl-1. Mean value of iron from RWSP is greater than that of RWSO.

However, both values are within the WHO standard

Manganese

Manganese was detected in both RWSP and RWSO with values ranging from 0.2 0.5mgl-1 in RWSO and 0.2-0.7mgl-1 in RWSP.

Copper

Copper was also detected in both RWSO and RWSP with values ranging from 0.20 - 0.08mgl-1 in RWSO and 0.20 – 0.09mgl-1 in RWSP indicating a higher value in RWSP than in RWSO.

Zinc

The value of zinc is from 0.12 – 0.3mgl-1 in RWSO while in RWSP it ranged from 0.06 – 0.50mgl-1 also indicating a higher value in RWSP than in RWSO.9

Generally, the results of metallic ion concentrations analyzed are higher in RWSP than in RWSO. This can be attributed to the fact that Port Harcourt is highly urbanized with many industries when compared to Omoku. This implies that the higher metallic concentration can be attributed to many industrial activities involving the use of iron, manganese, copper and zinc.

The metallic ion concentrations were observed to be lower at the period of high frequency rain (within the first five weeks) than at the period of low frequency rain within the last five weeks). This was also the case with temperature colour and electrical conductivity

Conclusion

This work has revealed anthropogenic activities arising from biomass burning, gas flaring from petroleum exploitation, automobile emissions, fossil fuel combustion, industrial effluent gases as sources of aerosols in the atmosphere. Analysis of rainwater from the two stations indicated higher anion concentration in RWSO than in RWSP while higher cation concentration were implicated in RWSP than in RWSO.

Both cation and anion including temperature, colour and electrical conductivity were higher when the frequency of the rain was low and vice versa. The pH rose with increase in rain frequency. The parameters however fall within the WHO permissible limits except manganese which is higher in Port Harcourt. With reduction in anthropogenic activities, there could be reduction in anthropogenic emissions.

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