ANALYTICAL ASSESSMENT OF ATMOSPHERIC RESIDUAL AEROSOL IN THE ENVIRONMENT

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BY

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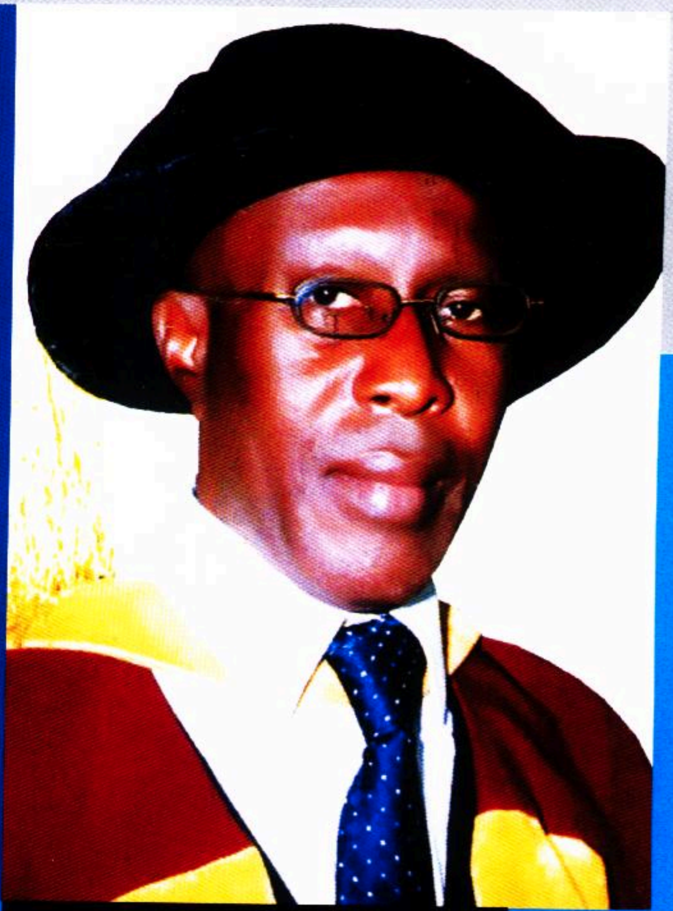

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Prof. Ubaezue Ugochukwu Egereonu

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Introduction

As man strives for better living standards through urbanization and industrialization, the Earth's environment, including the atmosphere is continuously degraded due to pollution. An environment, as defined in the Federal Environmental Protection Agency decree of 1988 now Federal Ministry of Environment includes water, air, land, plants and animals living therein and the inter-relationships which exist among these or any of them (FEPA, 1988).

The oxides of non-metals on dissolution in the atmospheric moisture precipitate as residual aerosol which constitutes unimaginable pollution in the environment. Acid rains as suitable as a corrodent devastates ornamental statues that adorn cities of the world, tarnish roofing sheets fences and cause changes in the composition of lakes with concomitant effects on the vegetation. In our continuation of monitoring the effects of gas flaring, this work assesses three satellite stations with a view to determining the threshold of the acidity due to residual aerosol dissolution with greater emphasis on heavy elemental presence. The atmosphere is composed of the following layers and heights.

1.0 The Troposphere

This is the region of atmosphere from the earth surface to the tropopause, having a height of from 6 – 12 kilometres and characterize by decreasing temperature with increasing attitude. Much of the mass of gaseous air pollutants are emitted in the Northern Hemisphere, hence the slow inter-hemispheric mixing time is of importance when considering the global consequences of atmospheric pollutants (Spedding, 1997).

The Stratosphere

In the stratosphere there's a systematic fall of temperature with increasing altitude characteristic of the region below it ceases, often given place to a more or less uniform temperature. It's height is from

12 - 50km. Temperature also varies with altitude and this is used to divide the atmosphere into layers. Properties of each of these layers have some relevance to air pollution chemistry although the properties of the troposphere as mentioned are of the greatest significance since it contains the air that sustains life (Spedding, 1977 and Audette, 1990).

The Mesosphere

This is a layer of the atmosphere lying between the stratosphere and mesosphere. The height of the mesosphere is between 50 and 80km.

The Thermosphere

This is the layer above the mesosphere of height ranging between 80 – 700km.

The Exosphere

This is the upper most layer of the earth's surface. This layer is from 700km and above. The exosphere is subject to ionization with seasonal variations. It is responsible for reflection of radio-waves.

The Lithosphere

This is the earth's surface. The Lithosphere is polluted through soil, industrial effluents and erosion. The solid portion of the earth is composed of rocks and minerals which in turn, comprise the continental masses and ocean basins. The rocks of the lithosphere are of three basic types: Igneous, sedimentary and metamorphic. Most of what we know about the lithosphere has been learnt through the study of the surface materials of the earth. However, by means of deep bore holes and seismological studies, geologists have gathered much valuable information about the earth's interior. The lithosphere has been divided into three district zones, namely the crust, the mantle and the core (Read and Watson, 1968).

The Hydrosphere

This comprises the seas, rivers and lakes, as well as groundwater which exists in the pores and crevices of the crustal rocks and soil. Most of this water is contained in the oceans, which cover roughly 71% of the earth's surface to an average depth of about 41cm. The waters of the earth are essential to man's existence and they are also of considerable geological importance. Industrial effluents and agricultural chemicals like herbicides and pesticides pollute the hydrosphere (Spedding, 1997).

2.0 Identification of Sources of Environmental Pollution

2.1 Agro-allied Chemical as Aerosols:

An aerosol is defined as being a dispersion of solid or liquid matter in air, some aerosols in agro-allied industries are found as herbicides and pesticides.

When natural aerosol is supplemented by pollutant aerosol in the form of smoke, ash, acid mist and soluble salts, the properties of the atmosphere may be adversely afflicted. Processes of absorption and scattering of light by smoke, $(NH)_4SO_4$ aerosols greatly affect visibility. Deposition of solid aerosols like soot and ash affect the surfaces of building. The deposition of acid mists, especially H_2SO_4 mists of carcinogenetic hydrocarbons from combustion processes have effect on human health. The aerosols exist in various sizes and these include the aitken particles, that is, particles of less than 0.1µm radius, large particles of radii in the range 0.1 to 1 µm, giant particles, that is, particles of radii greater than 1µm, dust, fumes and smoke. The tropospheric aerosol is of two major sources, the maritime and continental aerosols with the maritime aerosols predominating in the mid-ocean and the continental aerosols, predominating at the centre of the land masses. Man is concerned with the aerosol deposited over the land. The aerosol can remain airborne as long as the terminal velocity and gravity allow and when they deposit they change the colour of buildings, sculpture and exposed vehicles. The principal source of sulphur (iv oxide in the Kaduna metropolis is the Federal Superphosphate fertilizer company. The gas damages chlorophyll in plants causes the devastation of forest and causes respiratory ailments in human beings (Egereonu, 2003 and Egereonu et al. 2012c).

2.2 Biomass Burning

This is the burning of vegetation resulting in the release of Carbon (iv) oxide and water vapour. This is as a result of the elemental composition of vegetation. The release of Carbon (iv) oxide from biomass burning increases the concentration of atmospheric carbon (iv) oxide which results in the green house effect. The average diameter of a smoke particle resulting from biomass burning is about 0.075µm, that is, most of aitken particles. Most of smoke is made up of carbonaceous compounds, particularly tarry hydrocarbons and resins. The very small size of smoke particles enables them to penetrate building in the same manner with gases. Unlike gases, the smoke particles have a high "sticking" power and are found deposited on surfaces where air turbalance is high, for example, edges of window and door frames. The solid material set free when fuel is completely oxidized is known as ash (Onuchukwu et al. 1997 and Chung, 1984).

2.3 Gas Flaring

This involves the burning of natural gases by the petroleum refining industry. Natural gases like butane and propane on combustion yield Carbon (iv) oxide and water vapour. A simple calculation of the annual mass of CO_2 emitted by combustion shows that the change in CO_2 concentrations in the atmosphere is due to combustion and it represents about one half of the emitted fossil fuel CO_2 (Chung, 1984 and Looke 1997).

2.4 Industrial Chemicals

These include dangerous gases like the chlorofluorocarbons (CFCs) which are often used as coolants in refrigerators, air-conditioners and spray cans; halons are used by fire fighters and carbon tetrachloride used as a cleaning agent. CFC is broken down in the troposphere in the presence of light energy, for example:

$$CCl_2F_2 \xrightarrow{hv} Cl^{\cdot} + {}^{\cdot}CClF_2$$

$$CCl_3F \xrightarrow{hv} Cl^{\cdot} + {}^{\cdot}CCl_2F$$

The residual radicals react with the atmospheric oxygen to release all the chlorine either as $Cl^{\cdot}$ or ClO. Chlorine radicals react in the stratosphere with ozone atoms to produce oxygen molecule. The global use of CFCs by various regions of the world is in Table 1 (Spedding, 1997, Lavrov, 1978 and DOE, 1991).

Table 1: Global CFC: Use by Regions 1966

Regions	Share of total (%)
United States of America	29
Other industrial Countries	41
Soviet Union, Eastern Bloc	14
Other Developing Countries	14
China and India	2

Source: The Ozone treaty: A Triumph of All update from State, May/June, 1988.

The Nigeria National Petroleum refineries emit sulphur (iv) oxide, nitrogen (iv) oxide and particulates. The polluting effects of these substances are readily seen during harmattan when visibility becomes so poor as to warrant the disruption of scheduled flights in and out of the city airports.

The various cement factories in Nigeria are pollution sites. The Ewekoro Cement Company for example, had been in operation since

1960; cement dust from its towers had withered the surrounding vegetation, and polluted a nearby pond. The vegetation around the Shagamu Cement Company has also not been spared. Some investigation carried out has shown how notorious cement companies in Nigeria are in the pollution of the environment; they release dust into the atmosphere higher than level permitted WHO (Akingbade, 1991).

2.5 Soil degradation (Erosion)

This is a wearing down or destructive process. Degradation results from the wearing down of rocks by water, air and ice. It also includes the works of atmospheric weathering, glacial abrasion, stream erosion, wind abrasion and so on. Aggradations also known as deposition, result in the accumulation of sediments and ultimate building up of rock strata. The principal agents depositing these sediments are wind, ice and water (Mathew, 1964 and Read, 1968).

2.6 Volcanic Eruption

Some active volcanoes erupt, emitting gases, liquids and solids particles which pollute the atmospheric environment. The gases that are emitted from volcanoes are composed largely of water vapour, with varying amounts of carbon (iv) oxide, hydrogen sulphide and chlorine. During an eruption, these escaping gases may become mixed with vast quantities of volcanic dust, and often rise from the crater in great dark clouds which may be seen for many kilometers.

The liquids produced by volcanoes are the lavas which are great quantities of white-hot molten rock. Lava is more typically extruded from the crater in the top of the volcano, but it is not uncommon for the lava to break through the sides of the cone and escape by means of fissures developed along zones of weakness. Not all lavas are alike in their chemical and physical properties, and these properties may be reflected by the manner in which the volcano erupts. Because of the different characteristics of lavas, geologist have classified them as acidic, basic and intermediate. The acidic lavas are low in silica, less viscous, and dissolved gases can escape more readily from the more fluid lava. Intermediate lavas are those that fail in between the acidic and basic categories : a typical intermediate lava contains 50 to 60 present silica (Read and Watson, 1968).

3.0 Effects of Environmental Pollution

3.1 Acid Rain

Acid rain is that rainwater with a low pH value. Low pH value depicts high hydrogen ion concentration. SO_2 reacts with moisture to produce H_2SO_4.

$$SO_2 + O_3 \longrightarrow SO_3 + O_2$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

or

$$SO_2 + O_2 \longrightarrow SO_3 + O$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

H_2SO_4 falls as acid rain CO_2 dissolves in the water vapour of the stratosphere to form carbonic acid, H_2CO_3 which falls as acid rain.
No_2 dissolves in the water vapour of the stratosphere in the presence of oxygen to nitric acid which falls as acid rain:

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

Nitrogen (iv) oxide released into the atmosphere forms HNO_3 with moisture and falls as acid rain has become an issue of international concern (Howell, 1997 and Charison and Rodhe 1982).

Normal Rain is naturally acid with a pH = 5.6. Acid rain is one of the most devastating forms of pollution imaginable. It causes lung diseases, it threatens fresh water fisheries, agriculture and wild life and damages forests. Acid rain in known to cause havoc in the Niger Delta region of Nigeria; forests are being destroyed but the extent of destruction to both the terrestrial and aquatic ecosystems is not yet fully ascertained. Acid rain can be abated when industries attain the zero emission level and when gas flaring is halted (Egereonu, 2006).

3.2 On painted vehicles, buildings, leather and Papers

Smoke which is known to contain carbonaceous compounds such as tarry hydrocarbons and resins as the major combustion products coagulate and descend under gravity. This residual aerosol is known to stick on surfaces producing black sticky deposits. These deposits have been observed to constitute the black deposits on ornamental statues, building and objects such as cars packed long enough and exposed to the environment. The accumulation of these residues on these objects constitute an eyesore. These pollutants change the colour of vehicles, leathers and papers exposed for long to the atmosphere. The pollutants, responsible for these include, sulphurous, gases, oxides of carbon and nitrogen, phenols, organic acid residues, soil and elemental dust and some radioactive wastes (Speeding, 1997, Egereonu et al. 2012b and 2012c).

3.3 Global Warming

Trace gases present in the atmosphere is of very minute quantities is measured in parts per million volume (ppmv), parts per billion volume (ppbv) and at times parts per trillion volume (pptv) are known to contribute to changes in the chemistry of the atmosphere and earth's climate. Also it is evident that the chemistry and climate controlling factors are increasing in concentration with time. Typical of these green house gases are carbon (iv) oxide (CO_2), methane (CH_4), dinitrogen oxide (N_2O), Sulphur (iv) oxide (SO_2) and tropospheric ozone (O_3) which increase in concentration with time. Various sources of these gases include:

a. The burning of fossil fuels (sources of CO, CO_2 and NO_2)
b. Microbial metabolic activity (CH_4, NO, N_2O)
c. Photochemical reaction (O_3) and

d. Industrial effluent gases (CO_2, H_2S, CO, NO, SO_2 etc) include automobile exhaust.

These gases are produced directly by biomass burning, that is, the burning of the forests and savannah grass lands during clearing for agriculture. This practice is very much practiced in Nigeria. Much of the biomass burning and fossil fuel combustion and gas flaring is initiated by man, that is, of anthropogenic in origin. The result is that the earth is 33^0C warmer than it would have been and this could result in flooding of low lands where much of the human population is concentrated (Speeding, 1997 and Kaplan et al. 1998).

3.4 Green House Effect

This result when gases like NO, SO_2, N_2O, etc absorb infra-red radiation emitted from the surface of the earth thereby trapping some of these radiation and preventing them from escaping to space with the result that the planet is some 33^0C warmer than it would otherwise be (Spedding, 1997).

3.5 Carbon-monoxide (CO)

The poisonous action of carbon monoxide (CO) is fairly well known. It is colourless, odourless, tasteless and non-irritating, but it is very toxic. The only known damaging effects of CO at the concentrations found in the atmosphere are related to animal respiratory systems based on haemoglobin as an oxygen transporter. Even at low concentration of 0.04% of CO, one third of the haemoglobin is bound to CO forming carboxy-haemoglobin, death can occur from CO poisoning. Being present in air containing 0.5% of CO for 5-6 mins is mortally dangerous. The maximum acceptable concentration for CO is 30-$40\mu g/m^3$. Among the immediate effects upon humans are dizziness, blurred vision and distorted perception of time- certainly hazardous for drivers. Deadly level of CO may be reached within short periods in garages, tunnels and building above highways.

4.0 Analytical Assessment of Atmospheric Residual Aerosol

The increasing use of heavy metals has resulted in the influx of metallic substances in the environment. These metals are of concern because they are non-degradable and therefore persist. Although heavy metals are natural components of the environment, concentration of metals such as mercury, cadmium and lead could become potentially lethal hazard (Lexicon, 1989). One of the toxic metals is cadmium whose sources include batteries, phosphate fertilizers, mining, stabilizers and alloys (Earthwatch, 1995). Sources of other metal pollutant include mineral processing, manufacturing of inorganic products and large scale use of coal in power production (Lexicon, 1989).

The effects of acute cadmium poisoning in human include high blood pressure, kidney damage and destruction of testicular tissue and red blood cells are of serious concern (Water Research, 1995). The International Agency for Research on Cancer, has also classified cadmium as a probable carcinogenic element. Other heavy metals of interest are arsenic, zinc, copper and lead are produced through the large scale burning of coal. Lead from automobile and industrial emissions is absorbed into the body through inhalation. At present, the average blood lead levels in an urban adult are estimated at 75 to 100 times the natural level. It may result in anorexia and brain damage. The introduction of heavy metallic pollutant into the environment can occur in dissolved form as hydroxides, carbonates, sulphates, nitrates, phosphates and other related minerals. In particulate form, associated with suspended matter, the pollutant can under favourable hydraulic conditions, be deposited on the river bed (Water Research, 1995).

This work investigates the levels of some heavy metals and anions from some residual aerosol in the environment with a view to highlighting the effects or otherwise of the sources and the consequences of these elemental pollutants.

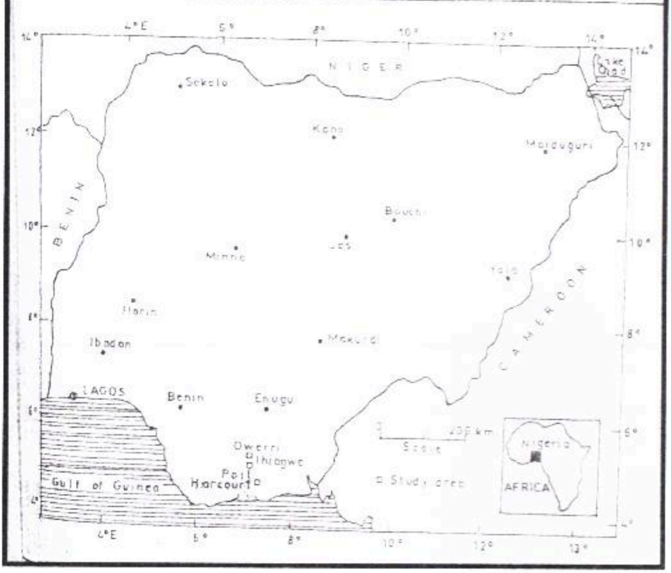
Sampling

Representative samples of the residual aerosol from three satellite stations were obtained from two species of economic trees. Samples were obtained from two species of economic trees. Samples were scrapped off from the leaves of *Mangifera indica* (Mango) and *Citrus sinesis* (Orange).

In addition, Mean Weakly Rainwater Supply (MWRWS) was obtained from each satellite station from rain gauges positioned in an equilateral triangular locations from sample stations as shown in figure 1,2,3. Rainwater Samples from Port Harcourt (RWSP) in River State and Rainwater Sample from Owerri (RWSO) and the University village – Ihiagwa

(RWSI) both in Imo State constituted the stations investigated.

Fig. 1 Location map showing the study area



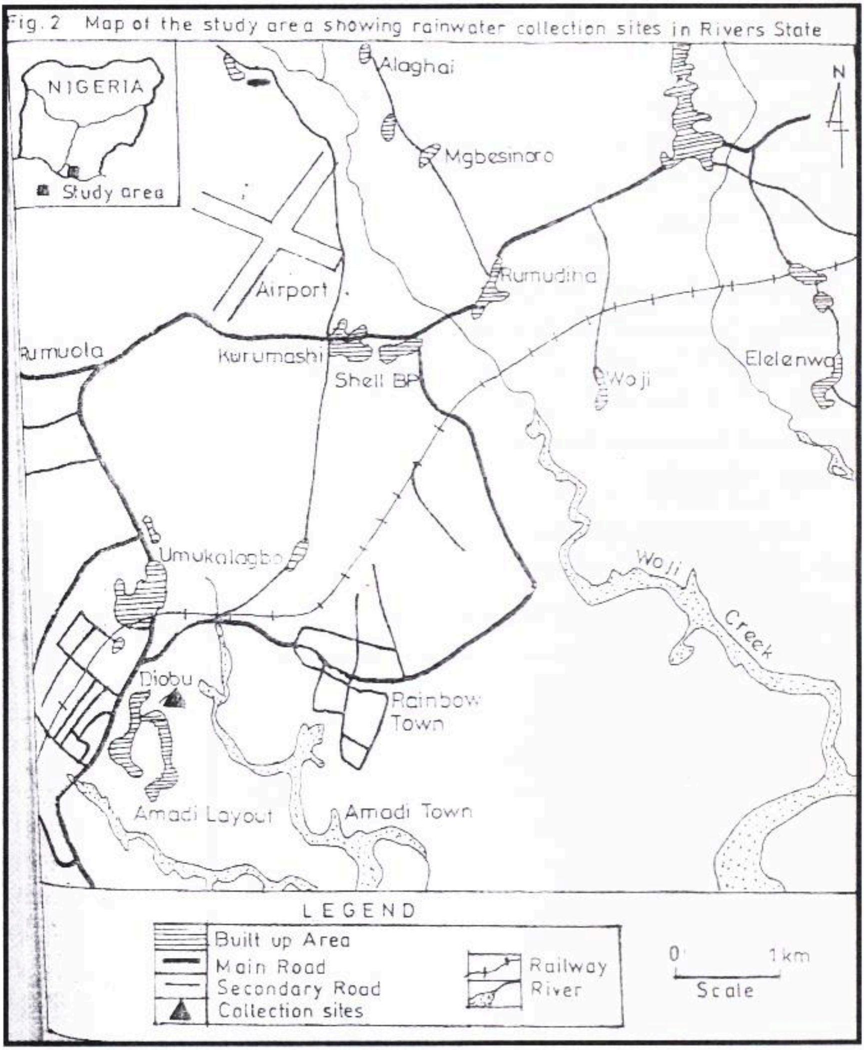


Fig 2: Map of the study area showing rainwater collection sites in Rivers State

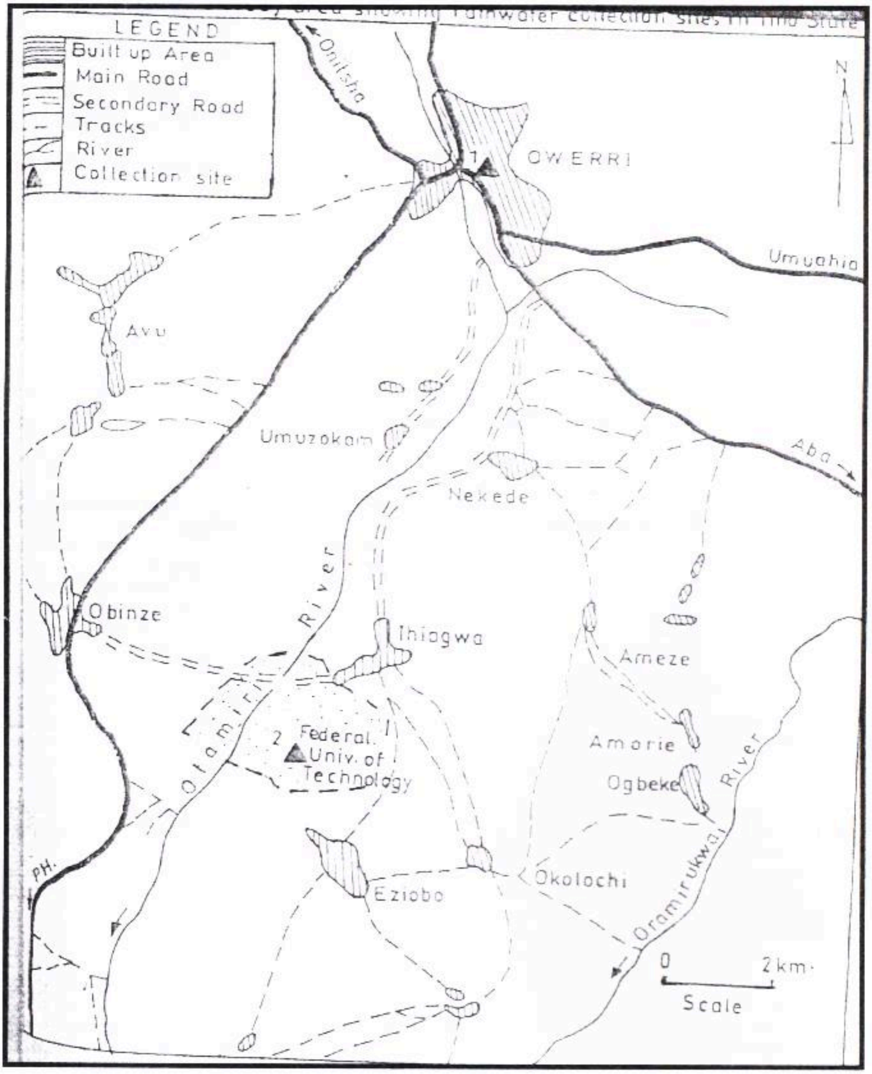


Fig 3: Map of the study area showing rainwater in Imo State

Environmental pollutants occur freely in the air as solid, liquid and gaseous or vapour mists in aerosol. These aerosol particles may accrete or coalesce on decomposition. When deposited on the surfaces of leaves they eclipse the stomata of the leaves thereby hindering light energy and gaseous exchanges and prevent photosynthesis. In consequence, these trees yield little or no fruits. The results of the analysis in Tables below show presence of metallic elements in mgL^{-1} which should have come from particulates in form of nitrate, sulphate, chloride and carbonate which were not able to dissolve in the rain drops and got deposited on the leaves as residues.

Table for Mean Analytical Data of the Aerosol Residual Deposit on Leaves from Owerri – The 1st Year.

Parameters	**MgL^{-1}**
Sodium	12.667
Potassium	12.11
Calcium	8.462
Iron	34.500
Cadmium	0.027
Lead	0.727
Mercury	0.005
Nickel	0.003
Phosphorus	3.164
%	
Inherent Moisture	4.45
Nitrogen Content	0.018
Carbon Content	50.38
Sulphur Content	0.015

Table for Mean Analytical Data of the Aerosol Residual Deposit on Leaves from Port Harcourt– The 1st Year

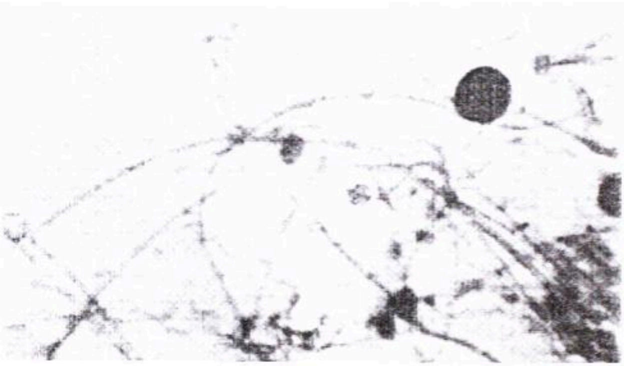
Parameters	MgL^{-1}
Sodium	13.243
Potassium	13.065
Calcium	8.896
Iron	36.000
Cadmium	0.031
Lead	0.753
Mercury	0.006
Nickel	0.004
Phosphorus	3.517
%	
Inherent Moisture	4.45
Nitrogen Content	0.025
Carbon Content	56.47
Sulphur Content	0.021

Table for Mean Analytical Data of the Aerosol Residual Deposit on Leaves from Ihiagwa– The 1st Year.

Parameters	MgL-1
Sodium	12.600
Potassium	12.104
Calcium	8.445
Iron	34.500
Cadmium	0.025
Lead	0.713

Mercury	0.005
Nickel	0.002
Phosphorus	3.145
%	
Inherent Moisture	4.45
Nitrogen Content	0.020
Carbon Content	50.36
Sulphur Content	0.014

Metallic ions such as Fe, Cd, Ni and Hg must have some maritime origin since these are present in oceans. The presence of phosphorus must have taken its source as phosphate sent into the troposphere as industrial emission of some fertilizer production and utilization in commercial farming. This could dissolve in the rain drops as phosphate and increase the phosphate concentration of rainfall. This is possible true for the high concentration of SO_3 and NO_2 in acid rain. Sodium, Potassium, and Calcium should have maritime origin as salts of chloride, sulphate and carbonate of sea water which on evaporation and condensation is incorporated in the rainwater. On biological culture of this solid aerosol revealed growth of fungi identified as rhizoids indicative of a Rhizopus species known as *Rhizopus nigricans*.



Substrate hyphae of this species is seen with highly branched rhizoids which function as anchoring and presumably absorbing structures. Features of these rhizodous fungi include the sporangium and fascicle of the sporangia arising from a group of rhizoids which are connected to another fascicle by means of a stolon. These features are indicative that the ungi is of the *Rhizopus nigricans*. This could be the cause of the degradation of most of the economic trees for example, *Mangifera indica* and *Citrus sinesis*. The mitigation of this environmental degradation could be effected using sulphur (iv) oxide gas which is enemical to the fungi growth. Therefore, it could be said that these deposits attracted the growth of this species of fungus.

Physical Measurement

Weakly average rainwater samples (RWS) was obtained from each satellite station from rain gauges positioned in an equilateral triangular locations from sample stations. Rainwater samples from Port-Harcourt (RWSP) in Rivers State, rainwater samples from Owerri (RWSO) and the University village Ihiagwa (RWSI) both in Imo State constituted these satellite stations under study. The measured RWS was shaken to ensure homogeneity, filtered and stored in labelled sample bottles with the following information, date of rainfalls, amount of rainfall and the location. The samples were collected between the months of February – July for the 2nd and 3rd years in order to obtain the trend of the concentrations of ions in the atmosphere.

Chemical Measurement

Sulphate Determination: Sulphate was determined by the Hatch corporation sulfaver 4 method adopted from the standard methods for the examination of water and waste water (Franson, 1978). The stored programme for sulphate 680 was entered into the DR2000 spectrophotometer at maximum wavelength of 450nm.

A clean sample cell was filled with 25cm^3 of sample with sulfaver 4 sulphate reagent powder pillow. This was swirled until dissolution and reaction was allowed 5 min. When the timer stopped after five minutes of the reaction, a second cell was filled with $25cm^3$ of the sample as blank. The blank was placed in the cell holder and the spectrophotometer was calibrated in the usual way.

Phosphate Determination: This was determined by the Hatch corporation phosphaver 3 phosphate method using the programme number 490 and wavelength 890nm and a DR2000 direct reading spectrophostometer. Sample cells were filled with $25cm^3$ of the rainwater sample. To one, was added phosphaver 3 phosphate reagent powder pillow. The sample cell was swirled for dissolution and introduced into the instrument for a reaction time of 2 min. the display gave the reading of the phosphate in mgL^{-1} phosphate. The reading from the blank was also recorded.

Nitrate Determination: This was also determined using the Hatch corporation Nitraver 5 nitrate method which was based on the cadmium reduction method using powdered pillows. This used programme number 355 of wavelength 500nm and a DR2000 was used for spectrophotometer read out. Sample cells were filled with $25cm^3$ of the rainwater sample. To one was added Nitraver 5 Nitrate reagent powder pillow. This was swirled to dissolve and then introduced into the instrument for a reaction time of one minute. The display gave the reading of the nitrate in mgL^{-1} nitrate nitrogen. The reading from the blank was also recorded.

Metallic ion determination: This was done using the Unicam Model 919 Atomic Absorption Spectrophotometer (A.A.S). The metallic ions determined include: Manganese, zinc, copper, iron, lead and cadmium. Stock solutions from which working standards were prepared by serial dilution as reported in Technical Bulletin (1937) using various cathode tubes specific for each element determined.

Results and Discussion

Figs. 1 and 2 are plots of pH versus rainfall (weeks) for the 2nd year and 3rd year respectively. A Philip analogy pH meter was used to monitor the pH of all the samples (Charlson and Rodhe, 1982 and Howel 1997). There are gradual increases with the frequency of the rains.

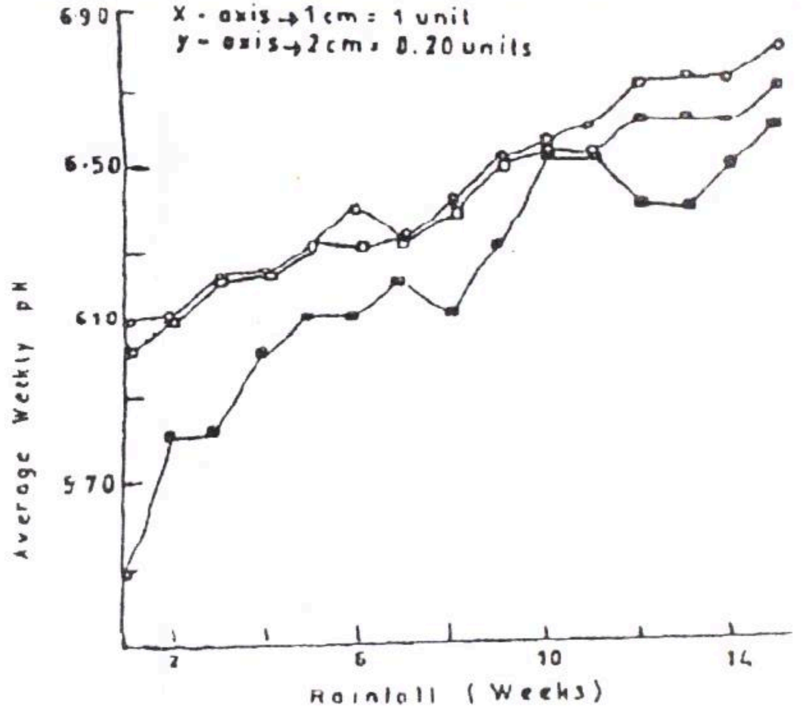


Fig. 1

Fig. 1

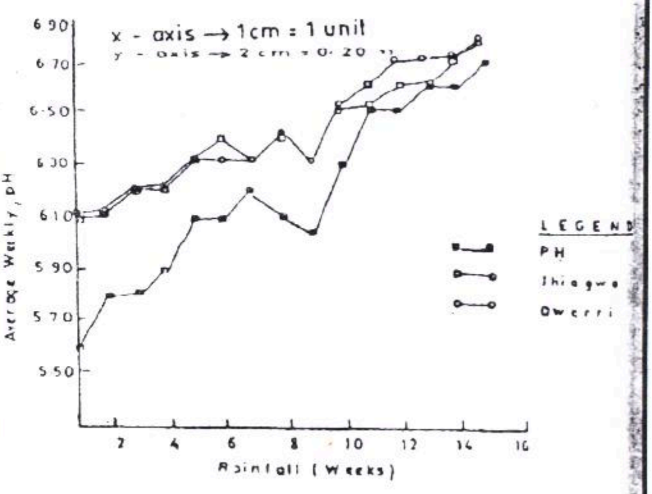


Fig. 2

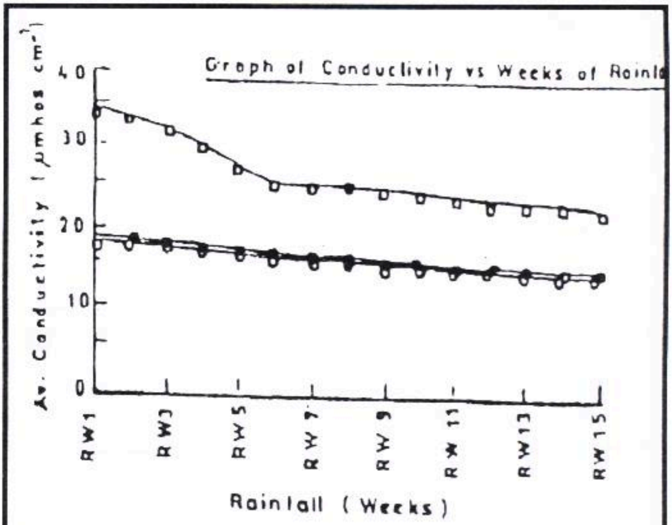


Fig. 3

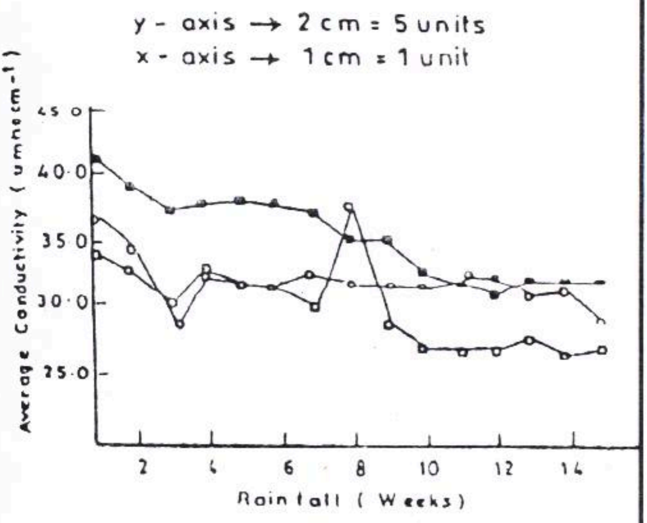


Fig. 4

Figs. 3 and 4 are plots of electrical conductivity versus weeks of rainfall for 2nd and 3rd years respectively. The conductivity (μScm^{-1}) was determined for all RWS. This indicates the concentration of ions in a sample. It is observed that the total ions in 3rd year was more than in 2nd year in each station. This could be seen from the significant increase in the sulphate concentration in 3rd year.

Sulphate in the atmosphere has its origin from gas flaring, fossil fuel combustion and automobile emissions. Sulphur is present in coal and petroleum as hydrogen sulphide, mercaptans, alkyl sulphides, alkyl sulphates, thiophens and as free sulphur. During which sulphur is oxidized to sulphur (iv) oxide, which on further oxidation gives sulphur (vi) oxide which dissolves in rain drops to produce tetraoxosulphate(vi) acid and precipitates as acid rain (Lavrov, 1978) by the reactions.

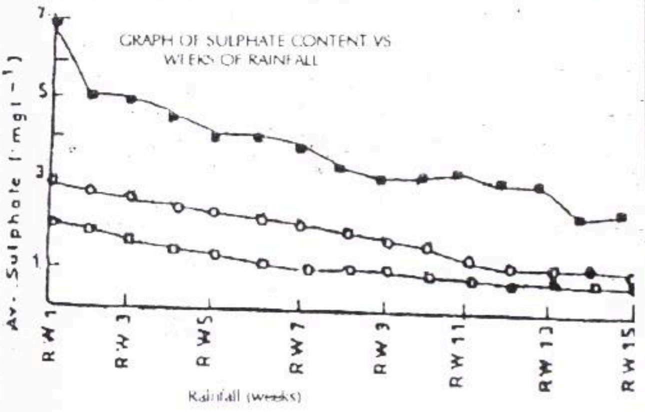

GRAPH OF SULPHATE CONTENT VS
WEEKS OF RAINFALL
Av. Sulphate (mgl−1)
7
5
3
1
RW 1
RW 3
RW 5
RW 7
RW 3
RW 11
RW 13
RW 15
Rainfall (weeks)

Fig. 5

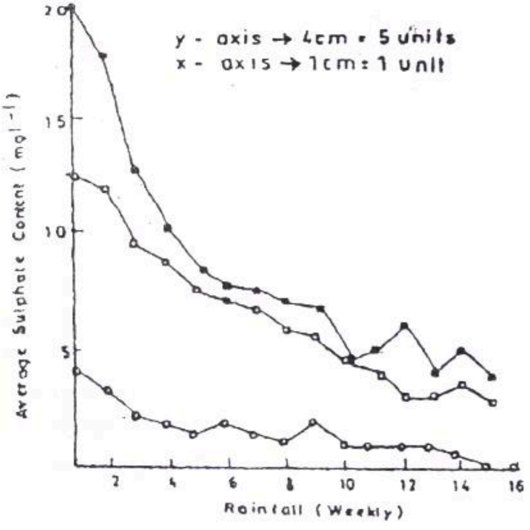

y - axis → 4cm = 5 units
x - axis → 1cm : 1 unit
Average Sulphate Content (mgl−1)
20
15
10
5
2
4
6
8
10
12
14
16
Rainfall (Weekly)

Fig. 6

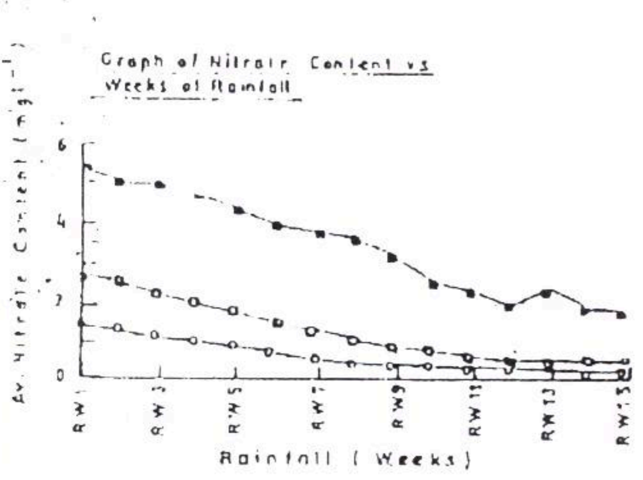

Graph of Nitrate Content vs Weeks of Rainfall
Av. Nitrate Content (mgl⁻¹)
6
4
2
0
RW1
RW3
RW5
RW7
RW9
RW11
RW13
RW15
Rainfall (Weeks)

Fig. 7

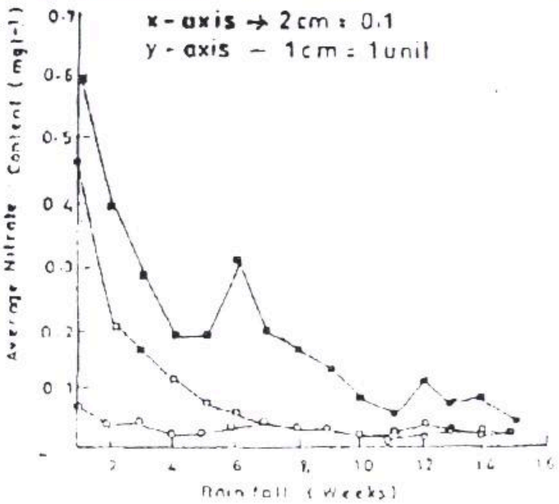

x - axis → 2cm : 0.1
y - axis – 1cm = 1unit
Average Nitrate Content (mgl-1)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
2
4
6
8
10
12
14
16
Rainfall (Weeks)

Fig 8

$$S(s) + O_2(g) \longrightarrow SO_2(g) \quad \text{.........................}1$$
$$SO_2(g) + O_3(g) \longrightarrow SO_3(g) + O_2(g) \quad \text{...............}2$$
$$SO_3(g) + H_2O(aq) \longrightarrow H_2SO_4(1) \quad \text{........................}3$$

Acid rain is one of the most insidious forms of pollution unimaginable because it alters the pH and affects aquatic lives in ponds, lakes, rivers and even the vegetation. Figs 5 and 6 indicate that the three stations have sulphate which decreased with the frequency of the rains. RWSP has the highest sulphate concentration depicting Port-Harcourt as an industrialized centre followed by Owerri.

Nitrate is emitted into the atmosphere initially as nitrogen (iv) oxide from gas flaring, biomas burning and fossil fuel combustion. With increased anthropogenic activity in the urban areas more nitrate aerosols are emitted into the atmosphere from some fertilizer companies. Nitrates dissolve in rain drops and precipitates as acid rain. Figs. 7 and 8 are graphs of nitrate against weeks of rainfall. Nitrate concentration increased with increased urbanization resulting resulting in RWSP having the highest then followed by RWSO and RWSI. These decreased with the frequency of the rains. Significant concentration of the nitrate was detected in 2nd year than in 3rd year. Oxides of nitrogen are primary pollutants which react in the atmosphere to form trioxonitrate (v) acid. This can affect the reactive nitrogen nutrients in the soil and ocean ecosystem. In addition, nitrogen monoxide takes part in the photochemical cycle of ozone. Tropospheric ozone is important in terms of atmospheric and biological perspective. Infact, acts as a green house gas and as a chemical oxidant which can cause injury to plants and animals. (Dignon et al. 1991, Heggi et al. 1990 and Spedding, 1997). The oxidation reaction are represented thus:

$$N_2O + h\nu \longrightarrow N_2 + O \qquad 4$$

$$N_2O + h\nu \longrightarrow NO + N \qquad 5$$

$$NO + O_2 \longrightarrow NO_2 + O \qquad 6$$

$$NO_2 + h\nu \longrightarrow NO + O \qquad 7$$

$$O + O_2 + M \longrightarrow O_3 + M \qquad 8$$

(M is any third body, usually N_2 or O_2)

$$NO + O_3 \longrightarrow NO_2 + O_2 \qquad 9$$

$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3 \qquad 10$$

Phosphate, like sulphate and nitrate, adds to the pH of the rainwater. RWSP rainwater has the highest PO_4^{3-} concentration followed by RWSO and RWSI. This shows that the concentration increased in the urban than in the rural. Port-Harcourt is an industrialized city, hence the high PO_4^{3-} concentration may have come from the fertilizer company fumes. This concentration decreased with the frequency of the rains. Probably due to the early heavy rains of 3rd year, phosphate was not detected but was detected in 2nd year.
Trace elements in the atmosphere exist in particulate and may be regarded in three ways:
1. Potentially toxic pollutants, 2. Nutrients and 3.Tracers of transfer mechanisms. These elements may be soil derived Materials blown from the ground, the oceans, volcanic eruptions, industrial and domestic pollution (Egereonu and Onuchukwu, 2000).

The results for the maximum, minimum, mean, the standard deviation etc of trace elements in rainwater are as shown in table 1-6. These concentrations are within the prevailing levels of many other industrial cities (Terhaar et al. 1967). The concentration of these metals in the collected samples was generally low except for the early rains when higher values were recorded Metal concentrations for 2nd year were in the order

Table 1: Analytical data on the chemical analysis of the Port-Harcourt rainwater in the 2nd Year

	Amount of rainfall (mm)	pH	Elect conductivity μScm^{-1}	SO_4^{2-} mgL^{-1}	PO_4^{2-} mgL^{-1}	NO_3^- mgL^{-1}	Mn^{2+} mgL^{-1}	Zn^{2+} mgL^{-1}	Cd^{2+} mgL^{-1}	Cu^{2+} mgL^{-1}	Fe^{2+} mgL^{-1}
Maximum	285	6.60	36.00	7.00	1.20	5.40	0.20	0.316	0.020	0.120	0.52
Minimum	100	5.50	23.60	1.80	0.01	1.96	0.091	0.021	0.020	0.050	0.040
Mean	205.3	6.190	27.540	3.655	3.537	3.537	0.019	0.086	0.020	0.011	0.046
Standard deviation	3.700	0.642	1.350	0.4940	0.486	0.486	0.035	0.076	0.037	0.027	0.055

Table 2: Analytical data on the chemical analysis of the Owerri rainwater in the 2nd Year

	Amount of rainfall (mm)	pH	Elect conductivity μScm^{-1}	SO_4^{2-} mgL^{-1}	PO_4^{2-} mgL^{-1}	NO_3^- mgL^{-1}	Mn^{2-} mgL^{-1}	Zn^{2+} mgL^{-1}	Fe^{2+} mgL^{-1}
Maximum	265	6.80	18.60	3.00	0.41	1.70	0.350	1.400	0.051
Minimum	100	6.10	15.65	1.85	0.01	0.43	0.060	0.057	0.040
Mean	195.9	6.43	16.863	1.778	0.108	0.838	0.225	0.556	0.047
Standard deviation	3.614	0.655	1.060	0.344	0.085	0.236	0.122	0.193	0.056

Table 3: Analytical data on the chemical analysis of the Ihiagwa rainwater in the 2nd year

	Amount of rainfall (mm)	pH	Elect conductivity μScm^{-1}	SO_4^{2-} mgL^{-1}	PO_4^{2-} mgL^{-1}	NO_3^- mgL^{-1}	Mn^{2-} mgL^{-1}	Zn^{2+} mgL^{-1}	Fe^{2+} mgL^{-1}
Maximum	268	6.70	19.20	2.00	1.00	3.00	0.091	2.964	0.075
Minimum	100	6.00	16.10	0.63	0.01	0.63	0.020	1.300	0.049
Mean	198	6.39	17.310	1.092	0.149	1.499	0.026	1.904	0.051
Standard deviation	3.633	0.652	1.074	0.270	0.099	0.316	0.042	0.356	0.058

Table 4: Analytical data on the chemical analysis of the Port-Harcourt rainwater in the 3rd year.

	Amount of rainfall (mm)	pH	Elect conductivity µScm^{-1}	SO_4^{2-} mgL^{-1}	NO_3^- mgL^{-1}	Zn^{2+} mgL^{-1}	Cu^{2+} mgL^{-1}
Maximum	267	6.52	441.0	20.40	0.60	3.480	0.100
Minimum	101	5.39	30.90	3.80	0.04	0.050	0.010
Mean	199.9	5.99	35.51	1.945	0.025	1.295	0.525
Standard deviation	3.632	0.632	1.539	0.331	0.041	0.086	0.187

Table 5: Analytical data on the chemical analysis of the Owerri rainwater in the 3rd Year.

	Amount of rainfall (mm)	pH	Elect conductivity µScm^{-1}	SO_4^{2-} mgL^{-1}	NO_3^- mgL^{-1}	Zn^{2+} mgL^{-1}	Cu^{2+} mgL^{-1}
Maximum	227	6.85	35.90	4.24	0.60	2.510	1.200
Minimum	56	6.06	28.50	0.32	0.01	1.100	0.020
Mean	178.40	6.58	31.45	1.704	0.025	0.882	0.525
Standard deviation	3.400	0.662	1.448	0.337	0.041	0.242	0.187

Table 6: Analytical data on the chemical analysis of the Ihiagwa rainwater in the 2nd Year.

	Amount of rainfall (mm)	pH	Elect conductivity µScm	SO_4^{2-} mgL^{-1}	NO_3^- mgL^{-1}	Zn^{2+} mgL^{-1}	Cu^{2+} mgL^{-1}
Maximum	215	6.99	34.10	12.80	0.22	3.050	0.100
Minimum	86	6.45	27.00	3.20	0.01	0.080	0.075
Mean	156.53	6.66	29.55	6.881	0.088	1.414	0.012
Standard deviation	10.435	0.665	1.404	0.667	0.077	0.307	0.028

Zn>Fe>Mn>Cu with their levels progressively decreasing with the frequency of the rains. Cadmium was only reported in Table 1 for one of the weeks and was never detected further. Maximum concentration of above 1.30mg^{-1} for copper was obtained for RWSO and 0.12mg^{-1}

for RWSP in 2nd year. Maximum concentration of 2.96mg^{1} for zinc was obtained for RWSI while above 0.30mg^{-1} was obtained for RSWP and RWSO in 2nd year. The same year maximum concentration of iron for the three stations was above 0.05mg^{-1}.

Metal concentration for 3rd year was in the order Zn>Cu with their levels progressively decreasing with the frequency of the rains. Maximum concentration of 3.48mg^{-1} for zinc was obtained for RWSO and RWSI. As a result of the wide uses of copper and zinc products, they were present in majority of all the rainwater sampled except in Table 3 of 2nd year. As a result of the discontinuation of tetralky lead in gasoline by the Nigeria National Petroleum Company, lead was not detected in all the rainwater sampled for 2nd year and 3rd year. Iron was not detected in the three stations in 3rd year but was detected in 2nd year.

The result of the two year sampling studies suggest that the annual soluble deposition may contribute to a notable percentage of the available fraction in the soil in respect of a number of elements. Under the influence of the harmattan wind, coupled with the high temperature reached by soils and the strong diurnal thermic turbulence resulting from these during the dry season, these are factors which favour the production of the dust and its suspension in the atmosphere. Thus, the air particulate levels of many elements are in excess of an order of magnitude greater than the levels that would, under normal conditions, be-recorded. The higher concentrations of trace metals (and anions) in the early rains may be owing to the aggregation of the metal particles and anions in the atmosphere. It may hence, be concluded that rainfall and dry sedimentation are the major routes for removing trace metals and anions from the atmosphere.

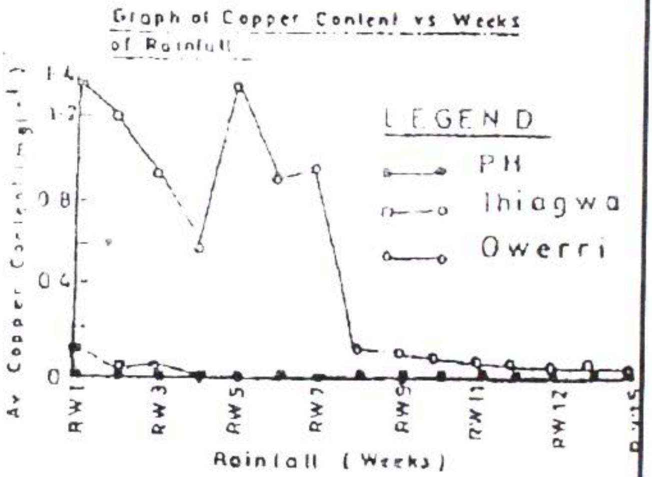

Graph of Copper Content vs Weeks of Rainfall
Av Copper Content (mgl-1)
1.4
1.2
0.8
0.4
0
LEGEND
PH
Ihiagwa
Owerri
RW1
RW3
RW5
RW7
RW9
RW11
RW12
Rainfall (Weeks)

Fig. 11

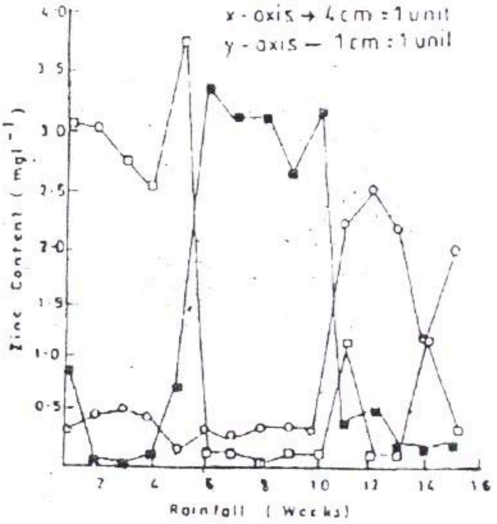

x - axis → 4cm = 1 unit
y - axis — 1cm : 1 unit
Zinc Content (mgl-1)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2
4
6
8
10
12
14
16
Rainfall (Weeks)

Fig. 10

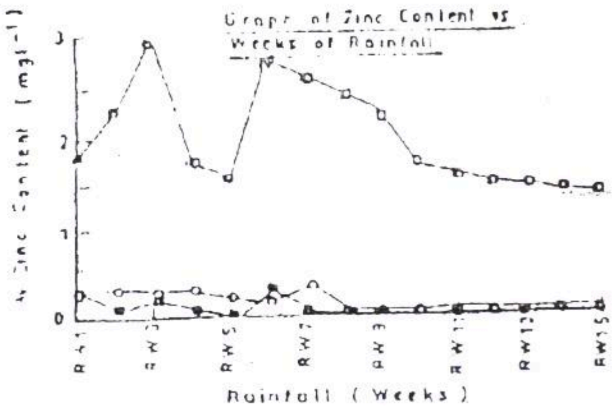


Fig. 9

Fig. 11

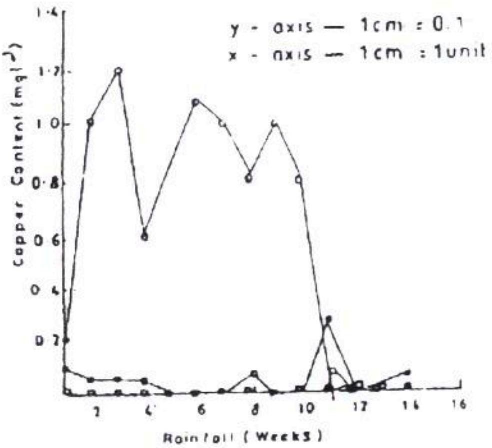


Fig. 12

Fig 9-10 shows the distribution of trace metals, anions, electrical conductivity, and pH. The results exhibit a range of concentrations between the early and subsequent rains, suggesting strong influence from anthropogenic sources. The distribution patterns for zinc and copper are similar as shown in figs. 9 and 10 for 2nd year and figs.11 and 12 for 3rd year respectively.

Tables 1 – 6 show the standard deviation of these metals in the stations for the period of study. Rains with low copper and zinc concentrations were more frequent than rains with high concentrations. Rainfall is one of the precipitation processes that washes down these products onto the surface of the land. The mechanism of wet deposition differs from that of dry deposition because the rates of dry deposition are dependent on pollution concentration and deposition velocity which, in turn, depend on the precipitation rate, the wash-out ratio and the ambient air concentration.

According to Ayodele (1996), the sources of the anions and cations in rainwater appear to be dust of which soil appear to be major contributor because of its concentration in the atmosphere during the dry season and pollution from industries. Therefore, the concentrations of these anions and cations are soil derived as the temporal effects are evident with the decreasing concentrations in the succeeding rains. Water as a result of its molecular structure, high di-electric constant and low electrical conductivity is capable of dissolving many substances.

Analysis of rainfall data from the different satellite stations, within the study period has shown a significant trend of increase for sulphate and zinc. The exceptionally high trace metal values have tended to be with the early rains that were accompanied with the strong gale-force winds. Meterological conditions affect the concentration of trace metals in rainwater. It has been observed that slow, even rainfalls are more effective in removing these metals from the atmosphere than brisk showers, although rain collected in thunder storms did sometimes contain a high concentration of these metals (Egereonu and Onuchukwu 2000).

5.0 Management of Urban Solid Waste

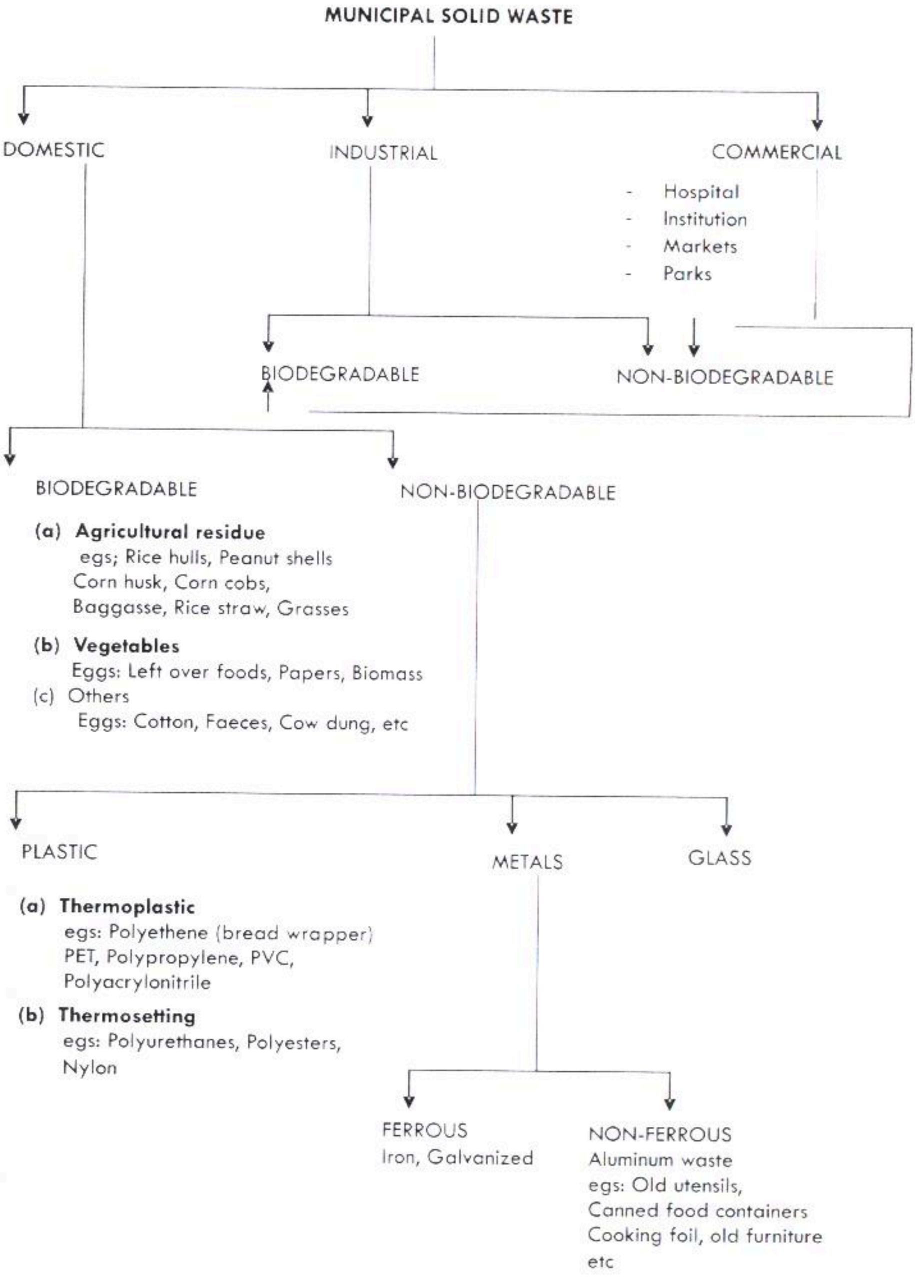
In Nigeria today, solid waste is a menace as dumping sites are seen everywhere even along major roads. Uncleared heaps of refuse may lead to the outbreak of epidemics. To get rid of refuse or indiscriminate dumping of wastes, there should be a proper co-ordination of the refuse disposal scheme by government. Government needs to double its efforts on public enlightenment campaign to ensure that members of the public adhere strictly to the environmental laws (Onuchukwu et al. 2006).

Also, the transit point for refuse collection must be close to the people, that is, should be a short distance for refuse collectors to dispose the garbage. While environmental sanitation corps must be encourage, the neighbourhood watchers should be involved in monitoring indiscriminate dumping of refuse (Agunwa, 2003). There are many suggestions on how to clear the dumping sites on the roads, but this is aimed at easy sorting of the solid waste and also converting the waste into more useful product through a chemical treatment, thereby making the nation and the environment healthier and safer.

Environmental engineers and scientist have agreed that there is need for new, searching reassessment of current policies for and methods of managing pollutants (Stumn et al. 1972). Metals, conservative elements, are utilized by many different types of industries in both developed and developing countries. Metal waste when released into the environment without restraint pose risk to human health and the environment and may accumulate in the food chain or sensitive ecosystem. The current pattern of disposal of solid waste to the environment, and the risk associated with such practices, appear to many to be adequate justification to reassess current policies and practices for solid waste management.

An observation of the Owerri Municipal council waste management, for example, reveals that the sanitary landfill method of solid waste disposal is not efficient. It was discovered that the sanitary landfill method technology wherein solid waste are place on land (typically underlain by impermeable soils) which protect the underground water, prepared with drainage surface runoff, and constructed with gas collection and ventilation of flaring system. Within the landfill, each day's solid waste is formed into cell and covered with soil to minimize water infiltration, migrate odours and limit vector breeding (Patterson et al. 1987, Egereonu, 2003 and Egereonu 2005). The amount of solid waste generated per household in Nigeria at present is increasing daily. Due to lack of waste management, individuals now resorted to dumping waste on our streets and roads. Proper categorization of our solid waste and chemical treatment of these wastes will enhance a healthy environment (Egereonu, 2005).

There is no hard and fast rule to the categorization of solid waste because waste comprises a wide categorizations. Solid waste can be generated from a wide range of sources including industrial, commercial, agriculture and domestic activities. A broader categorization of solid waste may include agricultural waste, hospital wastes, domestic waste, waste from a variety of industries, petrochemical waste, mining wastes, chemical waste arising from research and development and waste from automobile workshops (Vogler 1985).


MUNICIPAL SOLID WASTE
DOMESTIC
INDUSTRIAL
COMMERCIAL
- Hospital
- Institution
- Markets
- Parks
BIODEGRADABLE
NON-BIODEGRADABLE
BIODEGRADABLE
(a) Agricultural residue
egs; Rice hulls, Peanut shells
Corn husk, Corn cobs,
Baggasse, Rice straw, Grasses
(b) Vegetables
Eggs: Left over foods, Papers, Biomass
(c) Others
Eggs: Cotton, Faeces, Cow dung, etc
NON-BIODEGRADABLE
PLASTIC
(a) Thermoplastic
egs: Polyethene (bread wrapper)
PET, Polypropylene, PVC,
Polyacrylonitrile
(b) Thermosetting
egs: Polyurethanes, Polyesters,
Nylon
METALS
GLASS
FERROUS
Iron, Galvanized
NON-FERROUS
Aluminum waste
egs: Old utensils,
Canned food containers
Cooking foil, old furniture
etc

The domestic waste metals are usually consists of aluminum, tin and zinc as shown in Fig. 1. Most canned foods are stored in aluminum, tin and zinc containers. Aluminum waste fall under the category of non-ferrous metal and non-biodegraded domestic waste (Fig 1.). These metal waste can be converted to more useful products through chemical treatments. Aluminum wastes are chemically treated to form alum-a double salt. The high yields of the alum produced from waste aluminum cans shows that this method of alum production is very feasible. Alum produced from aluminum foil is of very low yield because the foil is not entirely aluminum but mixed with paper and other additives which are sources of impurities.

Table 7: Physicochemical data of rainwater from Onitsha

	Amount of Rainfall (mm)	pH	Elect conduct µScm^{-1}	Cl- mgL^{-1}	TDS mgL^{-1}	TSS mgL^{-1}	Total Hardness mgL^{-1}	Ca Hardness mgL^{-1}	Mg Hardness mgL^{-1}	Total Fe mgL^{-1}	NO_3 mgL^{-1}
Maximum	258	6.80	23.50	13.50	35.20	22.80	60	24	3.5	---	0.704
Minimum	180	6.00	18.80	8.90	24.10	19.60	42	17	25	---	0.189
Mean	219	6.40	21.23	11.87	30.08	21.06	52.3	20.9	30.7	---	0.406
Standard Deviation	29.67	0.23	1.07	1.26	3.69	1.29	4.57	1.43	1.97	---	0.225
WHO Standard		6.5-8.5	50	250	1000	500	500	70	0.3	15	

Table 8: Physicochemical data of rainwater from Nkpor

	Amount of Rainfall (mm)	pH	Elect conduct µScm^{-1}	Cl- mgL^{-1}	TDS mgL^{-1}	TSS mgL^{-1}	Total Hardness mgL^{-1}	Ca Hardness mgL^{-1}	Mg Hardness mgL^{-1}	Total Fe mgL^{-1}	NO_3 mgL^{-1}
Maximum	242	6.60	23.50	10.00	29.50	20.60	68	27.20	40.80	0.120	0.704
Minimum	180	6.10	17.20	7.40	22.10	17.20	46	18.40	27.60	0.001	0.189
Mean	210	6.39	18.95	8.76	25.84	18.70	56.4	22.56	33.84	0.060	0.406
Standard Deviation	24.67	0.11	1.72	1.70	2.63	1.77	6.27	2.77	3.76	0.037	0.09
WHO Standard		6.5-8.5	50	250	1000		500	500	70	0.30	15

The pH of rainwater in both areas is slightly acidic with mean value o 6.40 and 6.39 for Onitsha and Nkpor respectively and standar deviation of 0.23 and 0.11 from the mean respectively. For Onitsh the lowest pH value was 6.00 and 6.10 for Nkpor. The acidity of the rainwater could be attributed to anthropogenic emissions and bush burning.

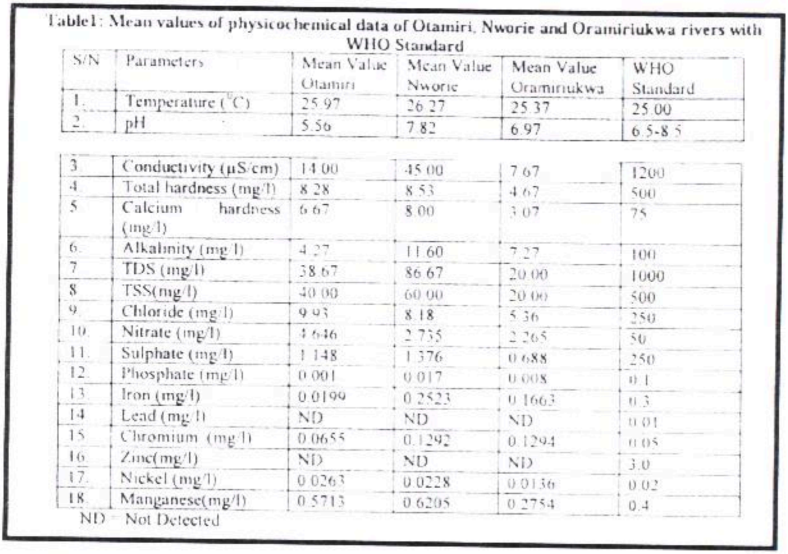


Table1: Mean values of physicochemical data of Otamiri, Nworie and Oramiriukwa rivers with WHO Standard

S/N	Parameters	Mean Value Otamiri	Mean Value Nworie	Mean Value Oramiriukwa	WHO Standard
1.	Temperature (°C)	25.97	26.27	25.37	25.00
2.	pH	5.56	7.82	6.97	6.5-8.5
3.	Conductivity (μS/cm)	14.00	45.00	7.67	1200
4.	Total hardness (mg/l)	8.28	8.53	4.67	500
5.	Calcium hardness (mg/l)	6.67	8.00	3.07	75
6.	Alkalinity (mg/l)	4.27	11.60	7.27	100
7.	TDS (mg/l)	38.67	86.67	20.00	1000
8.	TSS(mg/l)	40.00	60.00	20.00	500
9.	Chloride (mg/l)	9.93	8.18	5.36	250
10.	Nitrate (mg/l)	4.646	2.735	2.265	50
11.	Sulphate (mg/l)	1.148	1.376	0.688	250
12.	Phosphate (mg/l)	0.001	0.017	0.008	0.1
13.	Iron (mg/l)	0.0199	0.2523	0.1663	0.3
14.	Lead (mg/l)	ND	ND	ND	0.01
15.	Chromium (mg/l)	0.0655	0.1292	0.1294	0.05
16.	Zinc(mg/l)	ND	ND	ND	3.0
17.	Nickel (mg/l)	0.0263	0.0228	0.0136	0.02
18.	Manganese(mg/l)	0.5713	0.6205	0.2754	0.4

ND = Not Detected

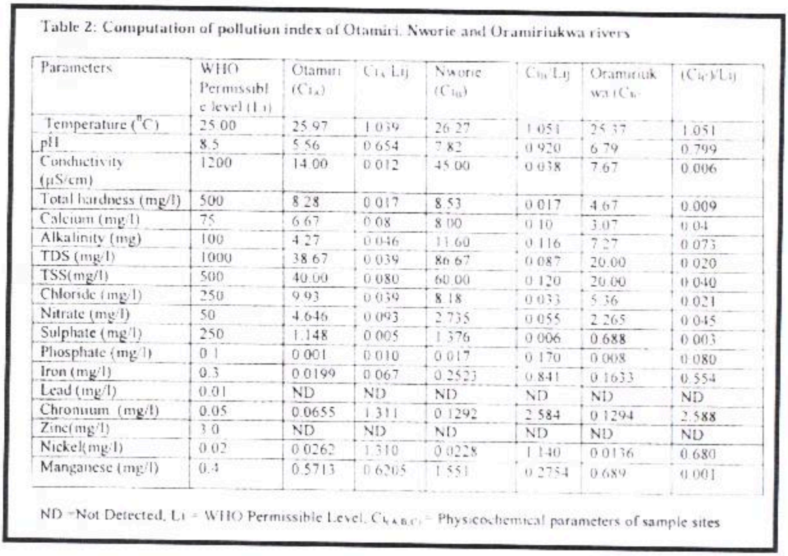


Table 2: Computation of pollution index of Otamiri, Nworie and Oramiriukwa rivers

Parameters	WHO Permissible level (Li)	Otamiri (C_{iA})	C_{iA}/Li	Nworie (C_{iB})	C_{iB}/Li	Oramiriukwa (C_{iC})	(C_{iC})/Li
Temperature (°C)	25.00	25.97	1.039	26.27	1.051	25.37	1.051
pH	8.5	5.56	0.654	7.82	0.920	6.79	0.799
Conductivity (μS/cm)	1200	14.00	0.012	45.00	0.038	7.67	0.006
Total hardness (mg/l)	500	8.28	0.017	8.53	0.017	4.67	0.009
Calcium (mg/l)	75	6.67	0.08	8.00	0.10	3.07	0.04
Alkalinity (mg)	100	4.27	0.046	11.60	0.116	7.27	0.073
TDS (mg/l)	1000	38.67	0.039	86.67	0.087	20.00	0.020
TSS(mg/l)	500	40.00	0.080	60.00	0.120	20.00	0.040
Chloride (mg/l)	250	9.93	0.039	8.18	0.033	5.36	0.021
Nitrate (mg/l)	50	4.646	0.093	2.735	0.055	2.265	0.045
Sulphate (mg/l)	250	1.148	0.005	1.376	0.006	0.688	0.003
Phosphate (mg/l)	0.1	0.001	0.010	0.017	0.170	0.008	0.080
Iron (mg/l)	0.3	0.0199	0.067	0.2523	0.841	0.1633	0.554
Lead (mg/l)	0.01	ND	ND	ND	ND	ND	ND
Chromium (mg/l)	0.05	0.0655	1.311	0.1292	2.584	0.1294	2.588
Zinc(mg/l)	3.0	ND	ND	ND	ND	ND	ND
Nickel(mg/l)	0.02	0.0262	1.310	0.0228	1.140	0.0136	0.680
Manganese (mg/l)	0.4	0.5713	0.6205	1.551	0.2754	0.689	0.001

ND =Not Detected, Li = WHO Permissible Level, $C_{i(A,B,C)}$ = Physicochemical parameters of sample sites

Lead and zinc were not detected at the three sample sites. The mean concentration of iron in Nworie and Oramiriukwa were 0.2523 and 0.1663mgL-1 respectively though they fell within the permissible level. These results suggest that the water bodies are at risk of high iron (Fe) contamination in the future if anthropogenic activities around these sample stations are left unchecked. The level of chromium in the three rivers fell outside the permissible limit with mean values of 0.0655, 0.1292 and 0.1294mgL^{-1} for Otamiri, Nwaorie and Oramiriukwa respectively. The contamination may be as a result of the mechanic workshop located close to these rivers. The mean values for nickel and manganese for the three rivers are given as 0.0263, 0.0228 and 0.0136mgL^{-1} for Otamiri, Nworie and Oramiriukwa respectively and 0.5713, 0.6205 and 0.275.mgL^{-1} for Otamiri, Nworie and Oramiriukwa respectively. The appreciably high values could be attributed to natural and anthropogenic activities.

Table 10 gives the pollution indexes of the three rivers by computing the parameters for water quality with the World Health Organization permissible levels. Each value of Ci/Lij shows the relative pollution contributed by the single item. A value of 1.0 is the critical value for each Ci/Lij. Values greater than 1.0 indicate a critical condition under which proper treatment is necessary before the water can be made use of. The overall pollution indexes Pij computed for Otamiri, Nworie and Oramiriukwa rivers are 1.04, 1.84 and 1.85 respectively.

Table 11: Levels of physico-chemical analysis of selected groundwater in Rivers State

LOCATION WHO	PORT-HARCOURT		AKPOR KINGDOM		ELELENWO		ELELE		OBIGBO		
Parameter	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Temperature (^{0}C)	26.4-24.6	25.4	24.24	24.0	26.5-26.1	26.25	25.7-24.7	25.08	26.2-24.6	26.38	25^{0}C
pH	6.60-5.40	6.26	6.60-6.40	6.50	6.06-4.60	5.84	6.10-4.95	5.45	6.62-5.90	6.334	6.5-8.5
Elect. Conduct (μscm^{-1})	18.0-16.3	37.9	117.2-12.8	140.35	16.1-8.1	17.50	17.5-12.0	15.05	56.9-19.3	38.03	100
Total dis solids (mgL^{-1})	48.2-8.7	7.75	58.6-6.3	20.1	9.5-7.9	8.55	8.1-6.0	7.5	27.6-8.3	18.05	1000
Alkalinity (mgL^{-1})	7.6-2.4	4.8	7.4-2.4	4.75	8.02.8	4.7	6.7-5.0	5.35	6.5-3.2	4.78	500
Calcium hardness (mgL^{-1})	12.0-4.9	7.13	12.8-3.1	6.48	11.2-4.6	6.98	6.4-4.3	5.18	12.32	6.73	500
Mag. Hardness (mgL^{-1})	3.0-1.3	1.8	1.5-0.9	1.65	28-1.2	1.78	1.6-1.1	13	3.0-0.8	1.8	
Total hardness (mgL^{-1})	6.0-1.5	8.88	16.0-4.0	8.13	14.0-5.8	8.75	8.0-5.4	6.48	15.0-4.0	8.55	500
Fe(mgL^{-1})	0.112- 0.00	0.112	0.911- .05	0.069	0.123- 0.056	0.103	0.168- 0.52	0.79	0.154- 0.59	0.11	0.3
Cr(mgL^{-1})	0.022- 0.00	0.093	0.031- 0 .00	0.007	0.031- 0.00	0.165	0.013- 0.00	0.003	0.017- 0.00	0.0008	0.05
Mn(mgL^{-1})	0.25-0.00	0.006	-	-	0.38-0.00	0.014	-	-	0.018- 0.00	0.009	0.3
Zn((mgL^{-1})	0.15- 0.00	0.07	-	-	0.192- 0.00	0.115	-	-	0.190- 0.00	0.048	1.5
Langelier sat.index	-3.66- (-4.99)	-4.13	-3.5- (-4.22)	-3.96	-3.54- (-4.24)	-4.02	-4.25 (-5.52)	-4.95	-3.40- (4.48)	-4.095	
Nitrate (mgL^{-1})	0.009- 0.008	0.0045	0.004- 0.001	0.0018	0.019- 0.001	0.0045	0.008- 0.001	0.003	0.026- 0.001	0.009	10
Sulphate (mgL^{-1})	2.50- 0.334	1.12	0.838-0.167	0.37	0.803- 0.167	0.350	0.834- 0.162	0.521	0.568- 0.10	0.247	400
Phosphate (mgL-1)	3.00- 1.16	2.00	1.33-1.253	1.43	4.00- 0.00	2.02	4.33-1.33	2.2	3.43-1.38	2.458	10
Chloride(mgL-1)	30.10- 18.46	7.48	17.04-2.84	8.52	17.33- 3.67	11.75	9.94-2.87	7.36	19.50-	10.29 2.10	250

The results of the analyses showed that all the samples from Port Harcourt and environs have negative langelier saturation index values ranging from 04.99 to -3.66. The least value of -4.99 was obtained for Rumukwuta while Rumuola has value of -3.66. Akpor kingdom has values ranging from -4.22 to -3.50, with Choba having the least value of -4.22 and Ozuoba -3.50. Elelenwo has saturation index ranging from -4.24 to -3.59. Eleme has saturation index ranging from -5.52 to -4.24 while Rumuoheneze has value of -3.59. Isiokpo has the least value of -5.52 while Obelle has value of -4.29. At Obigbo saturation index ranged from -4.48 to -3.40. Okoloma has the value of -3.40. From the results, it can be concluded that all the samples have corrosive potential. Langelier saturation index is a vital parameter in determining encrustation and corrosion potentials of water. (Garg, 2002).

Sulphate concentrations in the sample are within the acceptable limit 250mg^{L-1}. In Port-Harcourt the sulphate concentration ranged 0.334-2.5mgL^{-1} with a mean of 0.834mgL^{-1}. Akpor kingdom, Elelenwo and Obigbo have sulphate values range of 0.167 – 3.43mgL^{-1}. All nitrate values of groundwater within the study area are within the acceptable limit of less than10mgL^{-1}. Nitrate compounds are soluble in water. Nitrates in water comes from agricultural and industrial waste. And additional source is from NO_2 produced by lightening discharges and from bacterial actions, activities of micro organism or evaporation. Nitrate is taken out of natural water only through activities of micro organisms or evaporation. Nitrates in drinking water at levels above 45mgL^{-1} is a health risk for infants less than six months old. High nitrate levels in drinking water causes blue baby syndrome. High nitrate levels of nitrate also leads to eutrophication. Nitrate concentrations in the study ranged 0.001 – 0.026mgL^{-1}.

FINDINGS

In the light of World Health Organization standard, it could be inferred from the results that values of different parameters showed no pollution of the groundwater. The negative values of the Langelier saturation index obtained in all the samples showed corrosive tendency of the groundwater, Groundwater having corrosive potential has resulted in the failure of most wells.

Table 1: Physicochemical data of Groundwater investigations in Cross Rivers State, Nigeria

PARAMETERS	EFUT TOWN		AKIN TOWN		BIG QUA TOWN		IKOT ANSA TOWN		IKOT OMINI		WHO
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Temperature (°C)	24.50-24.30	24.64	24.50-24.100	24.26	24.70-24.40	24.56	24.80-24.50	24.66	25.00-24.20	24.56	25
pH	7.60-6.40	7.20	7.60-5.80	6.72	7.40-6.00	6.68	7.00-5.80	6.24	7.40-5.80	6.56	6.5-8.5
Conductivity (µ scm⁻¹)	22.00-18.00	20.00	30.00-19.00	24.20	40.00-21.00	30.20	50.00-18.00	30.40	40.00-15.00	28.80	400
Total diss solids (mgL⁻¹)	61.00-11.00	26.60	158.00-8.00	48.80	243.00-10.00	88.20	150.00-30.00	95.00	156.00-11.00	106.40	1000
Acidity (mgL⁻¹)	0.90-0.20	0.40	0.90-0.04	0.31	2.00-0.00	0.82	0.20-0.00	0.08	0.40-0.001	0.47	6.5
Alkalinity (mgL⁻¹)	6.00-3.00	4.40	71.00-32.00	35.80	240.00-10.00	94.40	172.00-14.00	97.20	[illegible]	161.80	100
Total Hardness (mgL⁻¹)	17.00-8.00	12.00	11.00-8.00	9.40	14.00-7.00	10.40	16.00-12.00	4.00	12.00-8.00	[illegible]	500
Calcium hardness (mgL⁻¹)	10.00-5.00	7.60	5.00-3.00	4.00	7.00-2.00	5.66	9.00-5.00	4.00	8.00-4.00	3.67	70
Magnesium. hardness (mgL	7.00-3.00	4.60	6.00-4.00	5.00	4.00-4.30	5.60	9.00-5.00	7.00	6.00-2.00	4.33	70
Iron (mgL⁻¹)	0.134-0.11	0.12	0.052-0.026	0.04	0.21-0.01	0.09	0.20-0.01	0.368	0.77-0.036	0.05	0.3
Sulphate (mgL⁻¹)	0.36-0.31	0.34	0.31-0.00	0.42	3.67-0.05	3.57	33.50-0.09	14.47	2.44-0.20	0.42	[illegible]
Chloride (mgL⁻¹)	21.22-8.12	19.59	32.65-15.01	28.57	33.65-13.12	22.47	34.00-20.00	[illegible]	25.00-21.22	27.40	250
Phosphate (mgL⁻¹)	2.67-4.58	1.79	2.46-0.33	1.21	2.67-0.90	1.78	2.64-0.80	1.72	2.57-0.05	0.77	0.1
Nitrate (mgL⁻¹)	[illegible]	0.037	0.11-0.10	0.26	0.11-0.01	0.056	[illegible]	0.074	[illegible]	0.064	45
Saturation Index	27.2-75.40	51.00	113.20-21.00	94.20	59.50-25.70	16.00	81.40-156	37.50	[illegible]	45.45	
Parameters	Akpa Buyo Town		Iwuru Town		Akamkpa Town		Awi Town		Odukpani Town		WHO
	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean	
Temperature (°C)	24.70-24.40	24.53	24.50-24.20	24.33	24.00-24.00	24.33	24.70-24.70	24.40	24.50-24.40	[illegible]	25
pH	7.00-6.40	6.73	7.00-5.80	6.57	7.40-5.80	6.53	7.40-6.80	7.10	7.20-5.80	[illegible]	6.5-8.5
Conductivity (µ scm⁻¹)	40.00-25.00	31.67	137.0-36.00	73.63	51.00-8.00	33.25	40.00-21.00	30.40	[illegible]	33.42	1400
Total diss solids (mgL⁻¹)	150.00-121.00	134.00	100.00-30.00	90.36	21.00-12.00	44.25	33.00-21.00	23.00	[illegible]	[illegible]	1000
Acidity (mgL⁻¹)	0.04-0.02	0.13	0.30-0.02	0.05	0.54-0.00	0.12	0.11-0.02	0.05	[illegible]	0.05	6.5
Alkalinity (mgL⁻¹)	50.00-30.00	106.00	172.00-16.00	32.33	50.00-30.00	44.75	72.00-32.00	8.00	[illegible]	[illegible]	100
Total Hardness (mgL⁻¹)	9.00-7.00	8.00	14.00-9.00	14.66	12.00-5.00	10.25	14.00-11.00	12.33	[illegible]	11.67	500
Calcium hardness (mgL⁻¹)	6.00-2.00	4.00	9.00-4.00	7.66	8.00-5.00	5.60	7.00-4.00	5.66	9.00-6.00	7.67	70
Mag. hardness (mgL⁻¹)	5.00-3.00	3.67	6.00-5.00	4.00	5.00-4.00	0.075	8.00-5.00	6.67	5.00-3.00	4.00	70
Iron (mgL⁻¹)	0.21-0.01	0.11	0.11-0.01	0.053	0.121-0.01	0.33	0.12-0.03	0.015	0.56-0.04	0.048	0.3
Sulphate (mgL⁻¹)	0.44-0.27	0.33	0.44-0.21	0.34	0.44-0.2	0.28	0.33-0.04	0.16	0.33-0.04	[illegible]	400
Chloride (mgL⁻¹)	11.20-0.23	0.79	32.00-20.30	27.66	32.00-18.00	25.40	18.00-9.70	13.85	33.00-20.00	23.33	250
Phosphate (mgL⁻¹)	0.65-0.47	0.24	6.33-0.33	2.37	1.43-0.33	0.31	0.43-0.21	0.31	0.34-0.11	0.22	0.1
Nitrate (mgL⁻¹)	0.11-0.08	0.08	0.11-0.01	0.32	0.33-0.21	0.12	0.50-0.03	0.28	0.34-0.11	0.32	45
Saturation Index	8.30-(-142.6)	-67.15	121.20-(-13.00)	55.10	98.30-(-112)	-6.85	106.50-20.7	42.90	95.00-(-27.2)	33.9	

Metalic ions like Zn, Cr, Cu, and Cd were not detected in the groundwater of Cross River State but rather Fe was detected. Values of the Fe obtained in the study area ranged between 0.04-0.09mgL^{-1}. Values obtained fell below the recommended value of 0.3 mgL^{-1}. The groundwater in Etut town has negative saturation indexes depicting corrosive nature of the groundwater as shown in the Table. Groundwater in Big Qua and Akpabuyo has more negative saturated index values indicating high corrosive and less encrustation in the area. Akin, Ikot Ansa, Ikot Omini, Iwuru, Akamkpa, Awi and Odupani towns showed high positive index value and less negative index value depicting more encrustation effect and less corrosive effect in the area. The positive saturation index showed that the groundwater is encrustating and negative saturation index showed that the groundwater is corrosive. The saturation index in the study area range from -159 to +131.6.

Alkalinity measurement is very important in this study in that it is involved in corrosion control. It must also be determined in order that langelier or saturation index can be calculated. Saturation index can be either negative or positive and rarely zero. A saturation index of zero indicates that the water is balance and is neither scale forming, that is, encrustating or corrosive. A corrosive water can react with the household plumbing and metal fixtures resulting in the deterioration of the pipe and increase metal content of water. The reaction could result in aesthetic problems. Such as bitter water, stains around basins or sinks and in many cases elevated levels of toxic metals.

6.0 Surface and Groundwater Pollution

6.1 Water Pollution and Its Sources

Water whether from underground or' surface sources found in nature is polluted, (Bhatia, 2010). The pollution is due to various reasons, namely from sewage, industrial wastes or from natural contaminants. Such water if supplied directly without treatment may not be used by consumers due to aesthetic or physiological reasons. Unwholesome water polluted by natural sources has caused great hardship for people are forced to drink it or use it for irrigation (Egereonu, 2012b).

Water pollution is a major global problem which requires ongoing evaluation and revision of water resources policy at all levels (international down to individual aquifer and wells). It has been suggested that it is the leading worldwide cause of death and diseases, (West, 2006). West, went further that water pollution account for deaths of more than 14,000 people daily.

When water in its original sources is contaminated by domestic, industrial or agricultural wastes it is sufficient to render the water unacceptable for its best usage, it is said to be polluted. "The substances causing these unfavorable alterations are called pollutants" (Ekpete, 2002). Water pollution is the contamination of water bodies examples lakes, rivers, oceans, aquifers and groundwater. It occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful compounds.

Although, water is an absolute necessity for life, there is an inherent health implication in the consumption of contaminated or polluted water. It can lead to many diseases and even death when contaminated with organic and or chemical pollutants (Bartran and Balance, 1996). But clean and unpolluted water is necessary for the maintenance of human health as well as quality of the environment (UNEP, 1996).

Heavy metals in trace concentration are one of the major sources of water pollution in rivers (Ojelabi et al, 2001). Toxic metals such as mercury, cadmium, arsenic, copper, lead and many other pollutants tend to accumulate in bottom sediments from which they may be released by various process of remobilization. These heavy metals are classified as conservative water pollutants because they are not broken down by bacterial action. Nature has provided no way to get rid of them. Some heavy metals and other substances are common components of natural waters and although some are essential for living organisms, yet they may become toxic when present in high concentrations (Egereonu et al. 2012a).

The contamination or spoiling of the water bodies could also be as a result of urbanization and industrialization. Although in industrialized nations, waterborne diseases as a result, of water pollution have been controlled; it is growing worse in poorer countries especially where population pressure has overtaxed the available resources to provide safe drinking water and to treat sewage. In addition to the acute problems of water pollution in developing countries, developed countries continue to struggle with pollution problems as well.

6.2 Groundwater Pollution

However, leachate from municipal, solid wastes, landfills is potential sources of contamination of surface water and groundwater, (Odukoya et al, 2002). Groundwater becomes polluted when materials seep through the soil and reach the water, which can happen when rainfall washes contaminants into the ground, when polluted surface water connects with groundwater, and when buried tanks or waste disposal sites start to leach.

Pollution of groundwater has gradually been on the increase especially in our cities with lots of industrial activities, population growth, poor sanitation, land use for commercial agriculture and other factors responsible for environmental degradation, (Egila and Terhemen; 2004). As investigated by Adeniyi and Mbagwu (1983); and Ajayi and Adelaye (1977); the water quality of some Nigerian groundwater shows that some of them are polluted especially those flowing through urban settlements. The concentration of contaminants in the groundwater also depends on the level and type of elements naturally or by human activities distributed through the geological stratification of the area. The presence of such contaminants in the groundwater above the recommended standard set by water quality regulating bodies like FEPA and WHO may result in serious health hazards.

6.3 Sources of Groundwater Pollution

The sources of groundwater pollution caused by human activities fall into two categories; point source pollution and non-point source pollution. Point source means that the pollutants can come from a single identifiable source examples leaky tanks or pipeline containing petroleum products, municipal landfills, leaky sewer lines, livestock wastes, leaks or spills of industrial chemicals at manufacturing facilities, spills related to highway or railway accidents etc. Non-point source means that the pollutants do not have a specific source but instead come from the cumulative effect of many number of activities; examples are fertilizer spill on agricultural land, pesticides on agricultural land and forests, contaminants in rain, snow and dry atmospheric fallout.

The sources of groundwater pollution could be natural and agricultural Egereonu, (2005), Roa et al. (1987), Gutter (1981), Egereonu and Ibe, (2003), Hallberg and Keeney (1992), Egereonu et al. (2012a), Egereonu et al. (2012b), Odemene, (1999) and Ibe et al. (2002).

6.4 Reducing Groundwater Pollution

As noted by Egereonu et al, (2012a); because groundwater movement is usually slow, polluted water may go undetected for a long time. Because of this, it is so expensive to clean up a contaminated aquifer if it can be done at all. It is preferable by far to prevent contamination from happening in the first place. Clearly, the most effective solution to groundwater contamination is prevention

Odoemelam, 1999 and Ibe et al. 2002). Methods of treating contaminated water include reverse-osmosis, ozonation, coagulation-precipitation, aerobic biological treatment and activated carbon. To protect our groundwater supplies, all levels of government in Nigeria should take some of the actions necessary and also ensure that the measures taken are fully effective. At the same time, universities and government research institutes should investigate what happens to water underground and what can be done to preserve it and even improve its availability to us. Both as society and as individuals we must keep in mind that groundwaters are susceptible to contamination.

6.5 Langelier Saturation Index for Groundwater

This is an equilibrium index used in determining the corrosive and encrustating nature of the groundwater (Garg, 2002). Parameters like pH, methyl orange alkalinity, coefficient of temperature, total dissolved solids and calcium hardness are used in the determination of saturation index. If the calculative value is negative the groundwater is corrosive but if positive it implies that the groundwater is encrustating, that is, it contains scales or crust. If the saturation index is zero. It means the groundwater is neither corrosive or encrustating. The expression is given as:

$$LSI = pH - pHS$$
$$pHS = 9.3 + \{(A+B) - (C+D)\}$$

Where A is the total dissolved solids (TDS), B is the temperature of the groundwater, C is the methyl orange alkalinity and D is the Calcium hardness. 9.3 is the correction factor and pHS is the saturation pH (Garg, 2002, Egereonu, 2006a and Egereonu, 2012a).

In Nigeria many wells have failed in recent years. A tube is deemed to have failed if it produces water below its capacity within its design life. encrustation can occur due to precipitation of carbonates, sulphates and silicates of calcium and magnesium or the precipitation of hydroxides, oxides and other compounds of iron and manganese (Garg, 2002 and Egereonu, 2003) such tube well can be resuscitated by chemical treatment, by leaching using carbonic acid, (H_2CO_3). For those wells that are corrosive polyvinyl chloride, PVC are used fully penetrating into the aquifer since acids are passive to PVC pipes.

Recommendation

The Vice Chancellor Sir, I will like to make the following recommendations:

1. The Otamiri River in FUTO should be harnessed for Hydro electric power as is in UniLorin and a section harnessed for fish pond. Also the water could be pumped into a treatment plant and made potable for human consumption, domestic and agricultural purposes.
2. The department of Chemistry should have a pilot laboratory equipped for teaching and production of soap, detergent, cosmetics, paints, water treatment, etc to help our students be on their own after graduation. The Chemistry programme should be a four (4) year programme as is done in our sister universities.

Conclusion

This work has revealed anthropogenic activities in particular, arising from biomass burning, gas flaring from petroleum exploitation, automobile emissions, fossil fuel combustion, industrial effluent gases, agro-chemicals and dust as a result of wind as sources of aerosols in the atmosphere. Analysis of rainwater from the three satellite stations indicated high residual aerosols in RWSP followed by RWSO and then RWSI. Ions detected in these samples are within the WHO permissible guideline. The pH which later increased with the frequency of the rains fell within the WHO permissible limit of 8.5. With reduction in anthropogenic activities there could be reduction in anthropogenic emissions.

The results of the physicochemical analysis carried out on Otamiri, Nworie and Oramiriukwu revealed that the water quality parameters investigated on the three rivers were well below and within the WHO acceptable levels. However, the values for chromium in the three rivers were above WHO standard indicating heavy metal pollution. The source of this pollution may include domestic, industrial effluent and agricultural activities around the river bodies. These activities must be checked to avoid future contamination of these water systems. Hence there is need for the Imo State Environmental Protection Agency (ISEPA) and Owerri Municipal Council to carry out continuous pollution monitoring, programme on the rivers, educate and sensitize the populace on the risk of discharging toxic materials into the water bodies.

The results of the boreholes within the Cross River State has an average temperature of $24.5^{\circ}C$. This average has also been found to remain approximately constant during the sampling period. This constancy of temperature displayed by water is an important advantage in irrigation. The Cross River State basin development authority is planning to embark on a large scale irrigation programme in the area. The groundwater is hereby recommended against surface water, which commonly fluctuate in temperature. Electrical conductivity ranges between $18\text{-}27\mu Scm^{-1}$ for all the towns. For Efut Town groundwater, the electrical conductivity is low, that is, between $18\text{-}12\ \mu Scm^{-1}$. The salinity in the study areas is less than $160mgL^{-1}$. The total hardness in the area ranged from $7\text{-}16mgL^{-1}$ indicating soft water which needs no treatment. The range also provides excellent irrigation processes which imply that the area has good groundwater. The groundwater in the area was found to be relatively diluted, having very little concentration of anions within the order of $C1^{-} > SO_4^{2-} > NO_3^{-}$. There was no level of cationic concentration with the exception of Fe which is within the WHO limit for drinking and domestic purposes. The result revealed low TDS value in indicating no salt water intrusion among the boreholes of the area. The groundwater in the area has two effects, corrosion and encrustation effects. It is advised that carbonic acid (H_2CO_3) be used to treat boreholes against encrustation.

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