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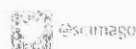
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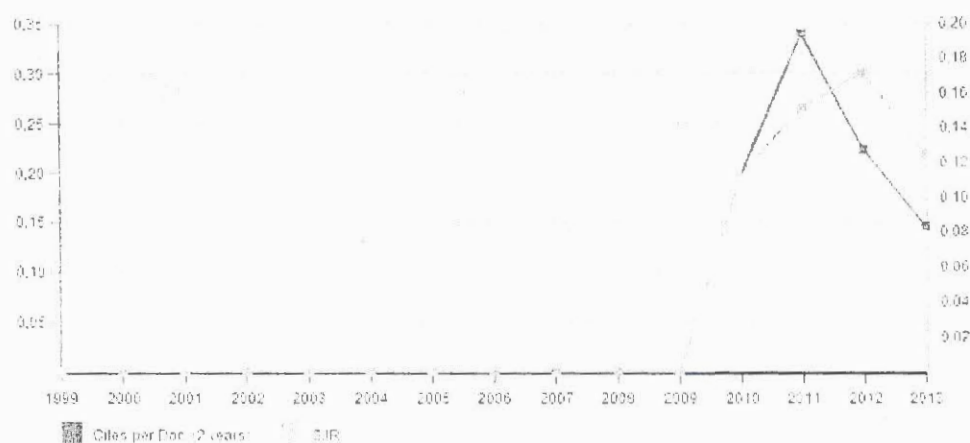
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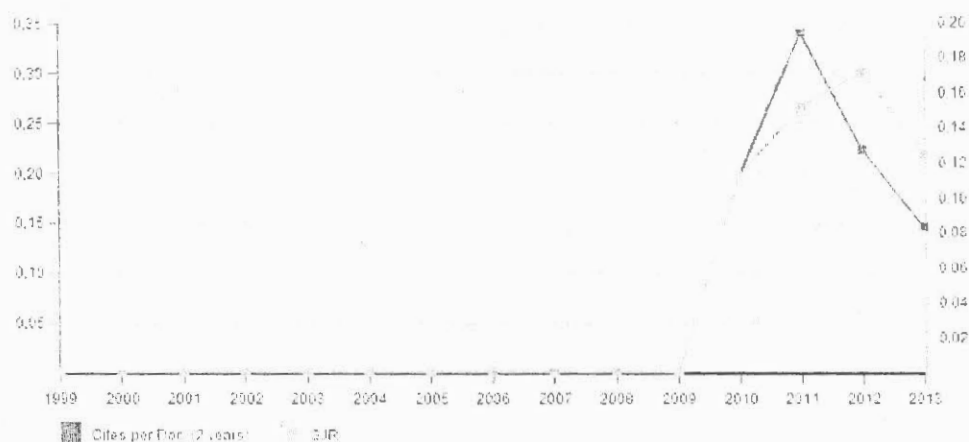
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Hydrogeochemical Study, Health Implications and Interpretation of Surface Water Analysis Around Rural Settlements of Itasin and Oki-gbode, Southwestern, Nigeria

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Abstract: A total of twelve water samples were collected from two rivers in Itasin and Oki-Gbode areas of Imobi, southwestern Nigeria, six (6) from each river and analyzed for chemical and physical quality parameters. The two water bodies serve the inhabitants of these communities as source of drinking water, agricultural and domestic uses. The hydrochemical parameters determined include major cations and anions using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the ion Chromatography methods to evaluate the water type, quality and usage. The physical analysis of the water samples were determined and the results indicate that the pH and Total Dissolved Solids (TDS) values range from 4.4–5.5 and 21.00–75.00 mg/L respectively. Electrical Conductance (EC) ranges from 32.31–115.39 mS/cm and Sodium Adsorption Ratio (SAR) from 1.62–3.39. Results of the chemical and physical analysis obtained for the river water samples were assessed and compared with World Health Organization (WHO) and Standard Organization of Nigeria (SON) standards in order to deduce if the water satisfies all the conditions for potability, irrigation and industrial use in low pressure boilers. Results obtained show that the water samples do not fit for drinking from the two standards employed, but can find uses in irrigation and for industrial purposes in low pressure boilers. The health implications deriving from drinking of these water bodies could be very devastating. For example, consumption of water having low pH over a long period of time may lead to metabolic acidosis, respiration may become deep and rapid in severe cases. Using Piper Trilinear diagram, the water samples were classified as Alkali/Earth Alkaline [$\text{Ca} - \text{Na} - \text{Cl} - \text{SO}_4 - \text{HCO}_3$] water type.

Key word: Water Quality, Piper/Trilinear Diagram, Sodium Absorption Ratio (SAR); Hydrochemical.

INTRODUCTION

Water is the most essential constituents of the human environment, Tebbutt^[1]. The water resources generate development in socio-environmental issue crucial to the society in general and more specifically for industries, agricultural activities and for public use. Surface water classifications are designations applied to surface water bodies, such as streams, rivers, and lakes, which define the best uses to be protected within these water (for example swimming, fishing, drinking water supply) and carry with them an associated set of water quality standards to protect those uses. There is no substitute for water in any of its uses. However, as much as water is important in life, where and when it is available, it must be kept safe and free of contamination and pollution for the survival of mankind. Until recently, surface water was the obvious

source of water but the advent of hand-dug wells and boreholes which are relatively recent development have almost shifted the supply of fresh water from surface water bodies to underground water supply. The chemical composition of water is important criterion that determines the quality of water. Water quality is very important and often easily degraded. While natural environmental processes provide a means for removing pollutants from water, there are definite limits. It is up to society to provide safeguards to protect and maintain water quality. Pollution of water comes from many sources. Municipalities and industries sometimes discharge waste disposals into water bodies that are used as public sources of supply. Surface run-off also brings mud, leaves, and decay vegetation together with human and animal wastes into streams and lakes. In turn, these organic wastes cause algae and bacteria to flourish. Pollutants deriving from these and many other

processes may enter surface or groundwater directly, may flow slowly within the groundwater to emerge eventually in surface water, or may run off the land. Hydrochemical assessment on the water samples shows how the dissolved substances (which could be heavy metals (trace elements), compounds etc) occur in water.

The proportions of these chemical parameters constitute indices of its proper use and quality. The improper disposal of refuse dumps and other pollutants, weathering and subsequent release of weathered materials also contribute to the chemistry of water. The World Health Organization (WHO) therefore established certain limits as minimum and maximum allowances for certain substance in water that is intended for drinking purposes.

In Nigeria, the National Council on Water Resources (NCWR), in 2005, recognized the need to urgently establish acceptable Nigerian Standard for Drinking Water Quality because it was observed that the "Nigerian Industrial Standard for Potable Water" developed by Standards Organisation of Nigeria (SON) (the only body responsible for developing National Standards in Nigeria) and the "National Guidelines and Standards for Water Quality in Nigeria" developed by Federal Ministry of Environment did not receive a wide acceptance by all stakeholders in the country, SON^[17]. Also, owing to the importance of water and the fact that water quality issues are health related, the Federal Ministry of Health, collaborating with the SON and working through a technical committee of key stakeholders developed a Standard, SON^[17], which was also used for this work.

2. The Study Area: The study area is around rural settlements where people depend on surface water both for consumption, domestic and irrigation purposes. It lies on latitudes $4^{\circ} 6'$ to $4^{\circ} 9' N$ and longitudes $6^{\circ} 35'$ to $6^{\circ} 37' E$ within Eastern Dahomey Basin, Fig 1. The stratigraphy of eastern Dahomey basin has been studied by various researchers such as Russ^[16], Omatola and Adekoge^[13] and Agagu^[11], Enu^[5] and Nton^[9] Fig 2. The lithostratigraphic units described are Abeokuta group. This is the oldest stratigraphic unit overlying the basement consisted of three formations namely; Ise, Afowo and Araromi formations.

The group is made up of sequence of continental sands, grits and coarse grained to medium grained sandstones and also with variable but thick interbedded shales, siltstones and claystones. The rock is soft and fragile but it is in some places cemented by ferruginous and siliceous material. The sandy facies are tar bearing and the shales are organic rich. Enu^[5]. The grains are well sorted, fine to medium grained siltstone at base overlain by shale. The bitumen is found seeping in most areas including the study area.

Overlying the Abeokuta group is the Imo group which consists of Ewekoro and Akinbo formations. The Ewekoro formation is essentially a fossiliferous limestone, shale, marls with a sandy base as it grades into Abeokuta formation while Akinbo consists of grey fossiliferous shale and claystone units^[11].

The claystones are concretary and are predominantly Kaolinite, while the base of the formation is defined by the presence of glauconitic bands with lenses of limestone. Oshoshun formation is the next stratigraphic unit. This formation composes of massive phosphate bearing shale with interbedded sandy unit overlying Akinbo formation^[15]. It is characterized by a dull brown and brick red sandy mudstone and claystone. Underlying this is the sandstone unit of Ilaro Formation^[7], while the youngest sedimentary formation in the Basin is Benin Formation or coastal plain sand consisting of series of soft poorly sorted, clayey sands, and sandy clay sandstones showing cross bedding.

However, the geology of the study area is mainly sandstone of the Afowo formation. The grains are well sorted, which is of medium sizes and small component increases progressively from bottom to top. Natural seepage of hydrocarbon – bitumen is common especially along river courses.

Methodology: Twelve (12) water samples were collected from the two rivers, six (6) from each river for laboratory analysis following a systematic procedure. A three-in-one pH meter was used to determine the pH and TDS of the water samples while conductivity meter was employed for the determination of electrical conductivity (EC). These parameter were determined *in situ*. Determination of hydro-chemical parameters such as concentrations of anions (Cl^- , SO_4^{2-} , HCO_3^- and NO_3^-) and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cu^{2+} and Fe) was done using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP – OES) at the Activation Laboratory, Canada. ICP-OES technique is a rapidly developing multi-elements method and is replacing even Atomic Absorption Spectrometry, AAS. Inherent advantages of the methods includes time saving, multi-element determination of a wide range of 40 – 70 elements, detection limit of 0.01%, better precision and accuracy.

Samples for cations determination were acidified immediately to avoid contamination and acidified samples were stored into 60ml bottles and unacidified samples into 120ml bottle. Total or four-acid digestion, comprising hydrochloric (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$) and hydrofluoric acid (HF), was used to decompose metal salts, carbonates, sulphides, silicates and some sulphates and sulfide.

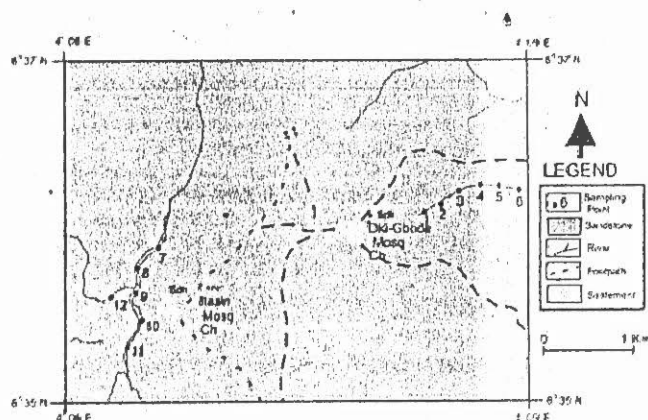


Fig. 1: Geological Map of the Study Area and Sampling Sites.

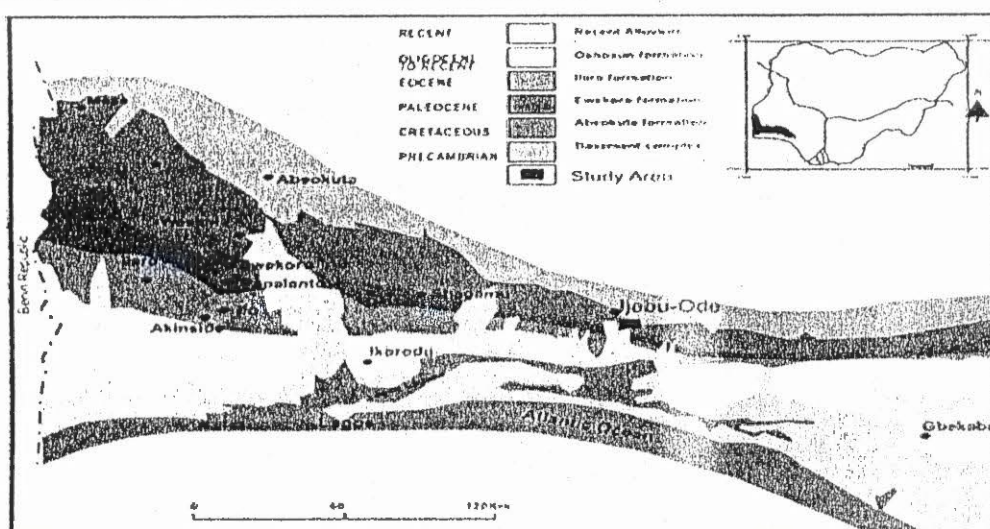


Fig. 2: Stratigraphy of Nigeria Portion of Dahomey Basin with Map of Nigeria Inset (Modified After Billman 1992).

3.1 Geochemical Results and Interpretations: The results of chemical analysis carried out on the samples were compared to WHO and SON standards. The concentration of cations, in mg/L, in the river waters range from 1.50-9.30 for Na, 0.42-6.23 for Fe, 0.50-10.90 for Ca, 0.20-4.70 for Mg, 0.20-4.70 for K and 4.0-35.0 Cu (Table 1). These were compared with the WHO^[21] standard minimum permissible level for drinking water and SON^[17] standard for drinking water in Nigeria. On the account of this, K and Fe concentrations in the water fall within the range of WHO^[21] but far above SON^[17] standard while Cu is above the WHO and SON standards.

The concentrations, in mg/L, of the anions in the river water range as follow; HCO_3^- from 8.0-23.0, NO_3^- from 0.70-3.80, SO_4^{2-} from 1.70-5.30 and Cl⁻ from 12.0-64.0 (Table 1). These fall below the WHO^[21] and

SON^[17] minimum permissible level for drinking water. From the results, the water under consideration is adjudged not suitable for consumption for falling far below the minimum permissible level of the two generally accepted standards used (Table 2). Deficiency and excess of some of these geochemical substances have been associated with chronic diseases world-wide such as respiratory damage in case of high intake of chromium; severe toxicity by arsenic ingestion, mental disorder, kidney problem and gastrointestinal tract problem caused by high level exposure to lead; anaemia, liver and kidney damage, and stomach and intestinal irritation as a result of high doses of copper; while long term exposure to cadmium is associated with renal dysfunction, obstructive lung diseases and lung cancer. Excess of NO_3^- could lead to the problem of infantile cyanosis or "blue blood" which could lead

Table 1: Results of Chemical Analysis for the Two Rivers

Sample Location	Na ⁺ (mg/L)	K ⁺ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Fe (mg/L)	Cu (µg/L)	HCO ₃ ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)
1A	9.3	4.7	10.9	4.5	0.45	6	13	0.8	1.8	22
2A	1.8	0.4	0.6	0.2	0.54	24	21	0.7	3.1	28
3A	2	0.2	0.5	0.2	0.42	6	8	0.8	3	60
4A	1.6	0.4	0.7	0.3	0.73	12	16	0.9	2.9	60
5A	2.4	0.4	1.1	0.4	1.83	8	17	1	4	52
6A	1.5	0.9	1.2	0.4	2.83	16	13	0.8	2	27
7B	3.8	1.2	6	2	4.42	4	22	1	1.8	12
8B	4.2	0.9	5.9	2	4.67	31	19	0.9	3.6	60
9B	4.6	1.1	6.1	1.9	5.64	8	21	1.1	1.7	64
10B	3.4	1.1	6.4	2	6.23	6	19	1.6	2.6	42
11B	4	1.3	6.5	2.1	6.06	35	23	3.8	5.3	26
12B	4.2	1.2	6.5	2.2	4.32	6.3	21	2.5	3	58

Table 2: Statistical results of summary of chemical and physical analyses with WHO and SON Standards

Measured Parameters	Present Study		WHO (2006) Standard		SON (2007) Standard
From the Present Study	Range	Mean	Min. Perm. Level	Max. Perm. Level	Max. Perm. Level
Ph	4.4-5.5	4.98	6.5(mg/L)	9.5(mg/L)	6.5-8.5
TDS (mg/l)	21-75	51.2	500(mg/L)	1500(mg/L)	500(mg/L)
EC (µS/cm)	32.31-115.39	7.72	400	1500	10000
Ca (mg/l)	0.50-10.9	4.37	75(mg/L)	200(mg/L)	NA
Mg (mg/l)	0.20-4.50	1.52	40(mg/L)	150(mg/L)	0.2(mg/l)
Na (mg/l)	1.5-9.30	3.57	10(mg/L)	<20(mg/L)	200(mg/L)
K (mg/l)	0.2-4.70	1.14	10ppm	15ppm	NA
Fe (mg/l)	0.42-6.23	3.18	5(mg/L)	10(mg/L)	0.3(mg/l)
Cu (mg/l)	4.0-35.0	13.53	0.1(mg/L)	2(mg/L)	1.0(mg/l)
Hardness(mg/l)	2.0-30.0	13.3	-	-	150(mg/L)
HCO ₃ ⁻ (mg/l)	8.0-23.0	17.75	200(mg/L)	600(mg/L)	NA
NO ₃ ⁻ (mg/l)	0.70-3.80	1.33	20(mg/L)	45(mg/L)	50(mg/L)
SO ₄ ²⁻ (mg/l)	1.70-5.30	2.97	150(mg/L)	250(mg/L)	100(mg/L)
Cl ⁻ (mg/l)	12.0-64.0	42.58	200(mg/L)	400(mg/L)	250(mg/L)

Min. – Minimum, Max. – Maximum, NA – Not Available

to infantry death. High contents of Fe²⁺ in water can also cause staining of laundry; metal pipes for reticulation, scaling in pipes, and it may give undesirable taste^[12,6,10].

High concentrations of some elements in water from the two rivers may not be unconnected with natural and anthropogenic activities in the area. Itasin

and Oki-Gbode and their environs are well known with natural seepage of bitumen also referred to as tar sand. The bitumen seeps and flows into the near-by streams and rivers while at some locations it seeps along river courses. It was also noticed that the resource is mined by the local dwellers for various purposes but commercial mining is not within the area. These

activities are expected to have significant effects on geochemical processes within the environs by way of increasing and/or decreasing the quantity of geochemical elements present, while the quality of water is adversely altered. Thus, the environment cannot be regarded as a natural one owing to the aforementioned activities and other anthropogenic influences.

3.2 Results and Interpretations of Physicochemical Tests on the Water:

The physicochemical analyses carried out on the samples include pH, TDS, Electrical Conductivity, EC, Hardness and SAR. The last three parameters i.e. Electrical Conductivity, EC, Hardness and SAR, are carried out for consistency of result and to ascertain the true characteristics of the water from different points. The results show that the pH of the water samples ranged from acidic values of 4.40 to slightly acidic value of 5.50. The lower values recorded might be due to decomposition of some organic matters or seepage of bitumen into the water from run-off.

The partial decomposition of these organic matters by bacterial and fungi has been recognised to produce various organic acids that are capable of lowering the pH of aqueous solution^[1,10]. Also, one of the associated impurities with hydrocarbon is hydrogen sulphide, hence its likely introduction to the two water bodies. The total hardness of water which ranged from 2.00 – 30.00 mg/L, falls within soft water classification of Todd^[10], Table 3. Generally, low Electrical Conductivity, EC, (32.31–115.39 $\mu\text{S}/\text{cm}$) and TDS (27.00–75.00 mg/L) values were measured showing that the surface waters are fresh waters. While the abnormal value obtained for the pH confirms the interaction of seeping bitumen with the surface water.

Physical parameters also determine the suitability of water for certain uses (for example domestic use). Notable damage could occur both to human being and utility from abnormal high or low values of these parameters. For example,^[12] noted that water with low pH ('acidic' water) may cause severe corrosion of metal casing used for reticulation. In like manner, long exposure to such water has been associated with metabolic acidosis whereby respiration becomes deep and rapid in severe cases,^[10].

The Sodium Adsorption Ratio (SAR) ranged from 1.62–3.39. The recommended water classification based on SAR is shown in Table 4. Mendel and Shifan^[8] suggested that waters having SAR of 0–10 can be used for agricultural soils while those having SAR range of 18–26 may produce harmful effects on agricultural soils. Thus, based on this classification, water from the two rivers are good for irrigation, which is one of the major uses of the water by the rural dwellers of the two communities.

3.3. Trilinear (Piper) Diagram: This can be used to classify water into various types based on the dominant cations and anions. It is graphical representation of water types modified after Piper (1944). For example, if calcium and bicarbonate are the dominant ions, then the water would be Ca-HCO₃ type. On this diagram, relative concentrations of major ions, in Meq/L are plotted on cations and anions triangles, and then the locations are projected to a point on a quadrilateral representing both ions, Deutsch^[9]. The quadrilateral was further divided to seven hydrochemical facies from, a – e by Tijani^[19] using the anions concentrations, Fig 3. Based on this, waters from Oki-Gbode area fall into the 'e' and 'g' types. This is known as predominantly SO₄ – Cl i.e. Alkali/Earth-alkali water.

However, Itasin water differs as it shows a predominantly Earth-Alkaline type (e), with higher alkali components, except in location 9 where a high sulfate, SO₄, of type 'c' was recorded. Cations concentrations show high Ca and Na contents. Hence, the overall results could be put as Alkali/Earth Alkaline water [Ca – Na – Cl – SO₄ – HCO₃] Fig 3. This reflects diverse effects of bitumen seepage, atmosphere precipitation, weathering, cation exchange processes and anthropogenic input as affected surface water quality of the areas. Earth-alkaline waters2)Earth-alkaline waters (with higher Alkali component) Predominantly HCO₃(d) Predominantly HCO₃, HCO₃ – SO₄(e) Predominantly SO₄ – Cl Predominantly SO₄ Alkali waters1-6 – Oki-Gbode water (f) Predominantly HCO₃ (g) Predominantly SO₄ – Cl 7-12 – Itasin water

3.4. Statistical Evaluations:

3.4.1. Correlation Coefficient: The determination of coefficient of correlation helps to evaluate the existence and extent of relationship between two variables. Association of some elements may lead directly to the interpretation of the likely sources of the elements. Na, K, Ca and Mg are strongly correlated to one another (Fig 4). It implies that same source could be inferred for these elements which mean that the process that introduced Na into the water is also culprit for other elements that are strongly correlated with Na. For the anions, HCO₃ correlates with NO₃ and NO₃ with SO₄.

We know that CO₂, nitrates and ammonia could be introduced from rain water which run-off into the stream. This may possibly be responsible for increasing acidity of the water. A few positive relationship exists between some cations and some anions, for example Fe versus NO₃ and HCO₃; and between Cu versus SO₄. Fe could be from ferruginous sandstone that constitutes part of the geology of the area. A better approach to understand the distribution of chemical elements made us to determine the flow path of these elements in the river water as shown in the Schoeller diagrams (Fig 5).

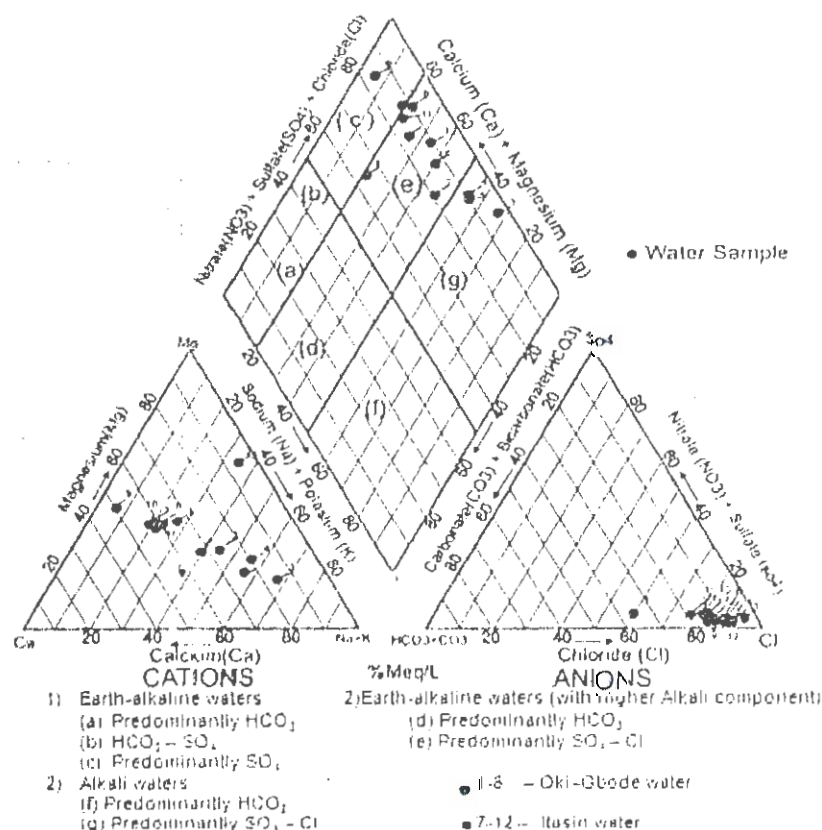


Fig. 3: Trilinear (Piper) Diagram plot of the Chemical Data Showing Different Hydro-chemical Facies in the study area.

Table 3: Water Classification based on TDS and Hardness (After Todd, 1980)

TDS (mg/l.)	Class	Hardness (mg/l.)	Class
<1,000	Fresh	0 - 60	Soft
1,000-3,000	Slightly Saline	61 - 120	Moderately Hard
10,000-35,000	Very Saline	121 - 180	Hard
>35,000	Brine	>180	Very Hard

Table 4: Classification of water based on SAR (After Mandel and Shifan, 1991)

SAR (%)	Water Class
<10	Excellent
10 - 18	Good
19 - 26	Fair
>26	Poor

The spatial distribution of the chemical elements denotes progressive increase in water mineralization for Itasin as against Oki-Gbode water. In the later, most cations, except for Fe, remain constant (Fig 5a); whereas, there is general increasing trend of cations concentration for Itasin water (Fig 5b). Also, the chloride composition shows an increasing sequence in

both water but more pronounced in Itasin than Oki-Gbode.

Thus, a main trend towards increasing salinity can be observed. Nitrate and sulphate concentrations are quite constant in both. Samples 5A and 6A have the highest Fe concentrations followed by sample 2A, while sample 12B has the highest chloride

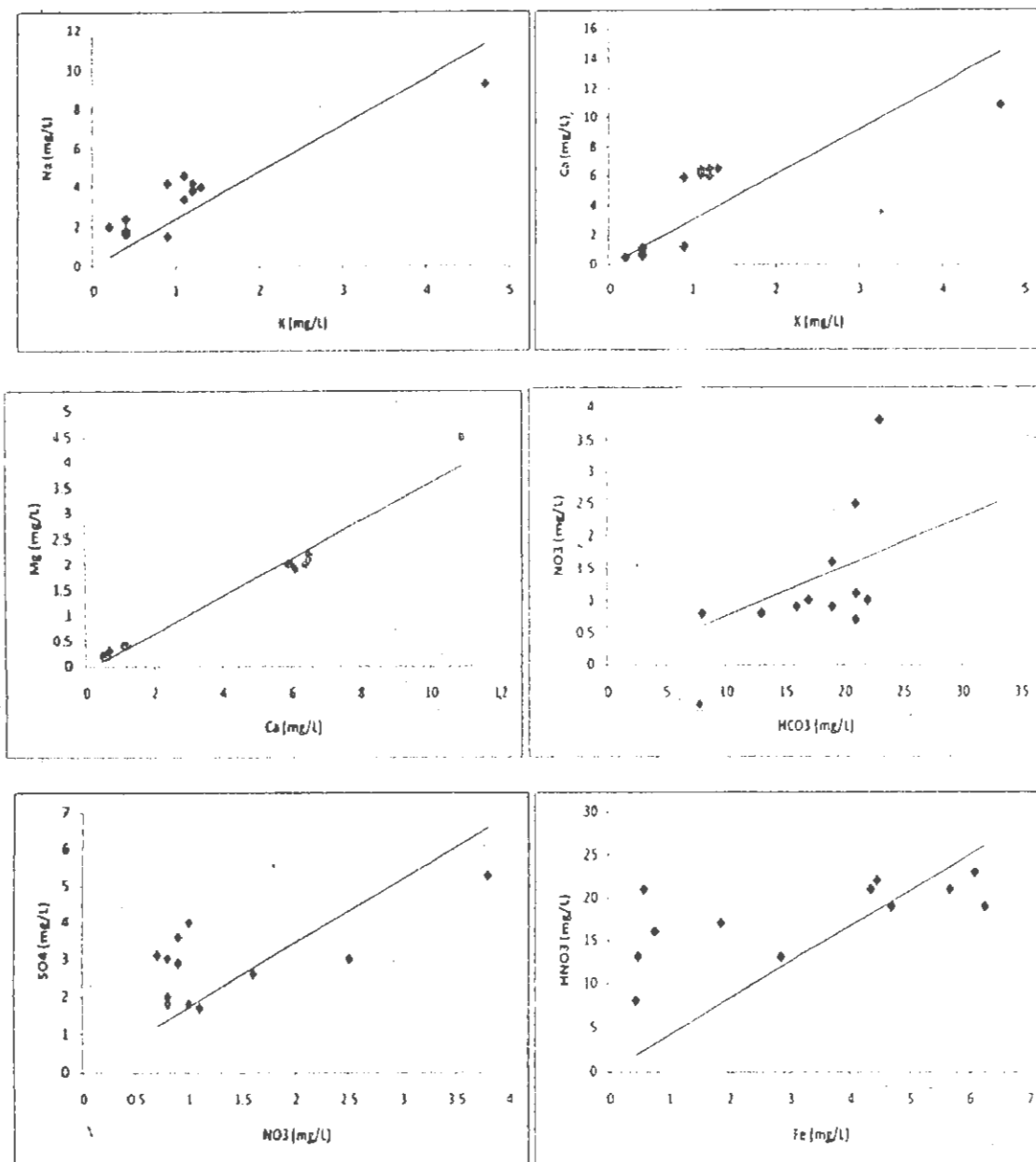


Fig. 4: Correlation Plot of some Chemical Parameters

concentration. Generally, there seems to be gradual increase of the chemical elements in Itasin water.

Higher enrichment of this water (river Itasin) above the other one (river Oki-Gbode) could possibly be explained in the fact that it flows from a far source cutting across different and wider geographical locations incorporating geochemical signatures from various sources along its path.

Conclusions: Physico-chemical assessment of water samples taken from rivers Itasin and Oki-Gbode in the study areas has been discussed here. Twelve samples were collected in all six from each river. The samples were analysed with Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and the ion Chromatography methods for cations and anions, while the physical parameters were determined, some *in situ* and others in the laboratory.

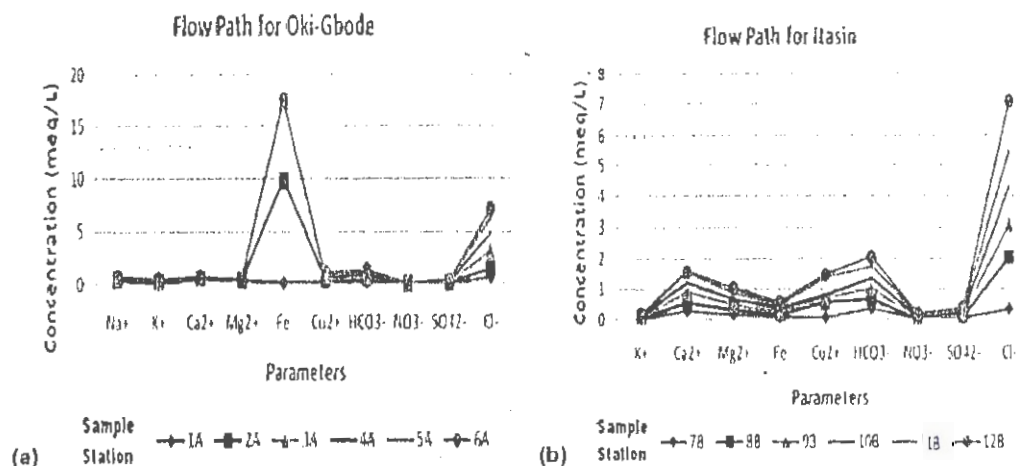


Fig. 5: Schoeller diagrams showing the hydrochemical composition flow paths for the two rivers

The results when compared with WHO and SON quality criteria for drinking water, shows very low degree of compliance. Chemical contents of Oki-Gbode water show lesser concentrations compared to that of Itasin. Statistical evaluations on the river waters indicates that there is general increasing trend of cations and chloride concentrations for Itasin water than for Oki-Gbode water.

Thus, Itasin water is more mineralized than its counterpart possibly because of its long flow history and wider geographic coverage. The high Fe content is highly undesirable and long exposure to it may give undesirable taste.

On the other hand, physical parameters determined also portend the water unsafe for human consumption. From the pH value, for example, the water samples were found to be acidic which has serious health implications. It is therefore recommended that the inhabitants of the study area be advised to desist from drinking water from the two rivers.

However, this could be difficult without alternative source of potable water which government must look into.

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Contamination assessment of surface and groundwater
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Contamination assessment of surface and groundwater within and around two dumpsites

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ABSTRACT: Geochemical analyses of groundwater and streams flowing around abandoned and active dumpsites in Lagos, Southwestern Nigeria were carried out. Results show that water samples have generally low total dissolved solids with average values of 163.75 and 153.4 for abandoned and active dumpsites, respectively. pH ranges from 3.96-8.34 while total hardness varies from 10-220 mg/L calcium carbonate (soft to slightly hard). Average concentrations of the dominant ions for abandoned and active dumpsites were 57.8 and 25.86 mg/L (Na) representing 40.7 and 46.3 % of the total cations respectively and Nitrate (av. 96.89 and 61.51 mg/L) representing 49.1 % and 40 %, respectively of the total anions. The pH, coliform count and concentrations of nitrate iron, manganese and sodium in most of the water samples were above the national drinking water standards proposed by the United States Environmental Protection Agency. Trace elements like silver, arsenic, beryllium, bismuth, cerium, cobalt, chromium, lithium selenium, tellurium, titanium, uranium, vanadium, tin and yttrium were below detection level for all the water samples while tungsten, thallium, molybdenum and lead were only present in surface and groundwater close to the dumpsites and also display values higher than recommended standards while copper, zinc, aluminum, barium and strontium were present in most of the samples. The pollution index among all sites varied from 0.009 to 1.26 and 0.106 to 6.25 for abandoned and active dumpsites, respectively while the water around most of the dumpsite areas exceeded the acute and chronic effect levels proposed by the United States Environmental Protection Agency in 2007.

Keywords: Anthropogenic; Environment; Pollution index; Trace elements

INTRODUCTION

The disposal of wastes generated by human activities within a municipality is generally an urban problem. The recognition of the connection between human activities and pollution and the need to protect human health, recreation and fisheries production led to the early development of water quality regulations and monitoring methods (Hem 1985; Jenkins *et al.*, 1996; USEPA, 2007). The existence of trace metals in aquatic environments has led to serious concerns about their influence on plant and animal life (Samarghandi *et al.*, 2007; Zvinowanda *et al.*, 2009). During their transport, the trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena (Akcay *et al.*, 2003; Abdel-Ghani and Elchaghaby, 2007; Abdel-Ghani *et al.*, 2009; Mohinddin *et al.*, 2010). One of the reasons these toxins are so harmful is that they become more

concentrated in successive trophic levels of a food web, a process called biological magnification (Woodwell, 1972; Grimanis *et al.*, 1978; Adams *et al.*, 1992; Campbell, 1996; Manly, 1996; Kaonga *et al.*, 2010). The need for socio-economic advancement has led to rapid expansion of the industrial sector in developing countries like Nigeria. These waste disposal sites and landfills are neither properly designed nor constructed. After some years a dumpsite undergoes biologically, chemically, geologically and hydro geologically mediated changes resulting in a weathering process consequently, it becomes point source for pollution of the aquiferous units close to them (Arienzo *et al.*, 2001; Manjunatha *et al.*, 2001; Altindag and Yigit, 2005; Awofolu *et al.*, 2005; Wang and Zhuo, 2005; Adeniyi *et al.*, 2008). The commonly used disposal methods of the solid wastes in the study area are open dumps, non-engineering sanitary landfill and incineration. When rain falls, the rain leaches pollutants from the

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waste disposal sites. Thus introducing toxins and contaminants into the soil, surface and groundwater and eventually plants that grow within the vicinity of the dumpsite (Awofolu *et al.*, 2007; Daka *et al.*, 2007). The overall implication of this is that the hydrochemical facies of groundwater changes in response to its flow path history, that is, underground water quality is dependent on pollution status of its environment (Olabaniyi and Owoyemi, 2006).

Geological and geomorphologic features

The geology of the study area fall within coastal plain sand of Dahomey Basin and is characterized by coarse, unsorted sands and clay lenses mixed together in varying proportions at varying depth. Depth to water ranges from land surface to about 10 m for first aquifer. Generally, the lithology is composed of medium to coarse grained sandy horizon interbedded with thin band of grey black clay which occur in minor proportion (< 20 m).

The study areas which are Isolo and Ojota dumpsites are both located in Lagos, southwestern

Nigeria (Fig. 1 a and b). Ojota disposal site is located in the northeastern area of Lagos. It is very massive with a topographical height of about 45.45 m (150 ft) from the sea level it has been in operation since 1992, still very active and it is very close to so many industries. The Isolo waste disposal site is situated at the northern part of Lagos metropolis. It is sited very close to a big canal which normally overflows its banks during the rainy season and a dominant percentage of the waste deposited here are domestic wastes. Also, the site has been abandoned for the past twelve years and therefore, it is no more active. This research has been done between 2007 and 2008.

MATERIAL AND METHODS

Water samples from boreholes, wells and streams were collected at several locations within and around the two dumpsites. Several sensitive parameters of water such as total dissolved solids (TDS), electrical conductivity and pH were determined during the on the spot sampling using the appropriate digital meters (e.g. water treatment works (WTW)-conductivity meter

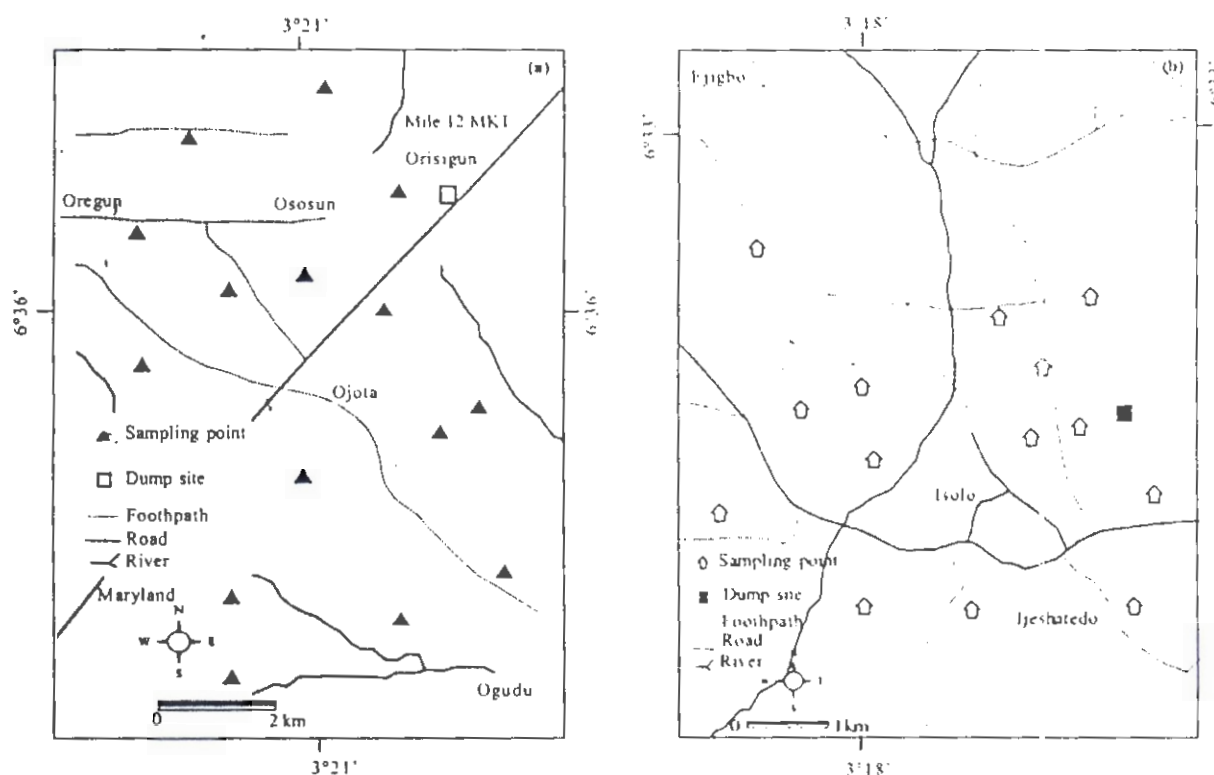


Fig. 1; Sample locations for a) Active dumpsite; b) Abandoned dumpsite

model L/92 and WTW- pH meter model pH 91). Water samples of approximately 125 mL were collected for multielement analysis; pressure filtered through 0.2 mm Nuclepore membranes and 3 mL analytical grade HNO₃ was added to bring the water acid solution to a pH ~ 2. The analysis of trace elements and cations in water were carried out using inductively coupled plasma-optical emission spectrometry (ICP-OES) while unacidified water samples were analyzed for anions concentrations using the DIONEX DX-120 ion chromatography techniques. All the analyses were carried out at the Actlabs laboratory, Ontario Canada. To check the accuracy, activation laboratories (Ontario, Canada) employed two internal standards (each run twice) and found that the errors were consistently minimal. Bacteriological analysis of the water samples was also carried out. Results were further compared with recommended standards and pollution index was calculated to determine the impacts of the two dumpsites on water quality.

RESULTS AND DISCUSSION

The summary of the concentrations of dissolved elements in streams and groundwater around both active and abandoned dumpsites in Lagos, Southwestern Nigeria were given together with national drinking water standards proposed by the US Environmental Protection Agency (USEPA) in may 2009 (Tables 1 and 2). pH values range from 3.96-8.34 with most of the samples slightly acidic and out of the USEPA (2009) standards as a result of dilution by leachates. Total dissolved solid is low generally with mean values of 163.62 and 153.38 while electrical conductivity (EC) showed mean of 301.63 and 311.21 for abandoned and active dumpsites, respectively. On this basis, the water can be classified as fresh (Todd, 1980). Major ions such as Fe, Mg, Mn, Na, Br and NO₃ in the water samples were higher than the limits of the above standards for samples close to the dumpsites, (Fig. 2). Concentrations for Au, Be, Hg, In, Ir, Nb, Os, Pd, Pt, Re, Rh, Ru, Sb, Se, Ta and Te were all below the detection limit for ICP-OES and therefore were not listed in Tables 1 and 2. The metals showed the following trends Zn > Al > Sr > Ba > Cu > Ni and Zn > Al > Ni > Sr > Ba > Cu for abandoned and active dumpsites respectively. The mean concentrations for samples taken around abandoned and active dumpsites were 551.5 and 398.76 for Zn, 4.71 and 72.06 for Ni, 52.35 and 43.76 for Ba, 32.59 and 15.29 for Cu,

182.4 and 264.7 for Al and 0.18 and 137.6 and 57.65 for Sr, respectively (Tables 1 and 2). W, Mo and Pb were found only in the two samples and both were above USEPA, 2009 standards. NO₃ ranges between 0.3-250.3 mg/L and 3.2 mg/L – 200 mg/L while coliform ranges between 0cfu/100 mL – 600 cfu/100 mL and 10 cfu/100 mL 600 cfu/ 100 mL for abandoned and active dumpsites, respectively. The large relative standard deviation values indicate that there is significant variability among the individual sampling sites around the two dumpsites. The wide range of concentrations most likely represents different point-source inputs from different materials in the dumpsites since chemical weathering of sedimentary rocks which is Coastal Plain Sands in the case of the study area are unlikely to provide such large spatial fluctuations in trace elements content. The variability of concentrations of these elements, as well as total coliform within the water suggests local anthropogenic input sources through domestic, municipal and industrial wastes within the dumpsites. The total concentrations of the elements were compared at several sampling sites and there was a slight overall trend of increase in the concentration of trace and major elements in the water samples within and very close to the dumpsites (Figs. 3 and 4). The large increase at these sites suggests a high elemental input into the water which is probably from the dumpsites. Leachate within the two dumpsites showed the highest values for most of the elements while the control samples taken far away from the sites showed the least (Figs. 3 and 4).

Pollution index

The pollution index was used in this study to evaluate the degree of trace metal contamination (Nishida *et al.*, 1982; Chon, *et al.*, 1991; Kim *et al.*, 1998; Emoyan *et al.*, 2005; Nier 2007). The tolerable level is the element concentration in the water considered safe for human consumption (Kloke 1979; Lee *et al.*, 1998). The USEPA national drinking water standards (2009) were used as tolerable level for water and the pollution index can be calculated by the formulae below

$$PI = \frac{\text{Heavy metal concentration in water}}{\text{Tolerable level}} \times \text{Number of heavy metals}$$

The PI among all sites varied from 0.009 to 1.26 and 0.106 to 6.25 for abandoned and active dumpsites,

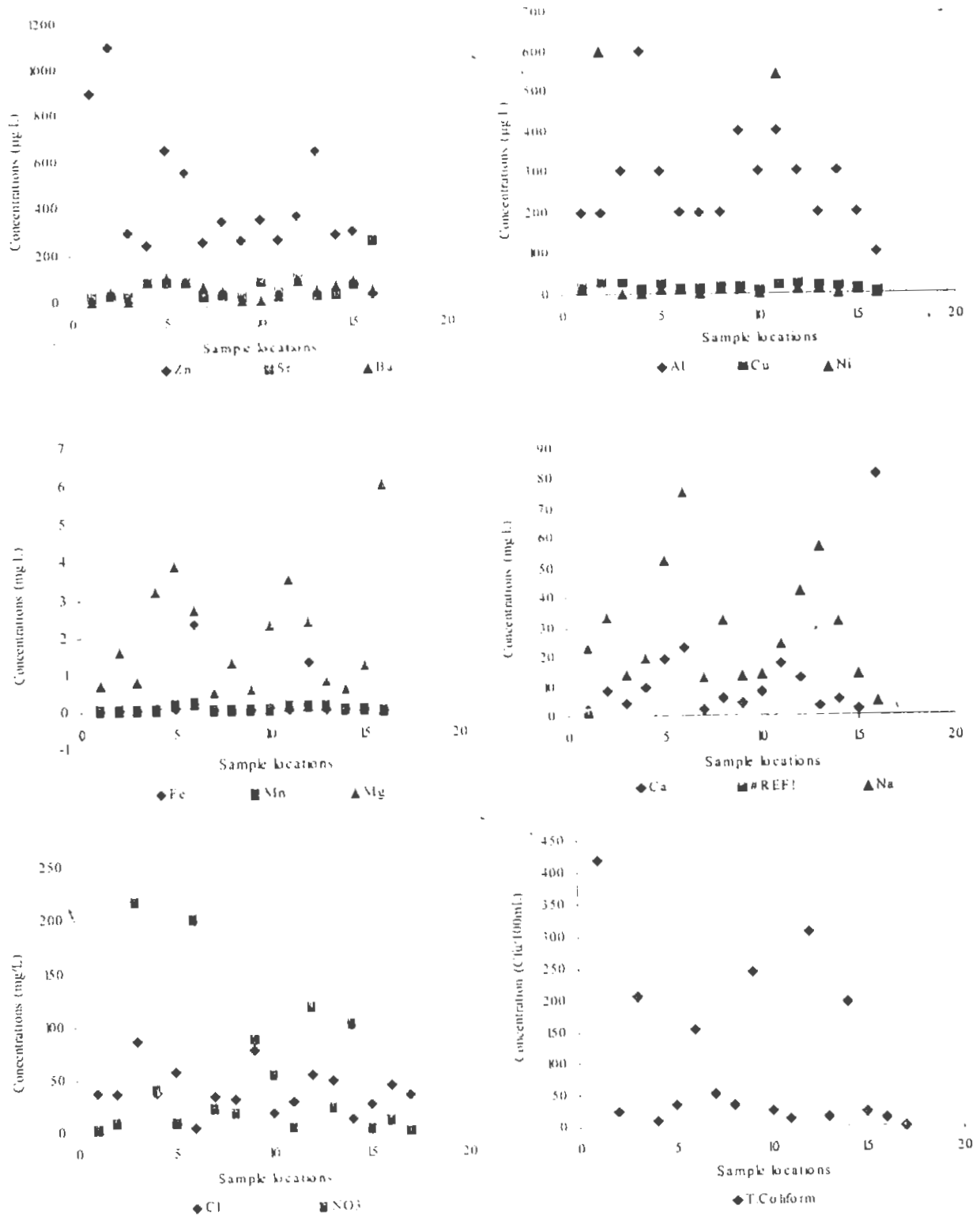


Fig. 4: Scattered plots of heavy metals against sample location around active dumpsite

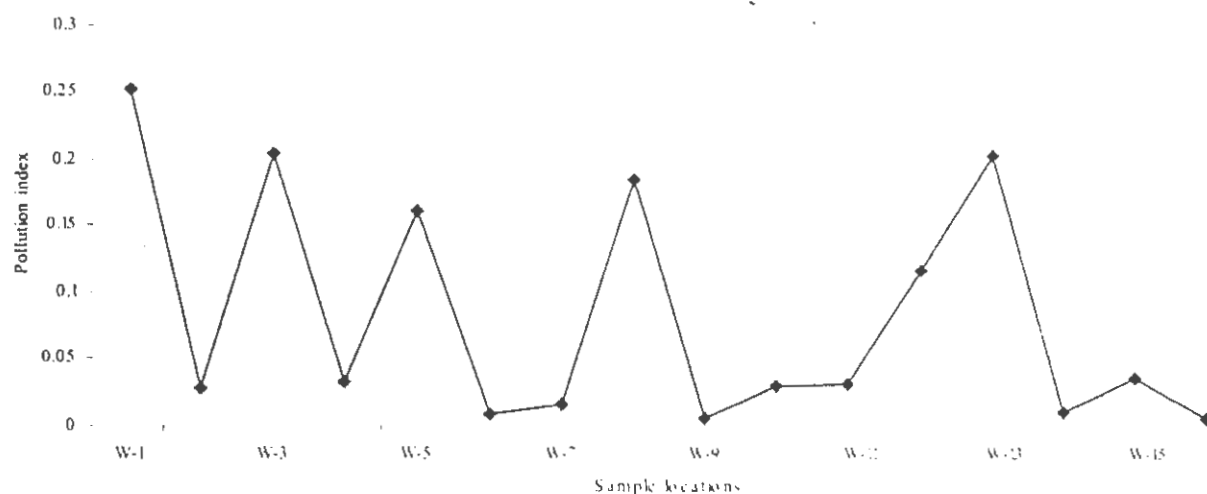


Fig. 5: Pollution index for abandoned dumpsite

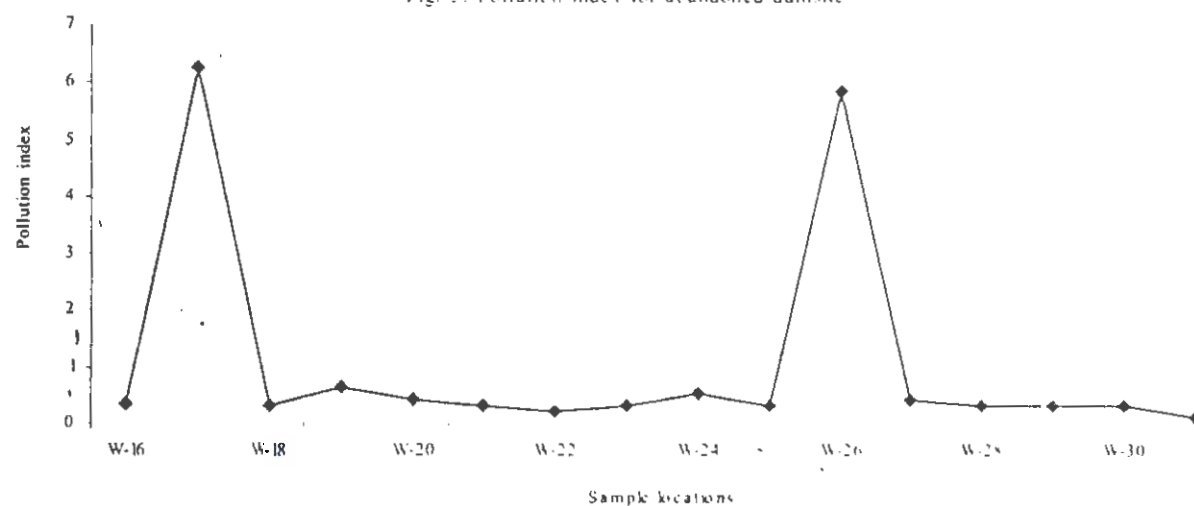


Fig. 6: Pollution index for active dumpsite

of these metals will pollute the water which serves as source of drinking water for some people while the possible trophic transfers especially at the downstream outside the urban areas where local inhabitants use the water in vegetable nurseries/ farming call for concerns.

CONCLUSION

Quality evaluation of surface and groundwater from Lagos Southwestern Nigeria, were discussed as a case study of anthropogenic influence of dumpsites in a typical urban environment of a developing country. From this study, it is clearly evident that lack of well constructed environmental friendly landfills and indiscriminate dumping of wastes to stream channels

have considerable influences on the heavy metal contaminations of surface and groundwater in the study area. The study revealed slight degree contamination of Al, Zn, Ba, Cu, B, Pb, Mo, W and Ni in the some water samples around the two dumpsites compared to the USEPA (2009) standards. Among the major elements, NO_3^- and Fe are the most critical in the water system. Also, total coliform counts were very high in all the samples. The pollution index among all sites varied from 0.009 to 1.26 and 0.106 to 6.25 for abandoned and active dumpsites, respectively while the water around most of the dumpsite areas exceeded the acute and chronic effect levels proposed by the US Environmental Protection Agency (USEPA, 2007).

Table 1: Summary of results of water samples within and around abandoned dumpsite

	Surface water	Groundwater	Leachate	Control	NDWS
pH	4.5-8.34(4.72)	3.96-8.05(5.54)	6.57	7.8	6.5-8.5
Conductivity	170-250(226.25)	40-730(255.2)	665	50	1400
TDS _s	116-186(164.75)	26-453(168.9)	408	30	1000
Hardness	10-48(29.25)	20-220(69.4)	70	67	
Total coliform	10-420(161.5)	0-600(98.8)	205	10	0
Ca	9.2-128(44.9)	1.2-45(14.85)	43.6	81.1	200
Fe	0.05-0.23(0.13)	0.03-0.34(0.095)	0.47	0.01	0.3
K	7.4-194(56.85)	0.3-12.4(4.025)	6.7	1.9	
Mg	3-63.1(18.25)	0.5-43.2(6.98)	2.2	6	50
Mn	0.09-0.16(0.12)	0.02-0.14(0.07)	0.06	0.01	0.05
Na	27.7-243(97.8)	4.2-84(29.7)	34.8	4.9	200
P	0.82-3.76(2.3)	0.22-2.24(0.84)	1.22	0.04	
Si	2.4-10.3(5.6)	2.5-8.4(5.05)	8.5	7.6	
S	5-24(14.5)	1-22(4.03)	9	5	
Cl	28.6-406(128.7)	12.8-29.8(21.54)	91.8	34	230
Br	0-0.61(0.18)	ND-0.61(0.177)	0.19	0.04	0.01
NO ₃	0.03-250.3(135.96)	0.02-120.3(39.8)	110.1	0.01	10
SO ₄	3.07-187(51.46)	1.13-76.4(29.69)	31.1	2.81	400
HCO ₃	0-38(12)	0-25(6.3)	7.8	45	
Al	200-1100(400)	ND-300(90)	300	100	87
Ba	40-100(65)	40-100(49)	80	40	1
Cu	4-46(21.5)	8-232(43.6)	16	4	1
Ni	0-20(7.5)	ND-15(3.5)	10	nd	0.02
Zn	525-1060(791.25)	30-960(384.6)	2330	30	5
Sr	50-670(227.5)	20-520(105)	120	250	0.01

*NDWS: National drinking water standards, *ND: Not detected, *Major elements in mg/L, *Trace elements in µg/L

Table 2: Summary of results of water samples within and around active dumpsite

	Surface water	Groundwater	Leachate	Control	NDWS
pH	4.28-6.75(5.1)	4.23-8.04(5.64)	4.89	7.92	6.5-8.5
Conductivity	122-603(302.6)	122-703(340.9)	50	30	1400
TDS	24-185(128.4)	86-424(197.3)	25	25	1000
Hardness	10-65(37)	22-102(51.2)	210	75	
Total coliform	12-308(111)	10-308(90.3)	208	5	0
Ca	2.3-23.1(12.16)	2.4-17.9(6.83)	8.5	81.1	200
Fe	0.04-2.36(0.52)	0.02-1.32(0.18)	0.06	0.01	0.3
K	1.2-21.7(9.1)	1-20.6(6.17)	5.5	1.9	
Mg*	0.5-3.9(2.32)	0.6-3.5(1.43)	1.6	6	50
Mn	0.02-0.21(0.1)	0.03-0.14(0.06)	0.06	0.01	0.05
Na	13.2-75.6(38.62)	13.4-56.7(26.08)	33.6	4.9	200
P	0.34-3.64(1.99)	0.02-2.32(0.86)	2.8	0.04	
Si*	4.4-9.6(6.56)	1.7-8.7(4.7)	4.7	7.5	
S	5-19(10.8)	2-17(6.8)	11	5	
Cl	12.5-54(44.95)	5.06-78.2(38.2)	87.2	34	230
Br	ND	ND	ND	ND	0.01
NO ₃	3.2-117.9(79.13)	2.41-200.01(51.62)	217.5	0.01	10
SO ₄	1.29-7.09(4.13)	1.19-9.86(4.3)	7.09	2.81	400
HCO ₃	0-103(20.5)	0-213(24.45)	0	45	
Al	200-600(300)	200-400(290)	200	100	87
Ba	40-100(72)	ND-80(56)	35	40	1
Cu	10-24(14.4)	8-26(17.1)	28	4	1
Ni	nd-19(6)	ND-540(65.5)	600	ND	0.02
Zn	240-645(405)	260-895(402)	1100	30	5
Sr	20-80(58)	20-100(44.4)	30	250	0.01

*NDWS: National drinking water standards, *ND: Not detected, *Major elements in mg/L, *Trace elements in µg/L

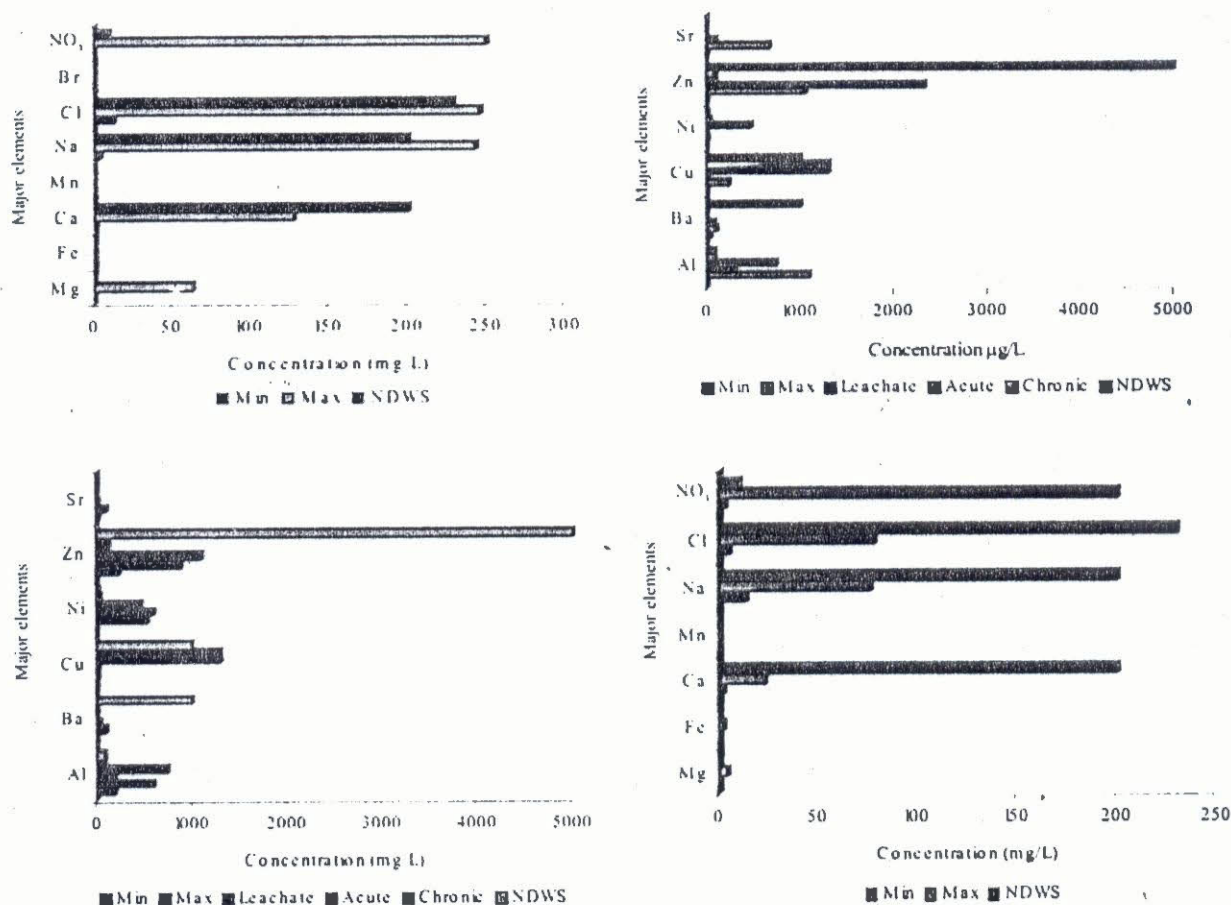


Fig. 2: Bar charts of heavy metals and some major elements concentration with acute, chronic and national drinking water standards proposed by USEPA (2009)

respectively. Concentrations of Al, Ba, Cu, Zn and Sr in most of the water samples were less than the given tolerable levels while Ni showed higher concentration in 1 and 2 samples for abandoned and active dumpsites, respectively (Figs. 5 and 6). Pi was below 0.1 at 4 and 6 samples representing (27.7% and 37.5%) of the total samples, between 0.1 to 0.3 at 6 and 8 samples (37.5% and 50%) and greater than 0.3 at 5 and 2 samples (33.3% and 12.5%) for abandoned and active dumpsites, respectively (Table 3). The pollution index for shallow well and leachate within the active dumpsite were as high as 5.42 and 6.05, respectively.

Fresh water acute and chronic criteria

The water around most of the dumpsite areas exceeded the acute and chronic effect levels proposed by the US Environmental Protection Agency (USEPA) in 2007 (Fig. 1). The tolerable acute and chronic levels

for fresh water are 470 and 52 µg/L for Ni, 750 and 87 µg/L for Al, 13 and 9 µg/L for Cu, 65 and 2.5 µg/L for Pb and 120 µg/L for both, for Zn. Among all the studied areas, 6.25%, 84.38%, 71.87% and 81.25% of water exceeded the acute and chronic limit of Ni, Al, Cu and Zn, respectively. For chloride only one sample from surface water exceeded the fresh water aquatic life acute and chronic criteria. The standard recommended for the consumption of water and organisms for human health by USEPA (2007) include 300 µg/L, 50 µg/L and 10,000 µg/L for Fe, Mn and NO₃, while 31.25%, 46.88% and 59.4% of total samples exceeded these values, respectively. The source of these metals may be attributed to anthropogenic activities from the various wastes at the dumpsites and dumping of wastes/rubbish on the stream channels. The environmental implication of water contamination lies in the fact that the adsorbed portion

Generally, the water contamination is related to anthropogenic sources mostly from different wastes within the dumpsites which are domestic municipal and slightly industrial in origin.

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