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GROUNDWATER QUALITY ASSESSMENT USING DESCRIPTIVE AND ASSOCIATED STATISTICAL ANALYSES IN ITORI DISTRICT OF OGUN-STATE SOUTH-WEST NIGERIA

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ABSTRACT: *Groundwater is a natural gift whose significance in all spheres of human endeavours cannot be underestimated. It also plays a critical role and indispensable contribution in the dilution and intake of a number of several nutritional and toxic trace elements in the body system of humans and other biological populations. This study has examined the concentration status of heavy metals in wells and boreholes of Itori within Ewekoro Local Government Area of Ogun State, South-West Nigeria. The existing and functioning 25 boreholes and 25 hand-dug wells in the area were physically and chemically sampled using Ion Chromatography (IC) for anions, Nitrate, Phosphates, Bicarbonate, Chloride and Sulphate were measured after chromatography separation utilizing conductivity detectors while Inductively Coupled Mass Spectrometer (ICP-MS) and Inductively Coupled Optical Emission Spectrometry (ICP-OES) were used for heavy metals and trace elements detection. The raw data obtained from the laboratory analyses were subjected to statistical treatment using SPSS software version 20.0. Results of the analyses revealed that the concentrations of Copper (Cu), Lead (Pb), Zinc (Zn), and Manganese (Mn) were within approved guidelines including WHO and NESREA maximum permissible limits with mean values of 0.02±0.01mg/L and 0.04±0.02mg/L; 0.004±0.0005mg/L and 0.0008±0.0004mg/L; 1.008±0.37mg/L and 1.60±0.89 mg/L and 0.01±0.009mg/L and 0.04±0.01mg/L, respectively for boreholes and wells. The proportion of Cadmium (Cd) was also very low, with a mean concentration value of 0.0002±0.0004mg/L and 0.0007±0.0005mg/L for boreholes and wells respectively. The value of chromium and cobalt were found to be significantly low (0.0001±0.0003mg/L) in boreholes only and largely undetected in wells while Iron exhibited elevated concentration mean values of 0.44±0.34mg/L and 0.54±0.32mg/L respectively for boreholes and wells which is above the permissible water quality set standards. The elevated values of the identified parameters notably DO, BOD, Alkalinity,* Cl^{-}, HCO_3^{-}, Zn^{2+}, *and* Fe^{3+} *in the groundwater system of the study area that were above the set standards are major concern to the health of the consumers which necessitates a proactive response from the communities.*

KEYWORDS: Concentrations, Chromium, Alkalinity, Permissible Standards, Chromatography.

INTRODUCTION

Heavy metal concentrations are associated with environmental media such as as air, water, soil, and rocks. In general terms, heavy metal depicts the cluster of metals and metalloids with atomic density greater than 4 g/cm^3 or 5 times or more, greater than water. Though, the major contribution of heavy metal with regard to personal and general wholesomeness has little or nothing to do with density but is highly linked with the chemical properties of the possible metallic element in the media (Duruibe *et al.* 2007). Notably lead, iron, cadmium, mercury and arsenic among the heavy metals constitute threats to human health and general wellness when exposed to them. It has been observed by different authors namely Sharma *et al.*, 2004; Prabu, 2009 and Ishola, 2019; Ishola *et al*., 2021 among others that heavy metals such as Cd, Ni, As, and Pb can be highly hazardous to plants, animals and humans and indeed, serve as cofactors and activators of biochemical reactions. Heavy metals are highly persistent in the natural environment because they are natural components of the lithosphere as they can neither be created nor destroyed. Different ecological responses and industrial activities like mining activities, volcanic eruption, sewage system, indusial activities, coastal erosion, soil erosion and general runoffs are potential sources of Environmental pollution by heavy metals coupled with old mine sites and this pollution has been recorded to gradually reduce with increasing distance away from mining sites and other sources where the environmental hazards are experienced (Mildvan, 1970; Ishola, 2019; Ishola *et al*., 2021). These aforementioned Environmental media are agents of conveyance and principal distributors of heavy metals. The metallic constituents are either transported as dissolved species in water or as an integral part of suspended substances through water bodies like rivers and streams where dilution and migration occur resulting to the most virulent and detrimental health effects on biological system (Duruibe *et al.*, 2007). Most importantly, to a small extent, these metals find their ways to the body system of humans through several intakes and biological pathways via food, drinking water and air. Though, some of these heavy metals (e.g. Copper, Selenium, Zinc) serve as essential elements to maintaining and sustaining the metabolism of the human body system, when their concentration level is greater than the allowable thresholds, they can be consequently inferred be toxic and hazardous (Lenntech, 2011; Ishola *et al*., 2021). Consumption of contaminated water through lead pipes high ambient air concentrations near emission sources, or intake via the food chain and drinking channels are the probable sources of heavy metal poisoning or toxicity. Heavy metals could be very debilitating and hazardous to human health and wellness because they tend to bioaccumulate; rapid or gradual increase in the concentration level of a given chemical constituent in a biological organism can lead to bioaccumulation overtime compared to the natural concentration of chemicals in the environment (Lenntech, 2011). Heavy metals may also enter a water supply channels from domestic/household handling and industrial operations of wastes and sewage system, or through acidic rain resulting in the breakdown of rock particles and releasing heavy metals constituents as the products of weathering into streams, lakes, rivers, and groundwater systems through run-offs, seepages, and percolation (Lenntech, 2011; Ishola *et al*., 2021).

As earlier reported, many trace elements are necessary in small amounts for the normal growth and development of the biological cycles and efficient metabolism, but most of them become toxic at high concentrations. The principal sources of heavy metal pollution in urban areas of Africa are anthropogenic, while contamination from natural sources predominates in the rural areas (Lenntech, 2011; Ishola *et al*., 2021).

Anthropogenic Sources of pollution are associated with fossil fuel and coal combustion, industrial effluents, solid waste disposal, mining operations and metal. However, among these aforementioned anthropogenic pathways, the atmosphere tends to be of great threat to human health, as a result of the quantities of contaminants involved and the pervasive dilution and dispersion and exposure (Raikwar *et al.*, 2008; Sharma *et al*., 2004).

According to Ishola, 2019, the impact of these pollutants is confined mostly to the urban centres with large population density, mechanized operations, high traffic density and consumer-oriented industries. Natural sources of pollution include among others weathering of mineral deposits, bush burning, deforestation, and prevailing windblown dust. Among the heavy metals, the most serious effect of pollution is presently associated with lead (Pb) emission (Olade, 1987). Heavy metals like Fe, Cu, Zn, Ni and other trace elements are important for the proper metabolism of biological systems but their deficiencies or elevated levels could lead to a number of disorders. In recent years, contamination of food chain by heavy metals has become a serious issue in because of their potential accumulation in biosystems through contaminated water, soil and air. Therefore, a comprehensive analysis and understanding of heavy metal occurences, their accumulation in the soil and the possible effect of their presence in water, soil and on plant systems seem to be particularly important issues of present-day research on risk evaluations studies and environmental impact assessment (Sharma *et al*., 2004; Ishola, 2019). Itori is an agglomeration of autonomous communities within Ewekoro Local Government Area of Ogun State. it is a semi-urban centre with rapid development, commercial activities, growing educational institutions and service industries (Ishola, 2019). The absence of public treated-water supply for every household in the area has led to the proliferation of boreholes and shallow wells as a result of its high demand for domestic needs. The World Health Organization (WHO) once estimated that globally, every eight seconds, a child die from a water related disease and that each year, more than five million people die from illnesses linked to the consumption of unsafe drinking water (Anon, 1996; WHO, 1998; WHO, 2008). Water borne diseases, such as diarrhea, cause 1.5 million deaths a year, prominently among children in developing countries (JMP, 2008). WHO (2004) also reported that if sustainable safe drinking water and sanitation services were provided for all and sundry each year, there would be fewer cases of diarrhea episodes, 2.1 million fewer deaths caused by diarrhea, 76,000 fewer dracunculiasis cases, 150 million fewer schistosomiasis cases and 75 million fewer trachoma cases (Ishola, 2019). Therefore, the concentration of heavy metals in water sources (river, stream, well and boreholes) over the years has attracted concerns from epidemiologists and environmental health researchers due to its detrimental implications on biotic organisms especially man. The published work is loaded with discourses on heavy metal concentration and probable causes, and majority of these studies have examined the levels of these metals in water sources and other media in their respective ecosystems (Olade, 1987; Duruibe *et al.*, 2007; Prabu, 2009; Momodu and Anyakora, 2010; Nwankwoala *et al.*, 2011; Ishola, 2019; Ishola *et al*., 2019). However, despite the abundance of the past health reports on heavy metals, there is a dearth of information on the heavy metal current concentration status of wells and boreholes in Itori study area of possibly due to its lower traffic density, comparably lower population density, agrarian economy and emerging industries. Natural sources of pollution include weathering of mineral deposits, bush burning and windblown dust. Among the heavy metals, the most serious effect of pollution is presently associated with lead (Pb) emission (Olade, 1987). Heavy metals like Fe, Cu, Zn, Ni and other trace elements are important for the proper performance of biological systems and their deficiency or when in excess, could lead to a number of disorders. Food chain contamination by heavy metals has become a serious issue in recent years because of their potential accumulation in biosystems through contaminated water, soil and air. Therefore, a comprehensive analysis and better understanding of heavy metal occurrences, their accumulation in the soil and the effect of their presence in water, soil and on plant systems seem to be of particular interest in the present day research undertaken on risk evaluation studies and environmental impact assessment (Sharma *et al.,* 2004; Ishola *et al*., 2019). Itori district, being an agglomeration of distinct autonomous communities in Ewekoro Local Government Area of Ogun State, it serves as a semi- urban centre with rapid development, commercial activities and service industries (Ishola, 2019). The daily demands for potable public treated-water for households have led to the proliferation of boreholes and hand-dug wells (Obiora and Onwuka, 2005). The concentrations of heavy metal in water sources (rivers, streams, wells and boreholes) have attracted concerns from multidisciplinary researchers due to its health implications on biotic organisms especially man. The published works of researchers on this subject matter and related independent studies at different times and varying locations have examined the levels of these metals in water sources (Olade, 1987; Duruibe *et al.,* 2007; Prabu, 2009; Momodu and Anyakora, 2010; Nwankwoala *et al.,* 2011; Ishola, 2019; Ishola *et al.,* 2021). However, despite the abundance of published literatures on heavy metal concentrations, there is a gap on heavy metal and potential toxic element evaluations in wells and boreholes needed to be filled which correspondingly necessitated this work (Ishola *et al.,* 2021). This study, therefore, assesses the heavy metal status of wells and boreholes in the area as well as the probable clinical conditions and general health implications associated with elevated concentrations of heavy metals.

STATISTICAL MODEL

The relative frequency of occurrences of the random variable p is indicated by the density function $f\ (p)$ where p is the representation of the concentration of both the elemental and physic-chemical parameters of the aquiferous zones sampled in the respective borehole locations of the study area. If $f\ (p_1) > f\ (p_2)$, then points in the neighbourhood of p_1 is more likely to occur than points in the neighbourhood of p_2. The population mean of a random variable p is defined as the mean of all possible values of p and is denoted by μ (*Ishola et al., 2016*). The mean is also referred to as the expected value of p or $E(p)$. If the density function $f\ (p)$ is known, the mean can sometimes be found but if $f\ (p)$ is unknown, the population mean μ would ordinarily remain unknown unless it has been established by past experience with a stable population. If a large random sample from the population represented by $f\ (p)$ is available, it is highly probable that the mean of the sample is close to μ. The sample mean of a random sample of n observations namely $p_1, p_2, p_3 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots p_n$ is given by the ordinary arithmetic average (*Ishola et al., 2016*).

$$\bar{p} = \frac{1}{n}\sum_{i=1}^{n} p_1 \qquad (1)$$

Generally, $\bar{p}$ will never be equal to μ; by this we mean that the probability is zero that a sample will ever arise in which $\bar{p}$ is exactly equal to μ. However, $\bar{p}$ is considered a good estimation for μ because $E(p) = \mu; var\ (\bar{p}) = \mu$ *and*

$$var\ (\bar{p}) = \frac{\sigma^2}{n} \qquad (2)$$

where $\boldsymbol{\sigma^2}$ is the variance of $\boldsymbol{p}$. in otherwords, $\boldsymbol{\bar{p}}$ is an unbiased estimator of $\boldsymbol{\mu}$ and has a smaller variance than a single observation $\boldsymbol{p}$**,** the notation ***E(p)*** indicates the mean of all possible values of $\boldsymbol{\bar{p}}$**;** that is, every sample concentration is obtained from the entire population of the formation or subsurface hydrogeological environment of the sampled location (Fig. 3), the mean of each is found, and the average of all the collected sample mean is calculated. If every $\boldsymbol{p}$ in the entire population is multiplied by constant $\boldsymbol{c}$, the expected value is also multiplied by ***c:***

$$E(cp) = c\,E(p) = c\mu \qquad \textbf{(3)}$$

The sample mean has a similar property. If $\boldsymbol{q_i = c^{p_i}}$ for i = 1, 2, 3, ……………,n**,** then

$$\hat{q} = \boldsymbol{c^{p_i}} \qquad \textbf{(4)}$$

The variance of the population is defined as

$$var\,(\bar{p}) = \sigma^2 = (p - \mu)^2 \qquad \textbf{(5)}$$

Equation 5 is the average squared deviation from the mean and is thus an indication of the extent to which the values of $\boldsymbol{p}$ (elemental and physico-chemical concentration) are spread, distributed and dispersed in the aquiferous zones of the study area. It can be shown that

$$\sigma^2 = E(p^2).\,\mu^2 \qquad \textbf{(6)}$$

The sample variance is defined as

$$S^2 = \frac{\sum_{i=1}^{n}(p_i - p)}{n-1} \qquad \textbf{(7)}$$

Equation (7) can further be expressed to be equal to

$$S^2 = \sum_{i=1}^{n} \frac{{p_i}^2 - \bar{p}_i{}^2}{n-1} \qquad \textbf{(8)}$$

The sample variance $\boldsymbol{S^2}$ is generally never equal to the population variance $\boldsymbol{\sigma^2}$; the probability of such an occurrence is zero, but it is an unbiased estimator for $\boldsymbol{\sigma^2}$**;** that is**,** $\mathbf{E}(\boldsymbol{S^2})$ indicates that the mean of all possible sample variances. The square root of either the population variance or sample is called the standard deviation (*Rencher, 2002* and *Ishola et al., 2016*).

If each $\boldsymbol{p}$ is multiplied by the constant **c,** the population variance is multiplied by $\boldsymbol{c^2}$**,** that is,

$$Var\,(cp) = c^2\sigma^2 \qquad \textbf{(9)}$$

Similarly, if

$\boldsymbol{q_i = c^{p_i}}$ where $\boldsymbol{i}$ = 1, 2, 3……………, n, then, the sample variance of z is therefore given by

$${S_z}^2 = c^2 S^2 \qquad \text{(Ishola et al., 2016).} \qquad \textbf{(10)}$$

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MATERIAL AND METHODS

Physiography and Regional Geology of the Study Area

Itori is located on a latitude of 6°56'22.44"N and a longitude of 3°13'14.38"E with an elevation of 27.25 Meters (89.42 Feet). Historically, the people of Itoriland, like other settlers in Ewekoro Local Government Area of Ogun State, migrated from Egbaland (Ishola, 2019). Today, Itori has over thirty thousand population with a highly organized communal system and well-behaved youths, unlike past few years when the population was less than five hundred and served as the headquarter of the entire Ewekoro Local Government Area of Ogun State (Ishola, 2019).

The physiography of the study area is characterized by extensive lowland, generally undulating with a gently sloping dissected escarpment generally known as southern uplands drained mainly by Ewekoro River which according to (Reyment, 1965 and Jones and Hockey, 1964) is obsequent, endorcic and forms a dense network all over the area with anstromatic pattern along its course. The vegetation is extensively the forest type, and falls within the humid tropical region (Reyment, 1965; Ishola et al., 2023). The soil is ferralitic and belongs to Oxisol order according to the USDA classification scheme (Gbadegesin, 1992 and Reyment, 1965). Late Albian and late Senonian are the lower and upper limits of the formation in the neostratype described by Okosun (1998). A late Senonian age has been suggested for the upper strata of the Abeokuta formation. Ewekoro limestone and the overlying Akinbo shale, according to Jones and Hockey (1964), are revealed to be of lateral equivalents of the Imo formation of eastern Nigeria. In terms of regional geology, the study area belongs to the eastern part of the Dahomey Basin extending from the Volta Delta (Southwestern Ghana) to the western flank of the Niger Delta in Nigeria (Ogbe, 1972; Ushie *et al.,* 2014; Ishola *et al.,* 2021). However, the general succession of the sedimentary rock units of Ogun State which consists of Abeokuta formation lying directly above the basement complex is that of underlying rock which comprises of Abeokuta Group, followed by Ewekoro, Akinbo, Oshosun and Ilaro formations respectively while on top of Ilaro formation is the coastal plain sands (Benin formation) (Ishola *et al.,* 2021).

Local Geology of the Study Area

The Ewekoro formation is the local geology in the study area which is generally consistent with the regional geology of eastern part of the Dahomey Basin; predominantly comprises of the non-crystalline and highly non-fossiliferous and fossiliferous limestone and thinly laminated fissile and probably non-fossiliferous shale (Adegoke, 1976; Ushie *et al.,* 2014; Ishola, 2019). It is the sedimentary terrain of southwestern Nigeria. Ewekoro formation consists of intercalations of argillaceous sediment. The rock is generally soft and friable but in some places it is often plastered by materials that siliceous and ferrigeneous types. The three informal formational units of Abeokuta group are Ise, Afowo and Araromi formations. The strata previously referred to as the Nkporo shale were renamed Araromi formation by Okosun (1998). The Abeokuta formation on surface outcrops comprises mainly sand with sandstone, siltstone, silt, clay, mudstone and shale interbeds. It usually has a basal conglomerate which may measure about 1m in thickness and usually consists of poorly rounded quartz pebbles with silicified and ferruginized sandstone matrix or a softly gritty white clay matrix. In outcrops where there is no conglomerate, a coarse, poorly sorted pebbly sandstone with abundant white clay constitutes the basal bed. The overlying sands are coarse

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grained clayey, micaceous amd poorly sorted and indicative of short distances of transportation or short duration of weathering and possible derivation from the granitic rocks located to the north. Ise-2, Afowo-1, Orimedu-1, Bodashe, Ileppawi, Ojo-1 and Itori boreholes provided the subsurface data of the Abeokuta formation (Okosun, 1998; Ishola et al., 2023). The formation thickness values of 849m, 898m, 624m, 54.4m and 888m were respectively acquired for Ise-2, Afowo-1, Ileppawi, Itori and Ojo-1 boreholes. Notably in the Ise-2 borehole, the formation is essentially constituents of an arenaceous sequence between 1261.5m and 2142.1m which in turn consists of sands, grits, sandstone, siltstone, clay and shaly materials. Very coarse loose sands with sporadic thin intercalations of multicoloured shale and limestone found within the interval of 1076m - 1907m which is made up of represent the formation in Ojo–1 borehole. The upper portion of the formation strata from 44m to 98.4m in the Itori borehole consists of coarse-fine and medium-grained sand, silt and sandy clay horizons. Basal conglomerates are also penetrated by Ise-2 borehole (Egboka, 1983; Ishola *et al*., 2019). Fig. 1 is the inset map showing political divisions of the study area within Nigerian continental environment, Fig. 2 shows the geological map of the Selected Locations of the Study Area within the Nigerian Part of Dahomey Embayment, and the maps of the investigated locations in the study area are shown in Fig. 3.

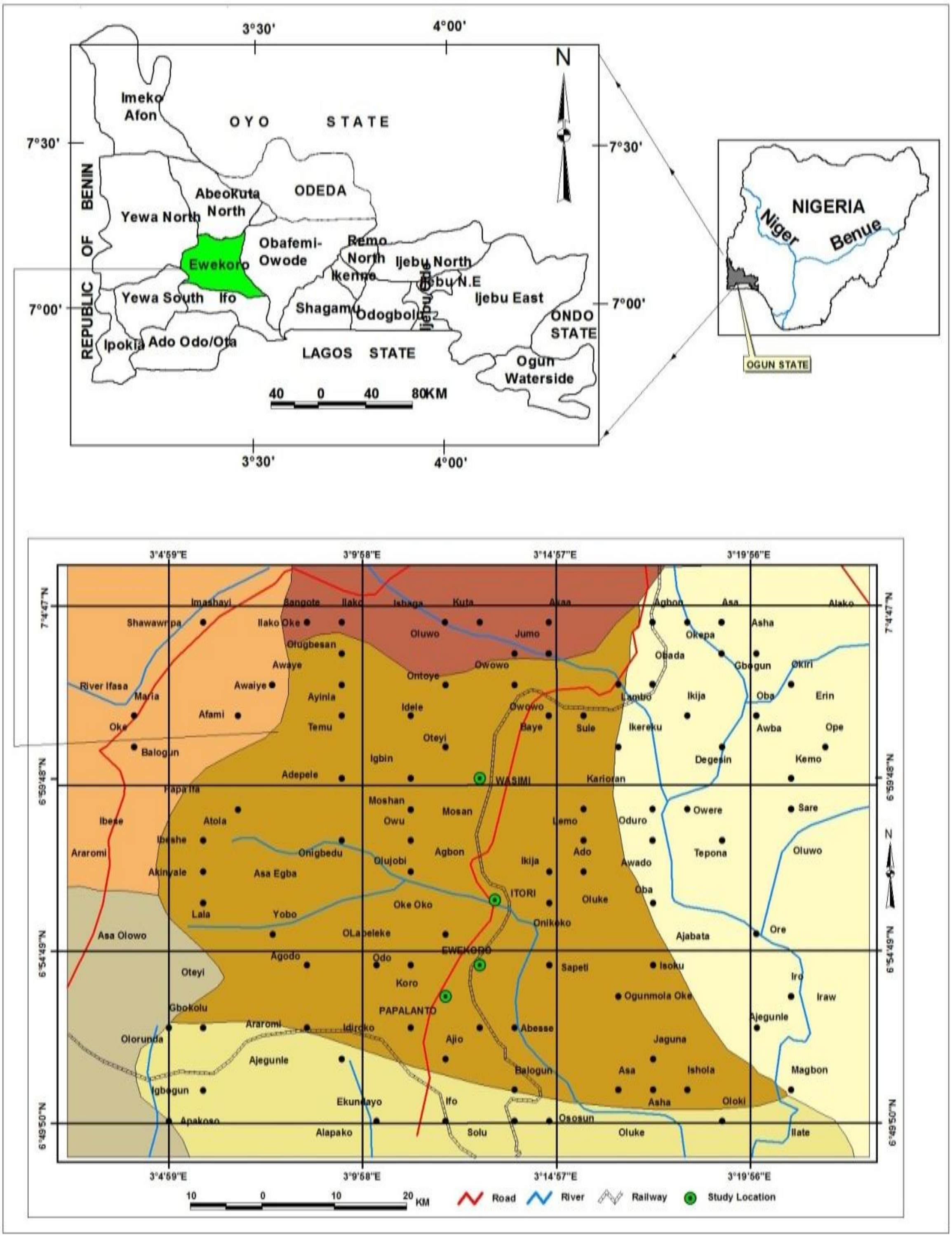

Fig.1: Inset Map showing the Study Areas in Ogun State within Nigeria Continental Domain (Arcview GIS 3.2A Environment, Ishola., 2019**)**

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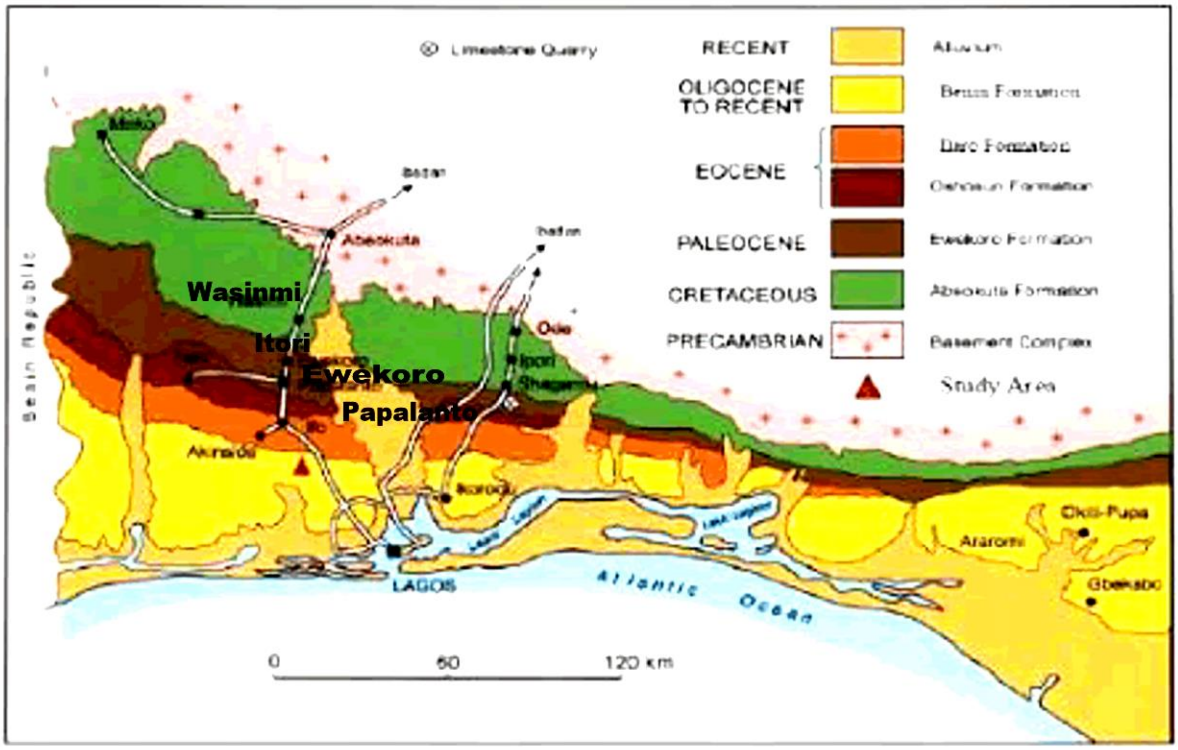

Fig. 2: Geological Map Showing the Selected Locations of the Study Area within the Nigerian Part of Dahomey Embayment (Billman, 1992; Modified by Ishola, 2019**)**

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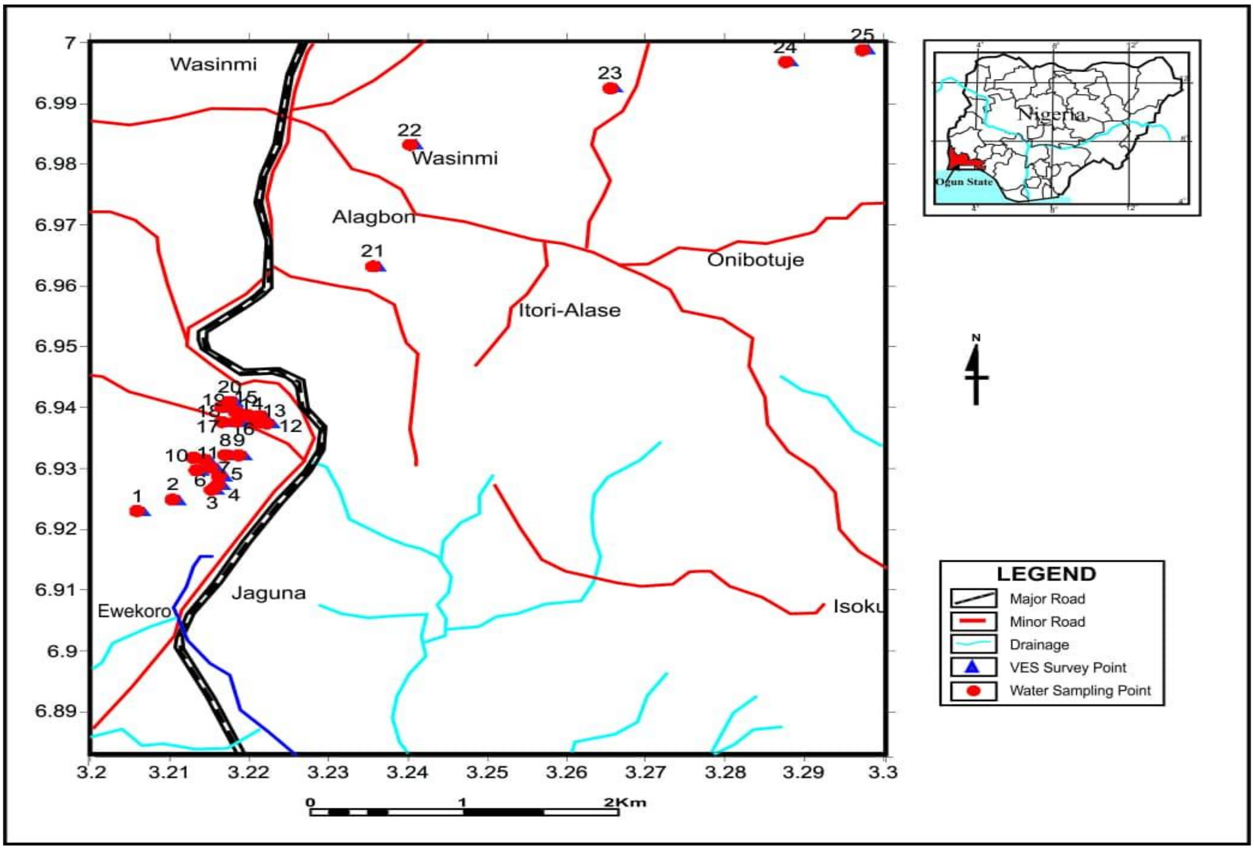

Fig. 3: Data Acquisition Map showing the Investigated Locations in Itori Study Area in Ewekoro LGA, Southwest Nigeria (Ishola, 2019**).**

Collection and Analyses of Subsurface Water Samples

Water samples were collected from existing and functional 25 boreholes at different and strategic sampling points within Itori communities. Most of the borehole water samples were obtained from private boreholes which serve as a source of household water supply, and also serve as a good source of livelihood for the families through sales to village buyers; a few others were a public borehole situated at a marketplace in the study area. Physico-chemical analyses were carried out on the water samples principally to identify and quantify the physical properties and chemical constituents of water. This includes pH, cations, anions, trace elements e.t.c. Determination of a water quality status is often realizable by extensive utilization of water chemistry analysis due to the possible interaction it has with its environment, which is predominantly the groundwork of studies of water quality, pollution, hydrology and geothermal waters (Ishola, 2019). .

Samples collected were immediately stored in clean air-tight, leak-proof plastic bottles and labelled appropriately while 1 ml concentrated HNO_3 per litre of sample was used for the preservation of the samples for metals. All water samples were consequently stored in an insulated cooler containing ice (maintained at 4 °C) and transported to the laboratory. Physico-chemical properties namely Electrical Conductivity (EC), Total Dissolved Solids (TDS), Temperature, Dissolved Oxygen (DO) and pH were determined in-situ using Hannah

Combo TDS/pH/EC/Temperature meter series multi-parameters (model HI991300), whereas Hannah (model HI9147) equipment was used for DO for the purpose of ensuring that they are not subjected to physical alteration such as temperature while JYD-IA DO meter was later used to measure BOD5 after the expiration of five days incubation. Other physicochemical parameters, bacteriological evaluation and metals levels were measured in the laboratory using standard procedures as reported by American Public Health Association (APHA, 1992; APHA, 1998; Ishola, 2019).

A very neat container (or that which the water samples to be tested has been rinsed with) was used for collection with the sensor on the meter dipped into it while the metre displayed the values it measured on a digital screen. The same procedures were repeated for other water samples. These measured parameters were compared with WHO and other specification. The geographical coordinates of sample points were also taken with GPS mete and their location is indicated on the data acquisition map. Samples specifically meant for anion determination were collected in 500 ml bottles, unfiltered and unpreserved, and later stored below 8 ^{0}C prior to analysis while the third sampling bottles were used for the determination of microbial loads. Ion Chromatography (IC) was used to analysed for anions while Nitrate, Phosphates, Bicarbonate, Chloride and Sulphate were measured after chromatography separation utilizing conductivity detectors. Inductively Coupled Mass Spectrometer (ICP-MS) and Inductively Coupled Optical Emission Spectrometry (ICP-OES) were used for heavy metals and trace metals detection. Water samples were filtered to less than 0.45 µm using a Pall Corporation GN-6 metricell sterilised membrane to improve accuracy and prevent cloudiness of the water while ensuring that the minute particles of clay sizes were removed before analysis. When lower levels of contamination are present, ICP-MS provide lower detection limits for measurement while ICP-OES is useful for higher concentrations, such as cases of high levels of contamination. Furthermore, cell-based ICP-MS serves as a very veritable integration tool for the removal of possible interferences that might prevent the detection of contamination at its emergence. These analyses were ultimately carried out in order to study how concentration of elements in water samples has been affected by the activities in the study area. The depth measurements of the investigated boreholes and existing hand-dug wells were determined using Heroin Water level meter. All the laboratory sample analyses were conducted in the Central Laboratory, Institute of Agricultural Research and Training (IART), Obafemi Awolowo University, Moor Plantation Ibadan Campus.

RESULTS AND DISCUSSION

The outcomes of physico-chemical parameters of water samples from the fifty water facilities (25 boreholes and 22 wells) shows that pH of the water samples ranged between slightly acidic to hugely alkaline with a mean pH 6.66±0.16 in boreholes and 7.14±0.41 in wells as presented in Table 1. The nature of the water samples can be attributed to the presence of tiny shale intercalations in the aquiferous coastal plain sand (Afangideh *et al.*, 2011). The pH values are well within the maximum desirable limits of 8.5 by the permissible set standards including WHO and NESREA (WHO, 2006). The average values of Total Suspended Solids (TSS) and Total Solids (TS) are 0.34±0.10 and 0.60±0.29 for boreholes; 0.33±0.15 and 0.92±0.32 for wells respectively. Of all the sampled physic-chemical parameters, Dissolved Oxygen (DO), Biological Oxygen Demand (BOD) and Alkalinity (ALK) exceeded the recommended limits with the recorded mean value of 3.56±155.30 and 7.58±0.44;

17.88±1.13 and 17.80±1.79; 489.02±507.57 and 566.71±658.40 jointly for boreholes and wells respectively while the exhibited mean Alkalinity values being 489.02±507.57 for boreholes and 566.71±658.40 for wells; the quality of groundwater in the area will be exceptionally good if minimum treatment is given to the water to reduce these properties and making it totally harmless and ideal for human usage and consumption (Afangideh *et al.,* 2011; Ishola *et al.,* 2021). It was observed that the numerical value of standard deviation for the exhibited alkalinity was higher than the mean in both groundwater sources; this implies that the degree of dispersion of alkalinity is far higher in distribution than average distribution amidst other associated physico-chemical parameters in the groundwater system of the study area (Ishola et al., 2016). The chloride content of the borehole samples had a mean value of 122.04±118.17 for boreholes; less concentration value for WHO, NESREA and NSDWQ and 252.12±125.69 for wells; slightly above WHO, NESREA, and NSDWQ but far above USEPA and NAFDAC recommended limits (Table 1). However, Total Hardness of the water samples ranged from 12.50 mgL^{-1} to 25.94 mgL^{-1} with a mean value of 17.46±3.77 for boreholes and 14.44 mgL^{-1} to 27.92 mgL^{-1} with a mean value of 20.52±3.14 for hand-dug wells. These recorded values in both groundwater sources are below the WHO highest acceptable limit of 500mgL^{-1} implying the water to be soft and foamy (WHO, 2006). This indicates that the wells and boreholes in the area are suitable for washing (Table 1 and Table 2). Based on the contents of heavy metals in the sampled wells and boreholes, the value of manganese (Mn) ranged from 0.00 to 0.03 mgL^{-1} with a mean value of 0.01±0.009 for boreholes and 0.01 to 0.06 mgL^{-1} with a mean value of 0.04±0.01 for wells. These recorded mean values of Mn falls within the maximum desirable limit of the approved standards WHO inclusive. It signified that water obtained from the sampled wells and boreholes was meant to give a satisfactory taste and would not promote the growth of algae in reservoirs or collection tanks during storage due to the low concentration of Mn (Nwankwoala *et al.,* 2011). Zinc on the other hand could be considered as non-toxic, but elevated concentration in human system can cause system dysfunctions that can lead to growth impairment and reproduction of the biotic contaminants. The clinical experience and symptoms attributable to Zinc have been reported to include vomiting, diarrhoea, bloody urine, liver failure, kidney failure and anemia (Fosmire, 1990; Duruibe *et al*., 2007; Ishola *et al.,* 2021). Concentration of Zinc in the analyzed samples ranged from 0.40 to 1.74 $mgL^{-1}$with a mean value of 1.008±0.37 for boreholes and from 0.46 to 4.30 mgL^{-1} with a mean value of 1.60±0.89 for wells which is less than WHO maximum allowable of 5.0 mgL^{-1} for drinking water (Table 2). This indicates that the sampled water contain the right proportion of Zn which is an essential plant and human nutrient element. The low concentration further implies that the water does not have caustic taste, hence, good for consumption and other domestic uses. Lead has often been reported as the most toxic form of heavy metals (Ishola *et al.,* 2021); its inorganic forms are absorbed through ingestion by food, water and inhalation (Ferner, 2001). Human exposures to lead are linked with a wide range of biological effects and clinical conditions depending on the level and duration of exposure. Toxic biochemical effects in humans which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system are associated High levels of exposure (Duruibe *et al.,* 2007; Lenntech, 2011; Ishola *et al.,* 2021). The proportion of lead (Pb) in the sampled water facilities was very low; it ranged from 0.00 to 0.004 $mgL^{-1}$with a mean value of 0.0004±0.0005 in boreholes and 0.00 to 0.0008 mgL^{-1} with a mean value of 0.0008±0.0004 in wells indicating the safe contamination of Lead (Olade, 1987; Ishola *et al.,* 2021). Cd concentration was equally very small in both groundwater sources with a mean value of 0.0002±0.0004 and 0.0007±0.0005 in the sampled boreholes and wells respectively. Chromium has been highly beneficial in metal alloys as pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration while the long-term exposure can cause kidney and liver damage, and damage to circulatory and nerve tissue. Chromium often accumulates over time in aquatic lives, adding to the danger of eating fish that may have been exposed to high levels of chromium (Lenntech, 2011). In the sampled water sources, the proportion of chromium (Cr) was significantly low with a mean concentration of 0.0001±0.0003 in wells implying the lower presence of this metal in the sampled wells but remained completely undetected in sampled boreholes (Table 1 and 2). The concentration of Fe ranged from 0.04 to 1.20 mgL^{-1} with a mean concentration value of 0.44±0.34 in boreholes and 0.02 to 1.40 mgL^{-1} with a mean concentration value of 0.54±0.32 in boreholes making it higher than the approved recommended general standards of 0.3 mgL^{-1} (Table 1 and 2). It is worthy of note that if the water sources had been acidic in nature it could have further increase in the level of Fe in both groundwater sources (Edmunds *et al.*, 1992; Paschke *et al.*, 2001; Verplanck *et al.*, 2006; Ishola *et al.*, 2021). The obtained maximum concentration values of Elemental and Physico-chemical parameters were compared across concentration categories as displayed in bar charts shown respectively in Fig. 5 and 6 and supported by exploded doughnuts showing the contributive weight of EC and Alkalinity with Chloride and hydrogen carbonate in both groundwater sources (boreholes and hand-dug wells) of the study area shown in Fig. 7 and 8; this is complemented with the bubble plot displayed in Fig. 9; it expressed the dominance of bicarbonate anions distribution over other detected and analyzed parameters in the groundwater system of the study area.

Table 1: Descriptive Statistics showing the Concentration Values of Physico-Chemical and Elemental Parameters of Itori Boreholes (N=25)

Parameters	**Min**	**Max**	**Range**	**Mean±SD**	**WHO (mg/L)**	**NESREA (mg/L)**	**NSDWQ (mg/L)**	**USEPA (mg/L)**	**NAFDAC (mg/L)**
PH	6.40	6.86	0.46	6.66±0.16	6.5 – 9.5	7.00-8.50	6.50-8.50	6.50-8.50	6.50-8.50
TEMP (^{0}C)	26.00	28.00	2.00	26.52±0.77	27	NA	NA	27	27
EC(μScm^{-1})	550.00	710.00	160.00	614.32±56.93	1200	NA	900	1200	1000
DO (mg/L)	6.82	7.84	7.77	**3.56±155.30**	7.5	NA	7.5	NA	NA
BOD (mg/L)	16.70	20.96	4.26	**17.88±1.13**	10	NA	10	NA	NA
COD (mg/L)	24.10	36.20	12.10	**28.75±3.17**	NA	NA	NA	NA	NA
TDS (mg/L)	0.48	10.90	10.43	7.59±2.28	100	1500	500	500	500
TSS (mg/L)	0.15	0.61	0.46	0.34±0.10	< 10	<10	NA	NA	NA
TS (mg/L)	0.28	1.21	0.94	0.60±0.29	1500	NA	NA	NA	NA
TURB (NTU)	0.10	1.11	1.01	0.28±0.28	< 4	5.0	5.0	5.0	5.0
ALK (mg/L)	141.40	1446.10	1304.70	**489.02±507.57**	200	500	100	100	100
TH (mg/L)	12.50	25.94	13.44	17.46±3.77	< 200	100-300	500	NA	100
THC(mg/L)	0.00	0.41	0.41	0.07±0.12	NA	NA	NA	NA	NA

Na^{2+} (mg/L)	24.10	42.10	18.00	30.48±5.10	< 200	NA	200	NA	200
K^{+} (mg/L)	31.80	56.91	25.11	38.69±8.72	250	200	NA	200	10
Ca^{2+} (mg/L)	9.40	22.90	13.50	12.96±3.84	100	75	NA	75	75
Mg^{3+} (mg/L)	1.70	5.83	4.13	4.20±1.08	20	15	NA	20	20
Cl^{-} (mg/L)	34.91	360.50	325.59	**122.04±118.17**	250	200	250	100	100
NO_3^{-} (mg/L)	0.04	0.13	0.09	0.11±0.02	50	45	NA	10	10
NO_2^{-} (mg/L)	0.01	0.03	0.02	0.02±0.008	< 3.0	NA	NA	NA	NA
SO_4^{2-} (mg/L)	5.11	12.74	7.63	7.80±2.72	400	500	200	250	100
NH_4^{+} (mg/L)	0.44	1.74	1.30	0.95±0.36	1.50	NA	NA	NA	NA
PO_4^{3-} (mg/L)	7.20	10.72	3.52	8.35±1.08	NA	NA	NA	NA	NA
HCO_3^{-} (mg/L)	72.35	743.50	671.15	**334.65±289.19**	100	NA	NA	NA	NA
$MgCO_3$ (mg/L)	7.60	13.94	6.34	10.43±2.04	10	NA	NA	NA	NA
Cu^{2+} (mg/L)	0.00	0.05	0.05	0.02±0.01	2.0	NA	1.0	1.3	1.0
Pb^{2+} (mg/L)	0.00	0.0004	0.0004	0.0004±0.0005	0.01	0.01	0.01	0.01	0.01
Cd^{2+} (mg/L)	0.00	0.0002	0.0002	0.0002±0.0004	0.003	0.003	0.001	0.005	0.005
Mn^{2+} (mg/L)	0.00	0.03	0.03	0.01±0.009	0.1	0.2	0.5	0.4	2.0
Zn^{2+} (mg/L)	0.40	1.74	1.34	**1.008±0.37**	0.01	NA	NA	NA	NA
Fe^{3+} (mg/L)	0.04	1.20	1.16	**0.44±0.34**	0.3	0.3	0.3	0.3	0.3
Cr (mg/L)	0.00	0.0001	0.0001	**0.0001±0.0003**	0.05	0.05	0.05	0.05	0.05
Co (mg/L)	0.00	0.0001	0.0001	**0.0001±0.0003**	0.05	0.05	0.05	0.05	0.05
Ni (mg/L)	0.00	0.0003	0.0003	0.0003±0.0005	0.02	0.05	NA	NA	0.05
S (mg/L)	0.15	2.81	2.66	1.08±0.67	250	NA	NA	NA	NA
Al^{3+} (mg/L)	0.00	0.00	0.0004	0.0004±0.0005	0.2	NA	NA	0.2	0.5
I (mg/L)	0.02	0.07	0.05	0.03±0.01	NA	NA	NA	NA	NA
Si (mg/L)	0.00	0.02	0.02	0.002±0.006	NA	NA	NA	NA	NA

KEY

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Table 2: Descriptive Statistics showing the Concentration Values of Physico-Chemical and Elemental Parameters of Itori Hand-Dug Wells (N=25)

Parameters	**Min**	**Max**	**Range**	**Mean±SD**	**WHO (mg/L)**	**NESREA (mg/L)**	**NSDWQ (mg/L)**	**USEPA (mg/L)**	**NAFDAC (mg/L)**
PH	6.50	7.80	1.30	7.14±0.41	6.5 – 9.5	7.00-8.50	6.50-8.50	6.50-8.50	6.50-8.50
TEMP (^{0}C)	22.00	28.00	6.00	26.24±1.71	27	NA	NA	27	27
EC (μScm^{-1})	510.00	880.00	370.00	671.44±94.60	1200	NA	900	1200	1000
DO (mg/L)	6.70	8.16	1.46	**7.58±0.44**	7.5	NA	7.5	NA	NA
BOD (mg/L)	15.75	21.91	6.16	**17.80±1.79**	10	NA	10	NA	NA
COD (mg/L)	23.81	36.82	13.01	**29.88±3.57**	NA	NA	NA	NA	NA
TDS (mg/L)	0.68	10.44	9.76	6.29±2.94	100	1500	500	500	500
TSS (mg/L)	0.22	0.67	0.45	0.33±0.15	<10	<10	NA	NA	NA
TS (mg/L)	0.33	1.16	0.83	0.92±0.32	1500	NA	NA	NA	NA
TURB (NTU)	0.10	1.09	.99	0.26±0.25	< 4	5.0	5.0	5.0	5.0
ALK (mg/L)	144.70	2881.40	2736.70	**566.71±658.40**	200	500	100	100	100
TH (mg/L)	14.44	27.92	13.48	20.52±3.14	< 200	100 - 300	500	NA	100
THC (mg/L)	0.00	0.22	0.22	0.09±0.07	NA	NA	NA	NA	NA
Na^{2+} (mg/L)	24.61	51.82	27.21	37.33±7.42	< 200	NA	200	NA	200
K$^+$ (mg/L)	30.12	65.81	35.69	46.14±9.26	250	200	NA	200	10
Ca^{2+} (mg/L)	9.74	23.74	14.00	14.60±3.66	75	NA	NA	75	75
Mg^{3+} (mg/L)	2.84	10.86	8.02	4.73±2.27	20	15	NA	20	20
Cl$^-$ (mg/L)	34.92	380.11	345.19	**252.12±125.69**	250	200	250	100	100
NO$_3^-$ (mg/L)	0.11	0.13	0.02	0.12±0.007	50	45	NA	10	10
NO$_2^-$ (mg/L)	0.01	0.04	0.03	0.02±0.007	< 3.0	NA	NA	NA	NA
SO$_4^{2-}$ (mg/L)	5.11	18.68	13.57	9.51±3.12	400	500	200	250	100
NH$_4^+$ (mg/L)	0.12	1.46	1.34	0.87±0.34	1.50	NA	NA	NA	NA
PO$_4^{3-}$ (mg/L)	7.88	12.71	4.83	9.38±1.23	NA	NA	NA	NA	NA
HCO$_3^-$ (mg/L)	72.35	1440.71	1368.36	**236.28±299.76**	100	NA	NA	NA	NA
MgCO$_3$(mg/L)	6.91	15.22	8.31	9.75±2.10	10	NA	NA	NA	NA
Cu^{2+} (mg/L)	0.01	0.06	0.05	0.04±0.02	2.0	NA	1.0	1.3	1.0
Pb^{2+} (mg/L)	0.00	0.0008	0.0008	0.0008±0.0004	0.01	0.01	0.01	0.01	0.01
Cd^{2+} (mg/L)	0.00	0.0007	0.00	**0.0007±0.0005**	0.003	0.003	0.001	0.005	0.005
Mn^{2+} (mg/L)	0.01	0.06	0.05	0.04±0.01	0.1	0.2	0.5	0.4	2.0

Zn^{2+} (mg/L)	0.46	4.30	3.84	**1.60±0.89**	0.01	NA	NA	NA	NA
Fe^{3+} (mg/L)	0.02	1.40	1.38	**0.54±0.32**	0.3	0.3	0.3	0.3	0.3
Ni (mg/L)	0.00	0.03	0.03	0.007±0.01	0.02	0.05	NA	NA	0.05
S (mg/L)	1.00	7.40	6.40	3.36±1.71	250	NA	NA	NA	NA
Al^{3+} (mg/L)	0.00	0.01	0.01	**0.001±0.002**	0.2	NA	NA	0.2	0.5
I (mg/L)	0.02	0.08	0.06	0.04±0.01	NA	NA	NA	NA	NA
Si (mg/L)	0.00	0.02	0.02	**0.002±0.005**	NA	NA	NA	NA	NA

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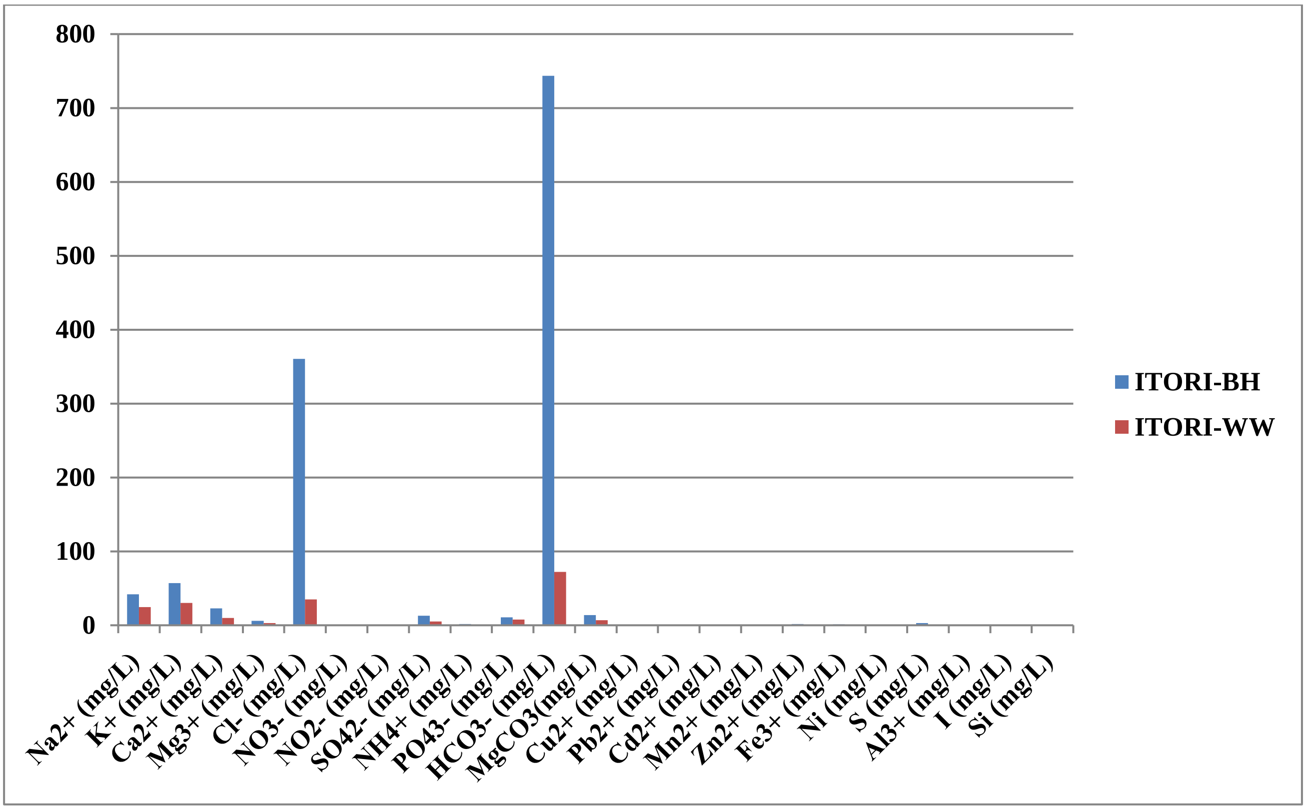

Fig. 5: Variation of Elemental Parameters of Itori Groundwater

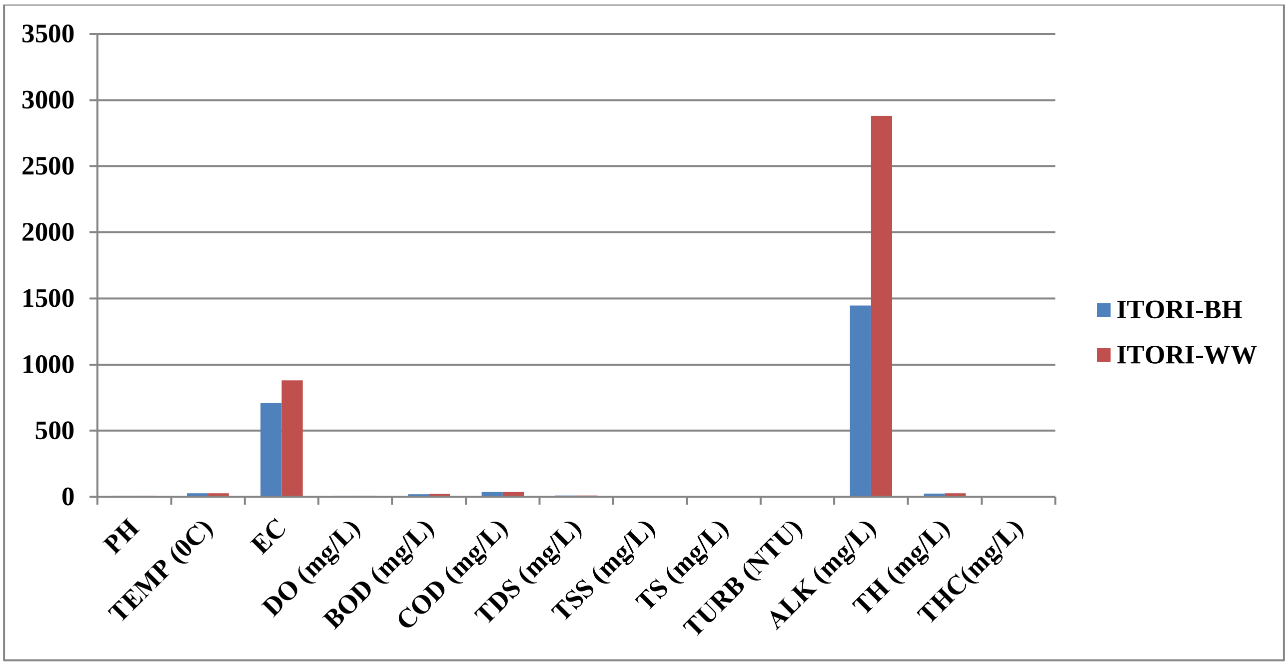

Fig. 6: Variation of Physico-chemical Parameters of Itori Groundwater

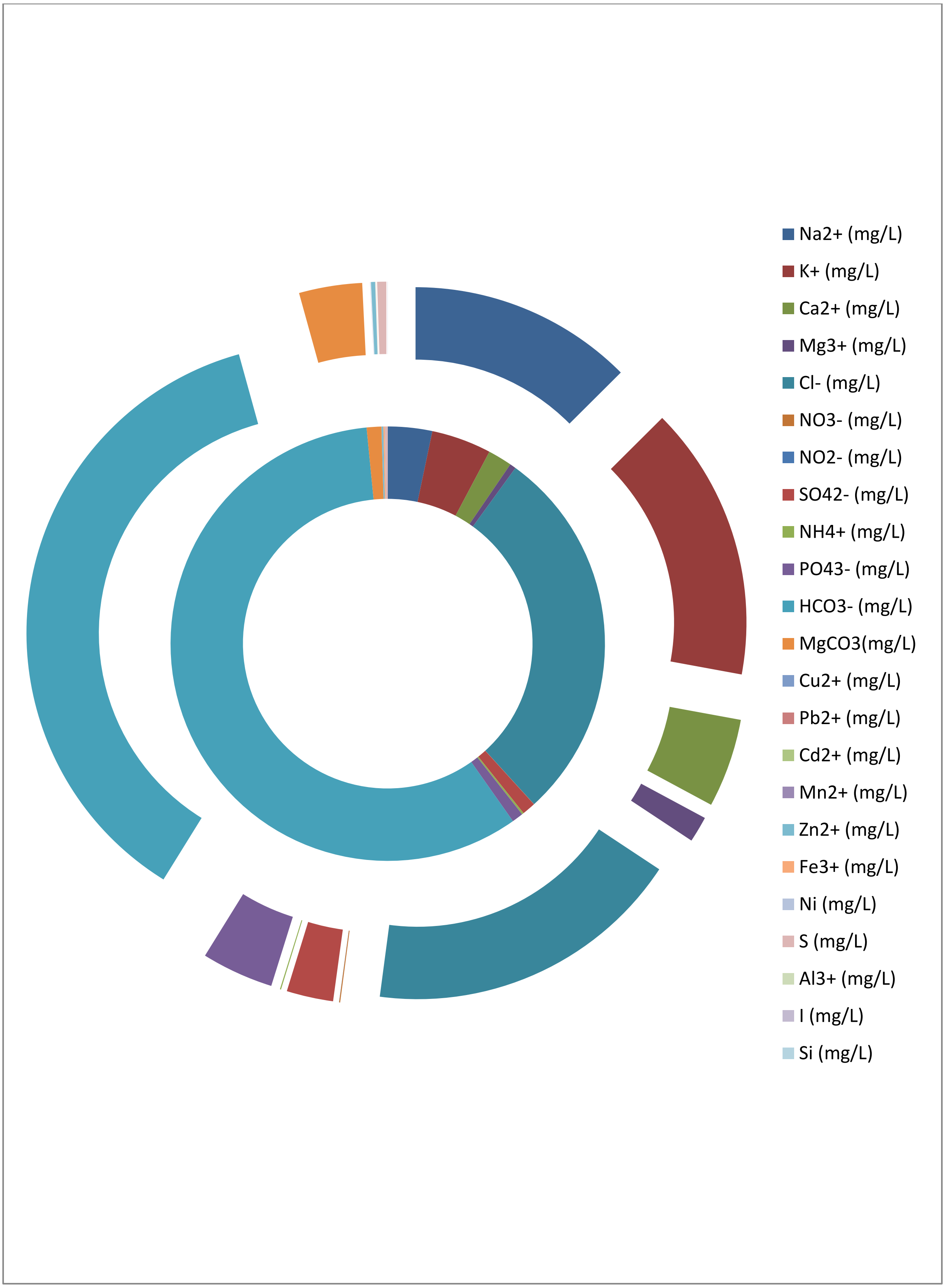

Fig. 7: Elemental Parameters of Itori Groundwater in Exploded Doughnut

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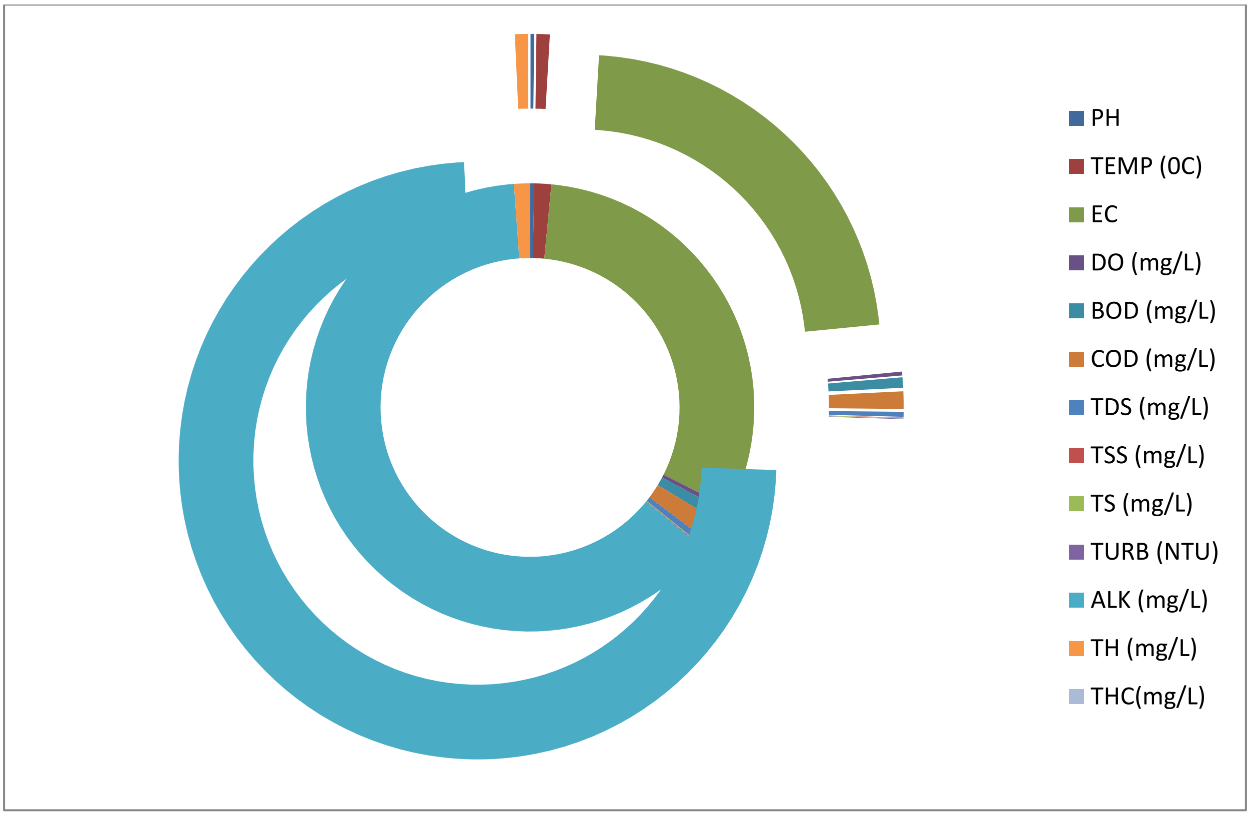

Fig. 8: Physico-chemical Parameters of Itori Groundwater in Exploded Doughnut

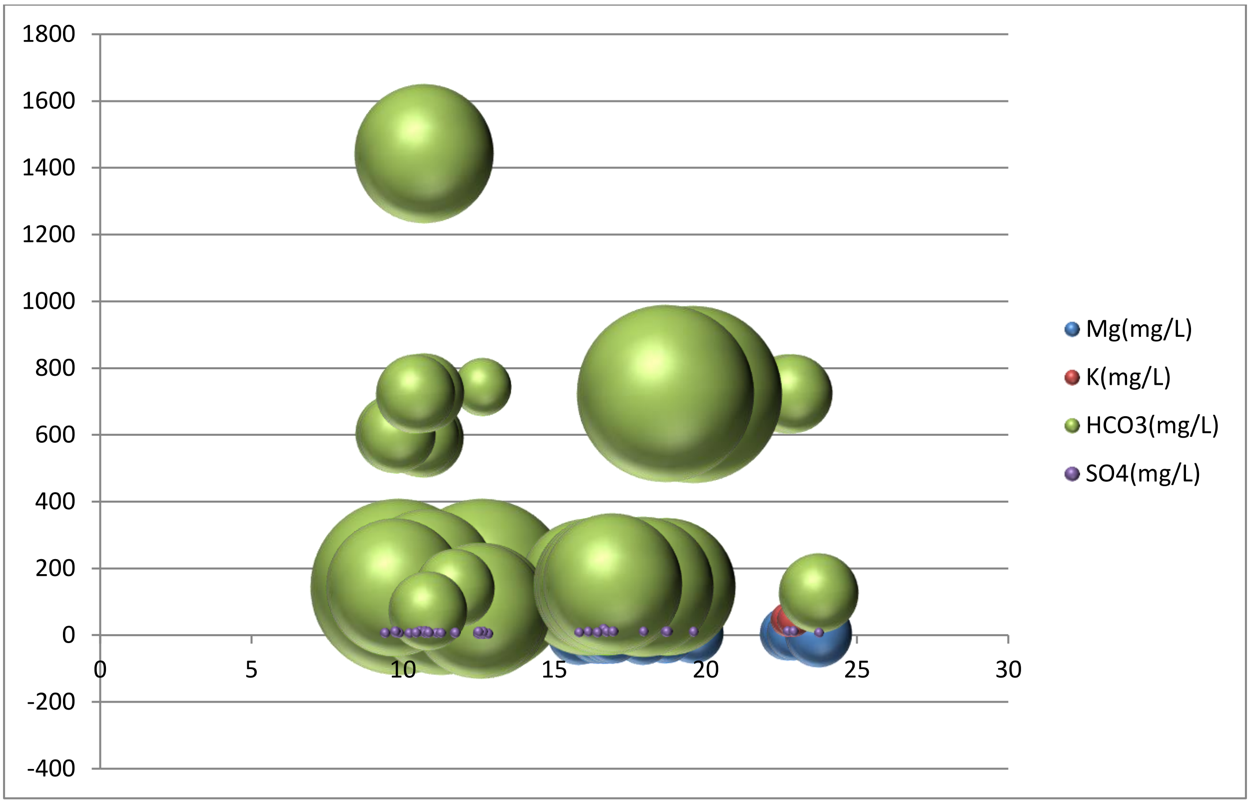

Fig. 9: Bubble plot showing the dominance of HCO_3^- in Itori groundwater system

CONCLUSION

Considering the outcomes of the sampled parameters; the significantly low concentration of heavy metal content except for a few elevated values of Fe^{3+} and Zn^{2+} concentration in the groundwater across the sampled wells and boreholes revealed the quality status of the groundwater sources (boreholes and wells) in the study area indicating the need for minor treatment and regular monitoring of the groundwater system of the study area. The generally low content also suggests that boreholes in the area though located far away from dumpsites, automobile shops and other common pollution sources. The invasion of heavy metals could ccome from other sources like run-offs, effluents among others. The result therefore implies that the quality status of water from facilities (wells and boreholes) had been affected. Though, most of the examined parameters are well within the approved set standards, including the WHO and NESREA maximum permissible limits for drinking water purposes but few others notably DO, BOD, Alkalinity, Cl^-, HCO_3^-, Zn^{2+}, and Fe^{3+} in the groundwater system of the study area were above the set standards and serve as major concern to the health of the consumers which necessitates a proactive response from the communities. To improve, maintain and sustain the present water quality status of groundwater sources in the area, routine monitoring and assessment of boreholes is recommended mostly to prevent the indiscriminate sinking of these facilities from to meeting the ever-increasing demands of people in the area by sanitary inspection officers. Also, the speciation of heavy metals and other elements (cations and anions) like Cd^{2+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Cl^-, HCO_3^{2-}, $MgCO_3^-$, and Zn^{2+} in the groundwater system of the study area in order to establish the newest forms of their occurrences is necessary. Therefore, results of water chemistry analyses using descriptive statistics and associated techniques have proven to be of extensive use in determining water quality status most importantly their concentration level, and the basic interaction it has with its environment which is the basis of the groundwork of studies of water quality, pollution studies, epidemics control, remediation techniques hydrology, geothermal waters overall water sciences and management.

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