

Hydrogeochemical Characterization and Groundwater Quality Assessment using Multivariate Classification Techniques in Papalanto District South-West Nigeria

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ABSTRACT

Papalanto district in Ewekoro Local Government area is one of the carbonaceous sub-basins of Dahomey embayment and supplies water to this part of Ogun State, South-West Nigeria. In this study the major hydrochemical facies were identified; the dominant water types are patterned in the following order based on the abundance of major contributive ions in relation to its corresponding cation abundance is $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. Emerging cationic concentrations indicate about 70% of the groundwater samples to be either lower than or well within the present allowable limit of 200, 150, 200 and 12 mg/L respectively of the approved national and international standards including WHO and NESREA. The samples in both groundwater sources (boreholes and wells) are mixed $CO_3^{2-} + HCO_3^- - Cl^-$ dominant fluids. For chemical parameters of Papalanto boreholes, the rotation converged in 10 iteration leaving 6 components extracted which accounted for 91.61% of the total variance of the formation concentrations with the result of the relationship supported by the principal component scores of box data plotted on the respective positions of the components in rotated space while the rotation for the physico-chemical parameters converged in 13 iterations of which 3 components were extracted which accounted for 86.32 % of the total variance observed. The components accounted for 42.46%, 29.05% and 14.82% of the total variance observed respectively for the first, second and third components suggestive of their hydrogeochemical impacts being traceable to two different origins. On the part of the Hand-dug wells, the rotation converged in 10 iterations with 6 components extracted, which accounted for 93.40% of the total variance observed. Hierarchical Cluster Analysis was used in identifying the similarities between the sampled sources based on the levels of the sampled parameters (Elemental and Physico-chemical) thereby grouping them into interpretable Clusters using the dendrogram for descriptor. The outcome of multivariate statistical analyses [Correlation Analysis, Principal Component Analysis and Hierarchical Cluster Analysis] gives an indication that most of the variations observed are elucidated by the possible anthropogenic pollutants that were predominant in the area.

Keywords: Boreholes, Water pollution, Hydrochemical facies, Papalanto, Multivariate Analysis

INTRODUCTION

The development and sustenance of any given society is incomplete without water availability (Ishola, 2019; Ishola *et al.*, 2021). Groundwater has become the major source of water supply for drinking, domestic,

household, agricultural, industrial, recreational, and environmental activities etc. This has led to an increase in the demand of water supply which is met mostly from the exploitation of groundwater resources. Today, groundwater quality is directly linked with

human safety and wellbeing because it serves as the most vital and unavoidable natural resource, which forms the core of the entire ecological system. The ultimate application of groundwater for varying purposes is dependent on the assessment of physical, chemical and bacteriological quality of groundwater. Variation in groundwater quality observable in any area has been a primary function of physical and chemical parameters that are greatly caused by natural processes such as the underlying geological formations and anthropogenic activities in such an area. In actual fact, industrial wastes and the municipal solid waste have emerged as one of the leading causes of pollution of surface groundwater system (Gupta *et al.*, 2009). Globally, many researchers have carried out different studies in different locations and at different times on groundwater quality and pollution sources influenced by industrial and natural process [Massoud *et al.*, 2006; Sue *et al.*, 2013; Mehdi *et al.*, 2014; Mohamad *et al.*, 2016; Nasrabadii and Abbasi, 2014; Ying *et al.*, 2014]. The underlying rationale governing the chemical characteristics of groundwater and possibly enhancing the varying observed anthropogenic activities are well documented in many urban and peri-urban areas of the world [Homoncik *et al.*, 2010, Marjani *et al.*, 2009, Ikem *et al.*, 2002, Cruikshank *et al.*, 1980, Eisen and Anderson (1980), Katz *et al.*, 1980, Kakar and Bhatnagar (1981), Flipse *et al.*, 1984, Cavallero *et al.*, 1985, Foster (1988), Dummer and Van Straaten (1988), Gosk *et al.*, 1990, Somasundaram *et al.*, 1992, Nazari *et al.*, 1993, Asubiojo *et al.*, 1997, Philips *et al.*, 1997, Mohan *et al.*, 2000;

Majudeswaran and Ramachandran, 2005; Yusuf, 2007; Mondal *et al.*, 2009; Joshi *et al.*, 2009; Srinivasamoorthy *et al.*, 2009; Jain *et al.*, 2010; Brinda *et al.*, 2012; Magesh *et al.*, 2012; Rajesh *et al.*, 2012; Sharma *et al.*, 2014; Selvan, 2015]. Groundwater contamination has been a major issue in any inhabited environment, especially in industrial urban centres (Ishola *et al.*, 2021). Papalanto is one of the growing industrialized districts and major cement producing and marketing location as well as the major sugar cane plantation for the entire South-West Nigeria. In due course, its industrial and agricultural glory gets fluctuated in terms of production due to various internal and external diseconomies which were adversely affected by the emerging government policies. On parity with cement industry, engineering industry mostly iron steel production also dominated the economy of the district in the past. As against the receding trend of the clay blocks industry, cement industry, ceramics and engineering industry still hold its unique position in spite of tremendous growth experienced in the country for the past few decades by different sectors of the economy. Papalanto has been a very busy area due to mining activities of limestone alongside with the predominant agricultural activities and rapid urbanization coupled with its endowed dense population in its surroundings areas (Ishola, 2019). Increased population, industrial mining and quarry operations make it essential to assess the quality of groundwater system in order to ensure the long-term sustainability of resources of the district (Uday *et al.*, 2018; Ishola, 2019). In this region, there is no proper or adequate drainage system. Hence, the sewage is

discharged into the river. Consequently, the polluted water reaches the diverse channels and flow paths which form the part of the Akinbo River, Alaguntan River and Eshe River systems. A decrease in various quality characteristics clearly indicates the possibilities of pollution due to industrial activities such as mining, fertilizer application, and foundries in and around Ewekoro Local Government Area, has also a strong impact on surface water and unprecedented implications on the underground water system. Earlier before now, most of the studies focused their attention on drinking and irrigation suitability on a few other regions of Ogun State thereby making the classification of hydrochemistry in Papalanto groundwater inadequate or grossly unavailable. Jeyaraj *et al.*, 2016 has accounted that a domestic and untreated industrial discharge is probably responsible for the high concentration values of Electrical Conductivity, COD, Alkalinity, and Turbidity. Furthermore, many of the earlier works in the area provide a preliminary and superficial assessment of groundwater quality without due characterization of the exact causative factors controlling the water quality and the samplings are random. But this present study has taken the large extent of the region covering the autonomous communities in this urban settlement, industrial zone, irrigational zones, for understanding of the water quality changes due to anthropogenic influences multivariate statistical techniques are consequently applied. The varieties of pollutants and contaminant seepages from multiple sources such as industrial outflows, agricultural cum irrigation return flow,

domestic discharges and hospital disposals aggregated the situation to be of water pollution and contamination impacts. Moreover, most of the wetlands in the district get dried up in dry season and serves as dumping yards for industrial wastes alongside the garbage dumping and other encroachments that have led to degradation of water bodies and ultimate depletion of the subsurface aquiferous zone. Deterioration of water bodies as well as the mismanagement of generated wastes is the inferred environmental problem in the Papalanto district.

Study Area

Hydrogeological Setting

Papalanto district of Ewekoro Local Government Area is approximately bounded by longitude $3^{\circ}13'E$ and $6^{\circ}54'N$ and harbours one of the largest outcrops of Ewekoro limestone that easily attracts global attention (Ishola *et al.*, 2019). The study area is located within the sedimentary terrain of south-western Nigeria and extends from Ibesse, 4km east of Papalanto along Papalanto-Shagamu road to Ogun River, 5km east to Iro community. The Ewekoro formation at the type locality is composed of 11m to 12m of limestone. It is sandy at the base grading downward into Abeokuta Formation. The Ewekoro formation is overlain of phosphatic glauconitic grey shale (Jones and Hockey, 1964). Subsurface investigation buttressed by some well information revealed a thick overburden of between 3m and 16m made up of silt, clay, sand shale with some alluvium and lateritic deposits in some places (WAPCO, 2001; Ishola *et al.*, 2019).

Limestones occur below this rock sequence with varying thickness and resistivity. The thickness of the limestone is between 3m and 40m; the thickest being at Fashola community (38.3m) and the thinnest at Jaguna (1.6m). The range of overburden thickness is between 2m to 16m while the limestone thickness ranges between 1.5m to 38.2m. The reserve estimation was calculated to be 7.75×10^8 cubic meters and adjudged to be of economic value if exploited especially around Fashola town. The limestone is classified (based on microfacies) into biomicrosparite, shelly biomicrites, algal biosparite and phosphatic biomicrites in that stratigraphic order (Fidelis *et al.*, 2014). 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 limestone and thinly laminated fissile and probably non-fossiliferous shale (Ushie *et al.*, 2014). It is the sedimentary terrain of southwestern Nigeria. Ewekoro formation consists of intercalations of argillaceous sediment. The rock is soft and friable but in some places cement by ferruginous and siliceous materials. The lithological units in Ewekoro formation are clayey sand, clay, shale, marl, limestone and sandstone (Ishola *et al.*, 2021).

On the lithostratigraphic nomenclature, the lithology of Ise and Afowo formations were defined by Omatshola and Adegoke (1981) which reveals a high degree of similarity; both as essentially sands and sandstones, but the latter contains thick interbeds of shales. This difference is not sufficient to warrant the establishment of separate lithostratigraphic

units. The two formations were later considered synonymous by Okosun (1998). In that study, it was observed that the Ise, Afowo and Abeokuta formations have similar lithologic and electric log characters. The uppermost beds of Abeokuta formation which crop out in Ijebu Ode area and in the shallow boreholes at Itori, Wasimi and Ishaga onshore consist mainly of fine to coarse grained sand and interbeds of shale, mudstone, limestone and silt. These lithofacies correlate well with the upper portion of the neostratotype in Ojo-1 borehole Okosun (1998).

The Abeokuta formation was defined by Jones and Hockey (1964) to consist of grits, loose sands, sandstones, kaolinitic clay and shale and was further characterized as usually having a basal conglomerate or basal ferruginized sandstone (Archibong, 1978; Okosun, 1998 and Chene, 1978). On the analyses of surface outcrops, Abeokuta formation 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. Coarse, poorly sorted pebbly sandstone with abundant white clay have been found to constitute the basal bed in other outcrops lacking conglomerates. The overlying sands are coarse grained clayey, micaceous and poorly sorted; indicative of short distances of transportation or short duration of weathering and possible derivation from the granitic rocks located to the north. The formation possesses a

thickness value of 849m, 898m, 624m, 54.4m and 888m in Ise-2, Afowo-1, Ileppawi, Itori and Ojo-1 boreholes respectively as obtained from the subsurface data on the Abeokuta formation as obtained from Ise-2, Afowo-1, Orimedu-1, Bodashe, Ileppawi, Ojo-1 and Itori boreholes by Okosun (1998). In the Ise-2 borehole, the essentially arenaceous sequence between 1261.5m and 2142.1m which consists of sands, grits, sandstone, siltstone, clay and shale constitutes the formation. The interval 1076m - 1907m which is made up of very coarse loose sands with sporadic thin intercalations of multicoloured shale and limestone represents the formation in Ojo-1 borehole. The strata from the 44m to 98.4m in the Itori borehole, which consists of coarse-fine and medium-grained sand, silt and sandy clay horizons, constitutes the upper portion of the formation. The Ise-2 borehole also penetrated a basal conglomerate.

Jones and Hockey (1964) revealed Ewekoro limestone and the overlying Akinbo shale to be lateral equivalents of the Imo formation of eastern Nigeria. The stratigraphy, depositional characteristics of limestone and clay/shale deposits with hydrogeological settings in South-Western Nigeria were equally investigated by other authors such as Omatshola and Adegoke (1991), Oladeji (1992) and Ishola *et al.*, 2021. Ewekoro formation belongs to tertiary formed Paleocene and Eocene; and the greater part of the depression is a potential artesian basin where groundwater can be sourced (Ishola, 2019). Kogbe (1976) and Adegoke *et al.*, 1972 described the stratigraphic and paleogeography of different sedimentary basins.

Also, Adegoke *et al.*, 1976 outlined the Albian and younger Paleographic history of Nigeria and summarized the nature and extent of transgressive, regressive phases as well as the nature of the sediment which also consists of intercalations of argillaceous sediment. The rock is soft and friable but, in some places, cemented by ferruginous and siliceous materials.

Although the water bearing rocks in large quantity are the sedimentary rocks, the basement rocks which underlies the area though hydrogeologically problematic appears to present relatively good ground water potential thought to be the reliable aquifers for small scale village, institution, industries and other water supply schemes. Offodile (1983) explained that the crystalline rocks are poor ground water regions with recorded average yield of 3960 liters /hrs (880gph) at average depth of 37.3m (123ft) and over 30% failure rate in water borehole drilling. Previous work shows that sedimentary aquifers give higher groundwater yield than the basement complex aquifer. Jones and Hockey (1964) evaluate depth, yield and specific capacity of tube wells which tap the Abeokuta formation, Ewekoro formation (Dahomey Basin) and coastal Plain sands with recent alluvium, in the Niger delta complex. These are important aquifer units in the Dahomey basin and Niger delta complex respectively. It is revealed that yields in excess of 10,000 l/hr are common as a result of lateral changes in lithology of the Abeokuta formation and coastal Plain sands. Egboka (1983) evaluates the various aquifer units in the Anambra basin, and on the basis of grain-size distribution. The Ajali sandstone is identified to have great

potentials for groundwater with a total discharge of $9.6 \times 10^5 \text{ m}^3 \text{ yr}^{-1}$. Although the water bearing rocks in large quantity are the sedimentary rocks, the basement rocks though may be hydro-geologically problematic appears to present relatively good ground water potential thought to be the reliable aquifers for small scale village, institution, industries and other water supply schemes. Uma *et al.*, 1989 considers accurate estimation of aquifer properties from grain-size distribution data crucial for successful groundwater development and management practices. However, this method is inadequate as its ability to define precisely, aquifer geometry and hydraulic boundaries is limited to sedimentary basins. By comparison, Offodile, (1992) is of that the idea that more productive aquifers occur in sedimentary geologic formations than in weathered and fractured crystalline rocks. Hydraulic conductivity of the Ajali sandstone in the Anambra basin was defined by employing the textural characteristics techniques (Yusuf, 2007; Tijani and Nton (2009). Nevertheless, recent experiences have shown that with the appropriate knowledge of the basic subsurface geology, detailed reconnaissance cum hydro-geophysical survey, and adequate hydrochemical evaluation with improved drilling techniques much better results of subsurface water quality status can be determined.

Site Description and Natural Vegetation

The natural vegetation of Ogun State which the study areas belong consists of the forest and the savanna which affect the floristic composition of the plant communities.

Human activities on the natural vegetation have reduced the original forest to secondary forest bush, regrowth and thickets. One very important impact of the quarry and mining activities in the area is deforestation which has led loss of vegetation cover necessitated by the need to move equipment to the quarry site, removal of the topsoil or (overburden) stemming of explosives and removal of blasted limestones. These effects are normally reduced by appropriate mitigating actions such as massive reclamation of the mined areas using new overburden materials and a forestation programme that involve planting of varieties of trees that can hold the soil structure well and could cover the exposed land well. Furthermore, Limestone mining in the entire Ewekoro Local Government Area of which Papalanto is a part had resulted into the conversion of many farmlands and human settlements into quarry sites. The house types on these sites are mainly the makeshift type built for use on no permanent basis. The few landowners on the factory site are resident on site to participate in cement business and could no longer engage in farming activities as it was before now. The West Africa Portland cement according to the management made frantic effort at resettling the displaced landowners in the estate that were built very close to the factory. Afterwards a programme of gradual takeover of the old farm site had started with some inhabitants completely relocated to new location far away from Papalanto while some others completely rejected the resettlement efforts. Since the resettling efforts were rejected by some of the landowners. In the course of using the quarry, farmers had been stopped from the site and the cutting/felling

of the trees continued, resulting into a large expanse of land exposed to rain water and wind. The lake created as a result of blasting of limestone and release of water within the weathered limestone deposit ordinarily should serve as habitat to fresh water fish, this has however not been developed (WAPCO, 2000; Ishola, 2019).

Fig. 1 shows the Geological Map of the Selected Locations of the Study Area within the Nigerian Part of Dahomey Embayment, Fig. 2 Displays the Google Earth imagery of the selected Investigated study area within in Ewekoro Local Government Area, Southwest Nigeria, the map of Ogun State showing the geology of the study areas is presented in Fig. 3, the inset map showing political divisions

of the study area within Nigerian continental environment is shown in Fig. 4, the maps of the investigated locations in the study area are shown in Fig. 5, and Fig. 6 is a basemap showing the location and accessibility of the study areas amidst the investigated points in Ewekoro LGA. The entire study area is generally accessible by major roads and several footpaths, although the road from Abeokuta town to the investigated area is tarred. In addition to Ewekoro-Papalanto road, the survey locations can equally be accessed through a major road from Lagos State through Sango-Ifo express road. The Global Positioning System (GPS) receiver was used in the field to obtain the spatial locations of the study area during sampling.

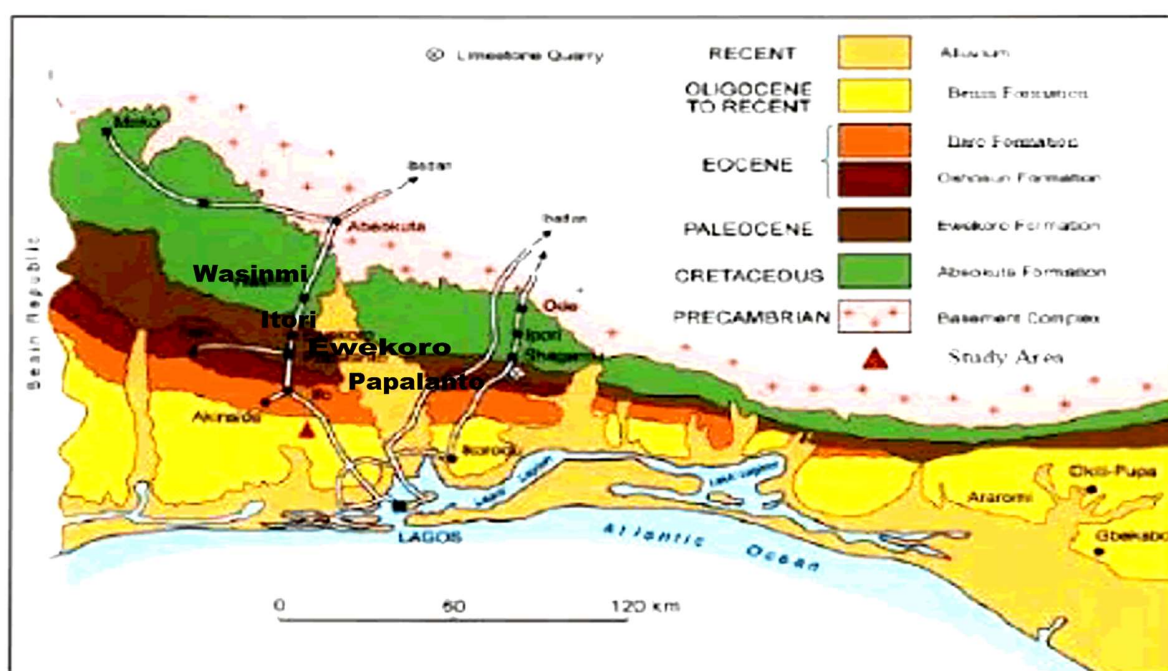


Figure 1: Geological Map Showing the Selected Locations of the Study Area within the Nigerian Part of Dahomey Embayment (Billman, 1992; Modified by Ishola, 2019).



Figure 2: Display of Google Earth Imagery of the selected Investigated study area within Ewekoro LGA, Southwest Nigeria (Ishola, 2019).

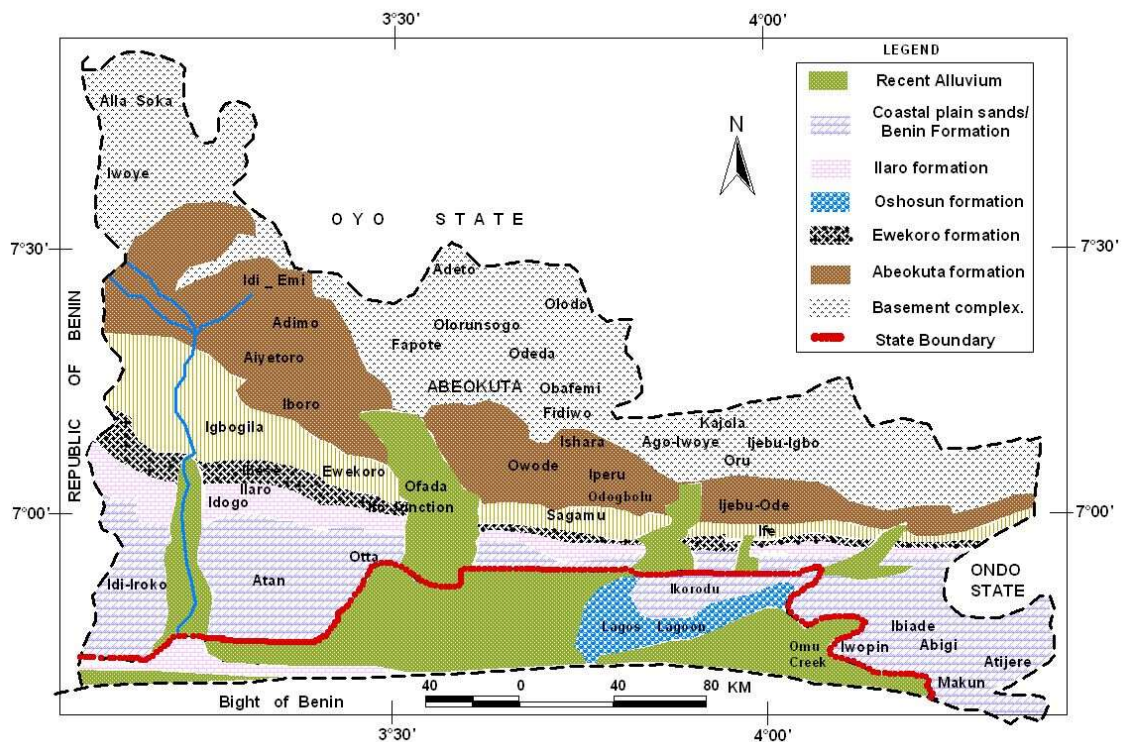


Figure 3: A Map of Ogun State showing the Geology of the Study Areas after Kehinde-Phillips (1990); Obiora and Onwuka (2005)

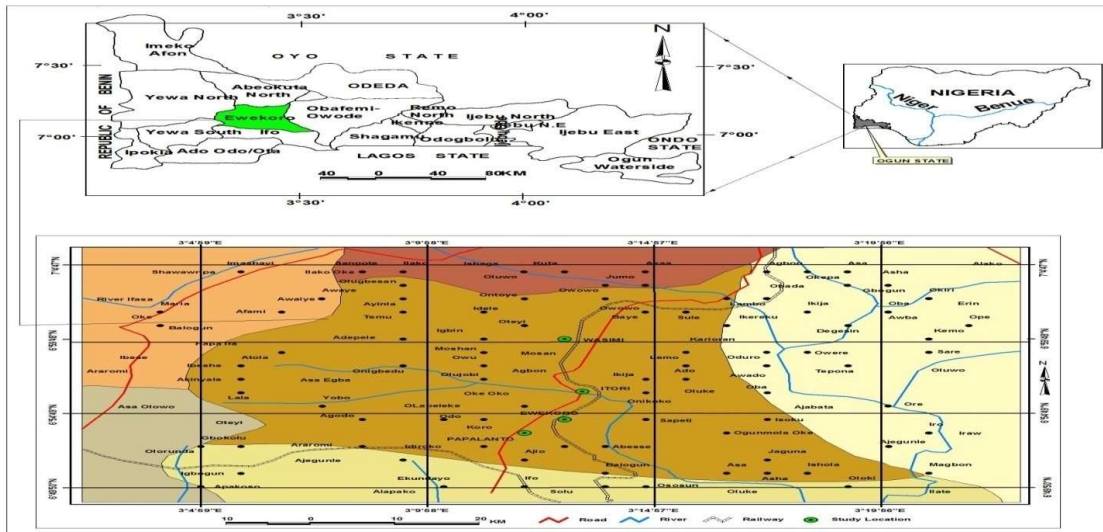


Figure 4: Inset Map showing the Study Areas in Ogun State within Nigeria Continental Domain using Esri Data/Nigeria Political Information in ArcView GIS 3.2A (Ishola, 2019).

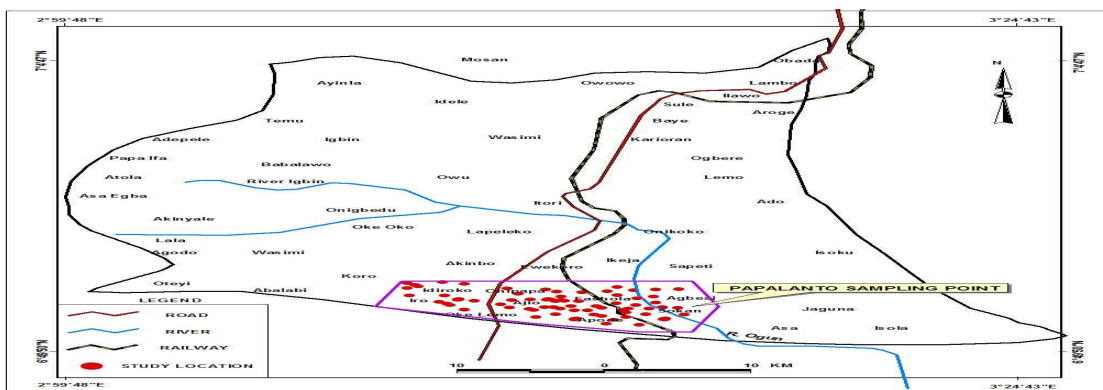


Figure 5: Data Acquisition Map showing the Investigated Locations in Papalanto Study Area in Ewekoro LGA, Southwest Nigeria (Ishola, 2019).

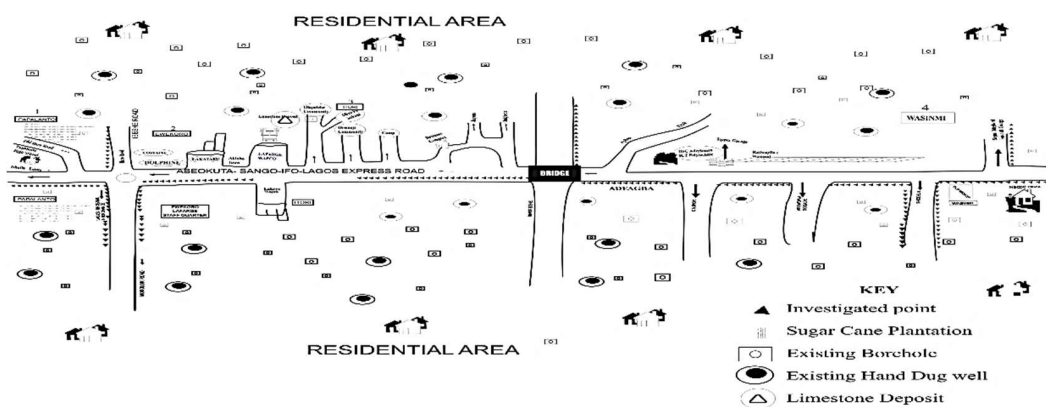


Figure 6: Basemap showing the Location and Accessibility of the Investigated Points in Ewekoro LGA, Southwest Nigeria (Ishola, 2019).

Hydrogeochemical Water Samples Collection and Analyses of Data

The study identified existing wells and boreholes as one that are frequently in use in the area while the procedure for data collection started with a reconnaissance survey to the area. Through this approach, 50 functional groundwater sources in dry season (25 boreholes and 22 wells) were randomly and strategically selected, with their coordinates recorded.

Water samples were collected in 1 litre plastic bottles. Prior to sample collection, all plastic bottles were rinsed thrice with the sampled water. After sampling, the containers were tightly covered. In addition, Physico-chemical analyses of the water samples were carried out to identify and quantify the physical properties and chemical components of water. This includes pH, TSS, Turbidity, Chloride Cations, Anions, Trace Elements, Total Hardness and so on were determined using standard methods (APHA, 1998). The samples collected were appropriately labelled and stored in clean air tight, leak proof plastic bottles in an ice-packed cooler, and immediately taken to the laboratory for analyses for heavy metals. Physico-chemical properties (Electrical Conductivity (EC), Total Dissolved Solids (TDS), Temperature, Dissolved Oxygen (DO) and pH were determined insitu using Hannah Combo TDS/pH/EC/Temperature meter series multi-parameters (model HI991300), whereas Hannah (model HI9147) equipment was used for DO in order to ensure that they are not subjected to alteration such as temperature. Water samples from the wells and boreholes were collected in a neat container (or that

which the water samples to be tested has been rinsed with) and the sensor on the meter was dipped in it while the metre displayed the values it measured on a digital screen. The same procedures were repeated for other water samples. Preparation of samples was carried out using acid digestion before 2ml of sample was injected into the machine by flow method. Detection limit set for each element varied from 0.02–0.1 µg/ml. 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. Water samples for anion determination were collected in 500 ml bottles, unfiltered and unpreserved, and stored below 8 °C prior to analysis. Ion Chromatography (IC) was used for anions. Nitrate, phosphates, bicarbonate, chloride and sulphate were measured after chromatography separation using conductivity detectors. Major metals and trace metals were determined using the Inductively Coupled Mass Spectrometer (ICP-MS) and Inductively Coupled Optical Emission Spectrometry (ICP-OES). In order to improve accuracy and to prevent cloudiness of the water, water samples were filtered to less than 0.45 µm using a Pall Corporation GN-6 metricell sterilized membrane. Minute particles of clay sizes were removed before analysis. ICP-OES is useful in measuring higher concentrations, such as high levels of contamination. When lower levels of contamination are present, ICP-MS provide lower detection limits for measurement. In addition, cell-based ICP-MS provides an additional tool for the removal of interferences that might prevent

detection of a contamination incident. The trace elements analyzed were Mn, Cr, Zn, Pb and Cd. These analyses were carried out in order to study how concentration of elements in water samples has been affected by the activities in the study area. The results obtained from the laboratory were subjected to analysis of variance (ANOVA) and Multivariate statistical methods such as Correlation Matrix, Principal Component Analysis, and Hierarchical Cluster Analysis were performed using IBM SPSS 20 software.

Results and discussion

Geochemistry and Water Quality Status

The mean value of PH for Papalanto borehole was 6.78 ± 0.11 while that of temperature was 26.56 ± 0.87 . The standard deviation values for both parameters showed that the variation between the measured values was not much. The pH of the groundwater in the study area varies from 6.4 to 6.87 with an average value of 6.78 ± 0.11 in boreholes and 6.70 to 7.85 with an average value of 7.11 ± 0.40 in hand-dug wells indicating alkaline nature of the samples; this was confirmed by the very high detected values of Alkalinity in the study area with a value range of 180.74 to 1481.11 and a mean value of 487.75 ± 515.95 in boreholes and a value range of 286.78 to 1711.11 with a mean value of 408.85 ± 391.94 in wells (Table 1 and Table 2). The EC values varied from 645.00 $\mu\text{S}/\text{cm}$ to 911.00 $\mu\text{S}/\text{cm}$ with an average value of 487.75 ± 515.95 $\mu\text{S}/\text{cm}$ in boreholes and 630.00 $\mu\text{S}/\text{cm}$ to 845.00 $\mu\text{S}/\text{cm}$ with an average value of 757.16 ± 56.61 $\mu\text{S}/\text{cm}$ in wells which is directly related to the ionic concentrations present in the

groundwater and its lower values contribute to lower salinity and total dissolved concentration. The TDS values are very low in the study area and vary between 6.90 to 8.98 mg/L with a mean value of 8.41 ± 0.71 mg/L in boreholes and between 7.80 to 10.40 mg/L with a mean value of 8.08 ± 0.66 mg/L in well for drinking purpose the maximum allowable TDS guideline value prescribed by the WHO (WHO, 2012) is 1000 mg/L. All the groundwater samples (both boreholes and wells) come under fresh water type (Table 1 and Table 2) and very much suitable for drinking purpose; as the value of TDS in them is far lower than 1000 mg/L. Suggestively, the lower TDS may be due to lack of serious percolation of channel water containing varying solids, agricultural wastes, and industrial seepages; most important sources of increasing dissolved solids in the groundwater could be traceable to the weathered country rocks. DO ranges from 6.70 to 7.84 with a mean value of 7.00 ± 0.32 in boreholes and 7.20 to 8.98 with a mean value of 8.56 ± 0.52 in wells making well water higher than the set permissible standards. The values of BOD ranges from 16.90 to 21.65 with a mean value of 20.02 ± 1.84 in boreholes and from 17.90 to 22.75 with a mean value of 19.76 ± 1.848 in wells thereby making both groundwater sources to be above the recommended limits of WHO standards. The recorded values of COD ranges from 25.00 to 38.88 with a mean concentration value of 32.38 ± 3.05 in boreholes and from 31.40 to 36.83 with a mean value of 34.38 ± 1.38 in wells. The concentrations of Ca^{2+} , Mg^{2+} , Na^{+} , and K^{+} ions vary from 12.10 – 28.72 (mean value of 24.02 ± 4.17 mg/L), 1.94 – 4.47 (mean value

of 3.47 ± 0.66 mg/L), 38.40 – 45.8 (mean value of 42.58 ± 2.04 mg/L) and 48.60 – 23 (mean value of 55.17 ± 2.60 mg/L) respectively for Papalanto boreholes and from 9.61 – 11.95 (mean value of 11.10 ± 0.75 mg/L), 4.24 – 9.99 (mean value of 7.42 ± 1.26 mg/L), 34.40 – 52.64 (mean value of 4.53 ± 4.03 mg/L) and 41.61 – 61.44 (mean value of 45.37 ± 4.94 mg/L) respectively for Papalanto wells. Thus, $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$ represents the ordered pattern of cation abundance. Not only that, but Cationic concentrations also indicate about 70% of the groundwater samples to be lower than the provisional allowable limit of 200, 150, 200 and 12 mg/L respectively. Among the anions, the chloride is the most dominant ion in the groundwater. The concentration of chloride in the study area ranges in value from 71.80 to 382.04 mg/L and with an average value of 314.80 ± 88.05 in boreholes making it above the highest allowable standard of WHO and 70.61 to 226.39 with an average value of 196.40 ± 56.00 in wells; making Papalanto wells lower than the allowable set standards. Chloride has been found to be one of the most important and contributive inorganic anions present in groundwater. Relatively, the higher concentration of chloride observed from the groundwater samples contributes approximately to about 85% to the total anionic concentration; most probably due to an influence of poor sanitary conditions, chemical fertilizers, irrigation return flow and industrial effluents. According to WHO (WHO, 2012), the maximum permissible limit of chloride value is 250 mg/L, from the study area, the mean concentration of the samples exceeds the permissible limit and unsuitable for drinking purpose. The

concentration of bicarbonate is observed from 90.37 to 778.62 mg/L with a mean value of 403.81 ± 318.40 in boreholes and 143.38 to 855.11 mg/L with a mean value of 203.94 ± 196.01 in wells making samples from both groundwater sources higher than the approved set standards; higher concentration of HCO_3^- when compared with chloride concentration in the groundwater infers that mineral dissolution must have also occurred in subsurface aquiferous zone. The concentrations of SO_4^{2-} were noted to range in values between 0.03 to 11.88 mg/L with an average value of 9.60 ± 3.65 mg/L in boreholes and 9.37 to 14.62 mg/L with an average value of 10.31 ± 1.32 mg/L in wells, which is a very significant environmental problem in many irrigated agricultural regions. Since the sulphate concentration is less than 400 mg/L in the groundwater samples; it indicates a lower impact of soluble salts accumulation in the soil, anthropogenic activity and lower sulphate fertilizer application. The range of NO_3^- is 0.12 – 0.14 mg/L with an average of 0.12 ± 0.008 mg/L in boreholes and 0.11 – 0.14 mg/L with an average of 0.13 ± 0.007 mg/L in wells making both results falling below the WHO recommended a value of 45 mg/L. The highest mean value of 403.81 ± 318.40 was recorded for HCO_3^- followed by 314.80 ± 88.15 for Cl^- while the lowest mean value of 0.0001 ± 0.0003 was recorded for Al^{3+} . COD, BOD and DO exhibit an increasing order of value concentrations of and $COD > BOD > DO$ respectively. The high value of standard deviation over the mean revealed a wide variation in the distribution of elemental constituents of the sampled parameters in the

hydrogeologic environment of the study area. Very high variability in the concentration of both the physico-chemical and elemental parameters (e.g. HCO_3^- , Ni, Cr, Co, Al^{3+} , Pb^{2+}) resulted in the standard deviation being higher than the mean values for such elements (Table 1 and Table 2). The concentration of NO_3^- does not exceed 10 mg/L in groundwater under natural conditions; beyond 10 mg/L is an indication of anthropogenic pollution; principally due to poor sanitary conditions, indiscriminate application of fertilizers for higher crop yields (SubbaRao et al., 2012; Ishola, 2019). Bubble plot with a 3D- effect resembles a scatter chart but compares sets of three values instead of two (Ishola, 2019). The third value determines the size of the bubble marker which is displayed with a 3D effect (Fig. 8); it displays the dominance of hydrogen carbonate concentration in the groundwater samples of the study area amidst other constituents. It gives an indication of chemical weathering in rock-forming minerals influencing the groundwater quality by dissolution of weathered rock through which subsurface circulations take place (Selvakumar *et al.*, 2015); the chemistry of groundwater in the Ewekoro geological formation in which the study area belongs is mainly controlled by geochemical mechanisms of a typical limestone formation (Sajikumar and James, 2016; Ishola, 2019; Ishola *et al.*, 2021). The display of samples falling outside these plots may be due to other processes of anthropogenic activities outside natural geological conditions, which addressed the similar observation of (Srinivasamoorthy *et al.*, 2008).

Geochemistry and Suitability for Irrigation Purpose

the osmotic pressure in the root zone which affects the agricultural soil and hence plants physically and chemically leading to reduced yield and consequently hindering the plant growth can be altered by the dominant presence of excessive amount of dissolved salts such as Sodium, Magnesium, Chloride and Bicarbonate that are primarily meant for irrigation purposes (Bob et al., 2016). Also, the growth and continuation of successful irrigation projects does not only depend on the supply of irrigation water to the land but also aim in controlling the solutes and alkali status of the soil (Oster, 1994). Hardness is an important factor in determining the suitability of water samples for various purposes; domestic, and irrigation purposes as is involvement in overall physico-chemical constituents of the water among others cannot be overemphasized. Sawyer *et al.*, 2003 reported the classification of water as soft, hard, moderately hard and very hard. Based on this classification scheme, total hardness of the groundwater samples indicates in the study area are very soft in nature while the maximum permitted limit of total hardness for drinking is specified as 500 mg/L (Sawyer *et al.*, 2003). However, for irrigational purposes, more than 1000 mg/L of hardness is also accepted. The EC values of the groundwater acquired from the study area simply measures up to 911 $\mu\text{S}/\text{cm}$ in boreholes and 842 $\mu\text{S}/\text{cm}$ in hand-dug wells making it to fall in the class of good to permissible (Table 3 and Table 4). The alkalinity of the water is high with corresponding low salinity level making it very conducive for irrigation purposes; high

sodium content and high salinity levels are bad for irrigation because sodium is a component of a harmful salt and also causes poor physical conditions of the soil. A high number of salts in irrigation water can also modify the osmotic pressure in the root zone, which in turn limits the amount of water absorbed by the plant and consequently hindering the effective and healthy growth of the affected plant (Ying *et al.*, 2014). Magnesium ratio also serves as an important parameter to assessing the suitability of water

quality conditions for the desired irrigation requirement. Excessive Magnesium content damages soil structure when water contains comparably more of sodium and high salinity (Chidambaram *et al.*, 2013). It has been reported that when magnesium ratio exceeds the value of 50, the water associated with such content could be considered to be harmful. Hence, it is unsuitable for irrigation, because it could harmfully affects the crop yield as the soils become more alkaline (Elango *et al.*, 2003).

Table 1: Descriptive Statistics showing the Concentration Values of Physico-Chemical and Elemental Parameters of Papalanto 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	6.87	0.47	6.78±0.11	6.5 – 9.5	7.00-8.50	6.50-8.50	6.50-8.50	6.50-8.50
TEMP (°C)	25.00	28.00	3.00	26.56±0.87	27	NA	NA	27	27
EC ($\mu S cm^{-1}$)	645.00	911.00	266.00	703.48±92.31	1200	NA	900	1200	1000
DO (mg/L)	6.70	7.84	1.14	7.00±0.32	7.5	NA	7.5	NA	NA
BOD (mg/L)	16.90	21.65	4.75	20.02±1.84	10	NA	10	NA	NA
COD (mg/L)	25.00	38.88	13.88	32.38±3.05	NA	NA	NA	NA	NA
TDS (mg/L)	6.90	8.98	2.08	8.41±0.71	100	1500	500	500	500
TSS (mg/L)	0.12	0.31	0.19	0.23±0.05	> 10	>10	NA	NA	NA
TS (mg/L)	0.66	0.99	0.33	0.86±0.10	1500	NA	NA	NA	NA
TURB (NTU)	0.10	1.11	1.01	0.24±0.33	< 4	5.0	5.0	5.0	5.0
ALK (mg/L)	180.74	1481.11	1300.37	487.75±515.95	200	500	100	100	100
TH (mg/L)	12.06	29.96	17.90	26.91±4.91	< 200	100 -300	500	NA	100
THC (mg/L)	0.12	0.21	0.09	0.19±0.03	NA	NA	NA	NA	NA
Na ²⁺ (mg/L)	38.40	45.87	7.47	42.58±2.04	< 200	NA	200	NA	200
K ⁺ (mg/L)	48.60	58.47	9.87	55.17±2.60	12	200	NA	200	10
Ca ²⁺ (mg/L)	12.10	28.72	16.62	24.02±4.17	75	NA	NA	75	75
Mg ³⁺ (mg/L)	1.94	4.47	2.53	3.47±0.66	20	15	NA	20	20
Cl ⁻ (mg/L)	71.80	382.04	310.24	314.80±88.05	250	200	250	100	100
NO ₃ ⁻ (mg/L)	0.12	0.14	0.02	0.12±0.008	50	45	NA	10	10
NO ₂ ⁻ (mg/L)	0.01	0.02	0.01	0.02±0.003	< 3.0	NA	NA	NA	NA
SO ₄ ²⁻ (mg/L)	0.03	11.88	11.85	9.60±3.65	400	500	200	250	100
NH ₄ ⁺ (mg/L)	0.80	1.78	0.98	1.47±0.28	1.50	NA	NA	NA	NA
PO ₄ ³⁻ (mg/L)	8.70	10.77	2.07	10.14±0.57	NA	NA	NA	NA	NA
HCO ₃ ⁻ (mg/L)	90.37	778.62	688.25	403.81±318.40	100	NA	NA	NA	NA
MgCO ₃ (mg/L)	8.72	13.98	5.26	11.54±1.40	10	NA	NA	NA	NA
Cu ²⁺ (mg/L)	0.00	0.03	0.03	0.02±0.01	2.0	NA	1.0	1.3	1.0
Pb ²⁺ (mg/L)	0.00	0.0006	0.0006	0.0006±0.0005	0.01	0.01	0.01	0.01	0.01
Cd ²⁺ (mg/L)	0.00	0.0004	0.0004	0.0004±0.0005	0.003	0.003	0.001	0.005	0.005
Mn ²⁺ (mg/L)	0.01	0.03	0.02	0.02±0.009	0.1	0.2	0.5	0.4	2.0

Zn²⁺ (mg/L)	1.11	1.85	0.74	1.43±0.25	0.01	NA	NA	NA	NA
Fe³⁺ (mg/L)	0.03	1.17	1.14	0.40±0.42	0.3	0.3	0.3	0.3	0.3
Cr (mg/L)	0.00	0.0004	0.0004	0.0004±0.0005	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)	0.38	2.47	2.09	1.41±0.65	250	NA	NA	NA	NA
Al³⁺ (mg/L)	0.00	0.0001	0.0001	0.0001±0.0003	0.2	NA	NA	0.2	0.5
I (mg/L)	0.02	0.04	0.02	0.03±0.008	NA	NA	NA	NA	NA

Drinking Water Standard Specifications given by WHO (2004), NESREA (2010), NSDWQ (2007), USEPA (2007) and NAFDAC (2011) and Statistical Information of ion Concentrations.

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Table 2: Descriptive Statistics showing the Concentration Values of Physico-Chemical and Elemental Parameters of Papalanto 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	6.70	7.85	1.15	7.11±0.40	6.5 – 9.5	7.00-8.50	6.50-8.50	6.50-8.50	6.50-8.50
TEMP (°C)	22.00	31.00	9.00	25.12±1.99	27	NA	NA	27	27
EC (μScm⁻¹)	630.00	845.00	215.00	757.16±56.61	1200	NA	900	1200	1000
DO (mg/L)	7.20	8.98	1.78	8.56±0.52	7.5	NA	7.5	NA	NA
BOD (mg/L)	17.90	22.75	4.85	19.76±1.48	10	NA	10	NA	NA
COD (mg/L)	31.40	36.83	5.43	34.38±1.38	NA	NA	NA	NA	NA
TDS (mg/L)	7.80	10.40	2.60	8.08±0.66	100	1500	500	500	500
TSS (mg/L)	0.35	0.53	0.18	0.45±0.04	> 10	>10	NA	NA	NA
TS (mg/L)	0.61	1.04	0.43	0.90±0.10	1500	NA	NA	NA	NA
TURB (NTU)	0.11	0.34	0.23	0.24±0.05	< 4	<5.0	<5.0	<5.0	<5.0
ALK (mg/L)	286.78	1711.11	1424.33	408.85±391.94	200	500	100	100	100
TH (mg/L)	14.84	29.76	14.92	19.34±3.61	< 200	100 -300	500	NA	100
THC (mg/L)	0.00	0.43	0.43	0.04±0.12	NA	NA	NA	NA	NA
Na²⁺ (mg/L)	34.40	52.64	18.24	41.53±4.03	< 200	NA	200	NA	200
K⁺ (mg/L)	41.61	61.44	19.83	45.37±4.94	12	200	NA	200	10
Ca²⁺ (mg/L)	9.61	11.95	2.34	11.10±0.75	75	NA	NA	75	75
Mg³⁺ (mg/L)	4.24	9.99	5.75	7.42±1.26	20	15	NA	20	20
Cl⁻ (mg/L)	70.61	226.39	155.78	196.40±56.00	250	200	250	100	100
NO₃⁻ (mg/L)	0.11	0.14	0.03	0.13±0.007	50	45	NA	10	10
NO₂⁻ (mg/L)	0.01	0.05	0.04	0.03±0.009	< 3.0	NA	NA	NA	NA
SO₄²⁻ (mg/L)	9.37	14.62	5.25	10.31±1.32	400	500	200	250	100
NH₄⁺ (mg/L)	0.11	0.75	0.64	0.17±0.17	1.50	NA	NA	NA	NA
PO₄³⁻ (mg/L)	8.60	9.85	1.25	9.25±0.42	NA	NA	NA	NA	NA
HCO₃⁻ (mg/L)	143.38	855.11	711.73	203.94±196.01	100	NA	NA	NA	NA
MgCO₃ (mg/L)	10.43	14.64	4.21	11.25±1.04	NA	NA	NA	NA	NA
Cu²⁺ (mg/L)	0.03	0.06	0.03	0.05±0.01	2.0	NA	1.0	1.3	1.0
Pb²⁺ (mg/L)	0.00	0.02	0.02	0.007±0.005	0.01	0.01	0.01	0.01	0.01

Cd²⁺ (mg/L)	0.00	0.0009	0.0009	0.0009±0.0003	0.003	0.003	0.001	0.005	0.005
Mn²⁺ (mg/L)	0.02	0.06	0.04	0.04±0.01	0.1	0.2	0.5	0.4	2.0
Zn²⁺ (mg/L)	0.84	4.23	3.39	2.31±1.26	0.01	NA	NA	NA	NA
Fe³⁺ (mg/L)	0.05	1.52	1.47	0.80±0.38	0.3	0.3	0.3	0.3	0.3
Ni (mg/L)	0.00	0.00	0.0006	0.0006±0.0005	0.02	0.05	NA	NA	0.05
S (mg/L)	1.14	5.25	4.11	3.28±1.41	250	NA	NA	NA	NA
Al³⁺ (mg/L)	0.00	0.01	0.01	0.002±0.004	0.2	NA	NA	0.2	0.5
I (mg/L)	0.00	0.06	0.06	0.04±0.02	NA	NA	NA	NA	NA
Si (mg/L)	0.00	0.04	0.04	0.01±0.01	NA	NA	NA	NA	NA

Drinking Water Standard Specifications given by WHO (2004), NESREA (2010), NSDWQ (2007), USEPA (2007) and NAFDAC (2011) and Statistical Information of Ion Concentrations.

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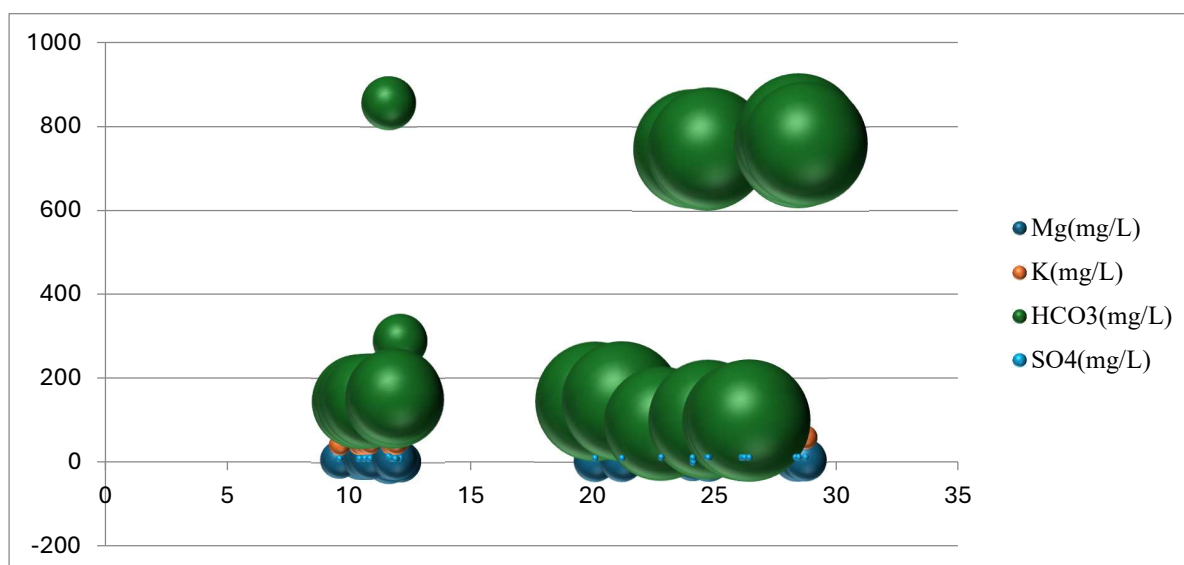


Figure 8: Bubble plot showing Dominant Hydrogeochemical Parameters of Papalanto (Ishola, 2019).

Multivariate Statistical Analyses

The contribution of Multivariate Statistical Techniques in facilitating the procurement of solution to the prevailing environmental problems and suggesting evidence for better and effective understanding of both natural and anthropogenic processes at different times and conditions cannot be ignored.

Correlation analyses (CA), Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA) have been broadly used as un-biased methods in the analysis of water-quality data for drawing meaningful information (Singh *et al.*, 2005). Pearson correlation analysis is commonly used to evaluate and establish the strength of a linear

relationship between two variables (Ishola, 2019). The correlation coefficients among various water quality parameters were calculated and presented (Table 5a, 5b, 6a and 6b). The resultant matrix illustrates that EC and TDS shows a good positive correlation with other physico-chemical parameters alongside with Na^+ , NO_3^- , and Al^{3+} ; K^+ , Ca^{2+} , Mg^{3+} , Cl^- , NO_2^- , NH_4^+ , PO_4^{3-} , MgCO_3^- , Cd^{2+} , Mn^{2+} , Zn^{2+} , Fe^{3+} , Ni and I; Ca^{2+} , with other elemental or chemical parameters, which indicates that these ions are mainly derived from multiple sources of both geogenic and anthropogenic provenance that may possibly include large amount of chemical fertilizers used in agriculture, domestic discharges, and industrial effluent. The PCA results comprising the loadings, Eigenvalues, percentage of total variance are summarized in Table 7a, 7b, 8a and 8b. PCA extracts correlations and reduces the amount of data into components that explain a portion of the total variance between chemical parameters. The extracted factors explained the total variance for the log-transformed data. The explained variance is mainly related to the chemical parameter loadings classified as 'strong' (> 0.75), 'moderate' (0.75 to 0.50) and 'weak' (0.50 to 0.30) (Udousoro and Umoren, 2014). The total variance with strong positive loadings particularly Ca^{2+} , Mg^{3+} , Na^+ , Cl^- , SO_4^{2-} and NO_3^- are better inferred to be related to evaporation and anthropogenic pollution sources from industrial effluents (Salinity, Cl^- , Na^+).

For chemical parameters of Papalanto boreholes, the rotation converged in 10 iteration leaving 6 components extracted

which accounted for 91.61% of the total variance of the formation concentrations (Table 7a). The first component accounted for 46.27% of the total variance observed and showed significant contribution by K^+ , Ca^{2+} , Mg^{3+} , Cl^- , NO_2^- , NH_4^+ , PO_4^{3-} , MgCO_3^- , Mn^{2+} and Zn^{2+} . The second component accounted for 14.45% of the total variance observed and is composed of very high factor loadings Cu^{2+} , Cd^{2+} and Cr and a low one for NO_3^- and NO_2^- . The third component accounted for 10.47% of the total variance observed and was significantly and moderately contributed Na^+ and SO_4^{2-} . The fourth component explaining the 9.49% of the total variance observed and has a high positive factor loading for NO_3^- and HCO_3^- and moderate associative loadings for MgCO_3^- and Ni. The fifth component accounted for 6.60% of the total variance observed and is composed of high factor loading for PO_4^{3-} , Pb^{2+} , Zn^{2+} and Fe^{3+} . Finally, the sixth component accounted for 4.33% of the total variance and cumulative variance of 91.61% which was significantly contributed Ni and Al^{3+} . The relatively high weights for NO_2^- on C1 and C2; NO_3^- on C2 and C4; PO_4^{3-} on C1 and C5; MgCO_3^- on C1 and C5 and Zn^{2+} on C1 and C5 lead one to believe that the aforementioned parameters have two different origins given that their weights on other components are very small. The result of the above relationship is supported by the principal component scores of box data plotted on the respective positions of the components in rotated space in Fig. 12a while on the physico-chemical parameters the rotation converged in 13 iterations of which 3 components were extracted which accounted for 86.32 % of the total variance

observed (Table 7b). The first component accounted for 42.46 % of the total variance with a high factor loading for pH, BOD, COD, TDS, and TH, the second component explains 29.05 % of the total variance observed and showed high factor loadings for DO and TURB. The third component accounted for 14.82 % of the total variance observed which was significantly contributed by pH, TEMP, EC, TSS, TURB and ALK. The significant weights for pH on C1 and C2 and TURB on C2 and C3 are suggestive of their hydrogeochemical impacts being traceable to two different origins. The result of the above associations is accompanied by the principal component scores of box data plotted on the respective positions of the components in rotated space in Fig. 12b.

For chemical parameters of Papalanto Hand-dug wells, the rotation converged in 10 iterations with 6 components extracted, which accounted for 93.40% of the total variance observed (Table 8a). The first component accounted for 41.50% of the total variance which was significantly contributed by Mg^{3+} , Cl^- , NO_3^- , NO_2^- , PO_4^{3-} , Mn^{2+} , and Fe^{3+} . The second component accounted for 22.09% of the total variance observed and was strongly contributed by Na^+ , Ca^{2+} , and PO_4^{3-} . The third component accounted for 13.20% of the observed variance significantly contributed by Al^{3+} and I; the fourth component accounted for 7.22% of the total variance observed and with high factor loading for PO_4^{3-} , Cd^{2+} and Mn^{2+} ; the fifth component accounted for 5.20% of the total variance and was significantly contributed by Ni and Si. The sixth component represent 4.20% of the total observed variance

positively contributed by for Pb^{2+} with a high factor loading. The presence of moderate loadings of PO_4^{3-} on C1 and C2 and Mn^{2+} on C1 and is a good suggestion of their dual sources given that their weights on C3, C5, and C6 are very small while on the physico-chemical parameters of the hand-dug well samples, the rotation converged in 5 iterations of 3 components were extracted which accounted for 87.65% of the total variance observed (Table 8b). The first component accounted for 39.96% of the total variance with a high factor loading for COD, TDS, TS and THC; the second component explains 21.16% of the total variance observed and showed high factor loadings for TEMP, EC and BOD. The third component accounted for 13.68% of the total variance observed which was significantly contributed by pH, and TURB and low contribution from THC. The fourth component accounted for 75.88% of the total variance observed which was significantly contributed solely by ALK. The degree of the above associations for the Physico-chemical parameters of the Hand-Dug Wells in the study area is accompanied by the principal component scores of box data plotted on the respective positions of the components in rotated space is shown in Fig. 13a and Fig. 13b.

The other contributing process is suggested as agricultural activities due to presence of NO_3^- , Mg^{3+} , PO_4^{3-} , and SO_4^{2-} in these factors. The other sources of NO_3^- may be derived from onsite sanitation, municipal wastes [Mohapatra *et al.*, 2011] and related to nutrient contamination owing to the unsewered urban environment and nearby agriculture practices over a period of decades

[Satyaji *et al.*, 2010]. The sources of Ca^{2+} , SO_4^{2-} and HCO_3^- may be due to dissolution of gypsum and calcium bearing minerals. The PCA loadings that explain the variability and correlative influence with K^+ and other variables that signified low positive and negative loadings can be possibly attributed to chemical weathering, leaching and dissolution of secondary salts in the pore spaces, agriculture effluents, and the usual sinks are plants and clays while notable factors contributive of the overall variance and reveals extreme negative scores that reflect areas that were essentially unaffected by the process. HCA analysis is highly resourceful for grouping water sample parameters by considering the similar level of concentrations in their chemical compositions. Cluster Analysis using the average linkage method based on the squared Euclidean distance is presented as dendrograms. The 'phenon' line is chosen at a linkage distance and the interpretation is subjective (Oyebog *et al.*, 2012; Ishola, 2019). Hierarchical Cluster Analysis was used in identifying the similarities between the sampled sources based on the levels of the sampled parameters (Elemental and Physico-

chemical) thereby grouping them into interpretable Clusters.

In the sampled boreholes of the study area, the dendrogram for the descriptor shows three identifiable clusters. Cluster 1 consists of Cd^{2+} , Cr, Pb^{2+} , Ni, Al^{3+} , NO_2^- , Cu^{2+} , I, NO_3^- , Mn^{2+} , Cu^{2+} , I, NO_3^- , Fe^{3+} , NH_4^+ , Zn^{2+} , Mg^{3+} , $^+$, PO_4^{3-} , MgCO_3^- and SO_4^{2-} as the dominant elements. Cluster two which linked Cluster 1 and Cluster 3 comprises of S, Ca^{2+} , Na^+ , K^+ and Cl^- as the adjoining elements with few elements from Cluster 1. Cluster 3 has HCO_3^- , Cl^- , K^+ and Na^+ its dominant elements. A significant subdivision which extracted Cluster 1 and 3 was clearly observed showing that their constituent elements are from different sources or origins (Fig. 13a).

On the physico-chemical parameters, the dendrogram for descriptor shows that 3 clusters were identified. Cluster 1 consists of TSS, THC, TURB, TS, pH and DO which are strongly associated with one another. Cluster 2 has TDS, TEMP, TH, COD, BOD, and EC as its adjoining constituent parameters. Cluster 3 consists of ALK as its main parameter. It is moderately associated with Cluster 2 (Fig. 13b)

Table 5a: Pearson Correlation between Elemental Parameters of Papalanto Boreholes

****.** Correlation is significant at the 0.01 level (2-tailed).

.* Correlation is significant at the 0.05 level (2-tailed).

Table 5b: Pearson Correlation of between Physico-chemical Parameters of Papalanto Boreholes

	Na ²⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	NO ₃ ⁻	NO ₂ ⁻	SO ₄ ²⁻	NH ₄ ⁺	PO ₄ ³⁻	HCO ₃ ²⁻	MgCO ₃ ⁻	Cu ²⁺	Pb ²⁺	Cd ²⁺	Mn ²⁺	Zn ²⁺	Fe ³⁺	Cr	Ni	S	Al ³⁺	I
Na ²⁺	1																						
K ⁺	0.162	1																					
Ca ²⁺	0.298	.888**	1																				
Mg ²⁺	0.290	.957**	.914**	1																			
Cl ⁻	0.443*	.791**	.820**	.772**	1																		
NO ₃ ⁻	.536**	0.409*	0.500*	0.435*	0.240	1																	
NO ₂ ⁻	0.356	.784**	.772**	.830**	.525**	.660**	1																
SO ₄ ²⁻	0.350	0.286	0.068	0.286	0.452*	-0.132	0.183	1															
NH ₄ ⁺	0.255	.974**	.891**	.971**	.833**	0.386	.808**	0.377	1														
PO ₄ ³⁻	0.164	.619**	.653**	.743**	0.230	0.480*	.706**	-0.094	.596**	1													
HCO ₃ ²⁻	0.231	.186	0.259	0.270	-0.031	.579**	0.297	-0.331	0.166	0.436*	1												
MgCO ₃ ⁻	0.204	.659**	.781**	.643**	0.442*	.794**	.726**	-0.241	.616**	.555**	0.522**	1											
Cu ²⁺	0.241	-0.068	0.205	-0.004	-0.096	.560**	0.397*	-0.285	-0.050	0.193	0.076	0.491*	1										
Pb ²⁺	-0.032	.260	0.099	0.240	0.078	0.045	0.362	0.566**	0.278	0.243	-0.498*	0.036	0.225	1									
Cd ²⁺	0.121	.543**	.525**	.520**	0.417*	0.654*	.756**	0.422*	.589**	0.254	-0.186	0.484	0.544**	.665**	1								
Mn ²⁺	0.336	.653**	.509**	.638**	0.504*	0.483*	.787**	0.458*	.720**	0.274	0.163	0.476*	0.200	0.360	0.738**	1							
Zn ²⁺	0.408*	.742**	.657**	.778**	.580**	.538**	.617**	0.407*	.750**	.649**	0.218	0.533**	-0.062	0.433*	0.349	0.471*	1						
Fe ³⁺	0.254	.510**	.516**	.555**	0.460*	0.158	0.407*	0.380	.513**	.560**	-0.317	0.231	0.061	0.674**	0.356	0.124	0.734**	1					
Cr	0.466*	0.451*	.592**	.550**	0.453*	0.490*	.728**	0.355	.523**	0.476*	-0.025	0.492*	0.686**	0.563**	0.846**	0.558**	0.440*	0.520**	1				
Ni	0.139	.529**	0.388	0.448*	0.340	.599**	.585**	0.343	.542**	0.162	0.145	0.594**	0.275	0.468*	0.704**	0.769**	0.581**	0.173	0.460*	1			
S	-0.191	-0.096	0.012	-0.097	-0.232	0.117	-0.110	-0.538**	-0.139	0.104	0.243	0.199	0.177	-0.277	-0.183	-0.184	-0.161	-0.188	-0.155	-0.112	1		
Al ³⁺	-0.603**	.195	-0.088	-0.022	0.023	-0.222	0.007	0.143	0.153	-0.378	-0.296	0.015	-0.219	0.221	0.333	0.363	-0.141	-0.268	-0.221	0.473*	-0.061	1	
I	0.319	.705**	.595**	.700**	.779**	0.124	0.417*	0.654**	.756**	0.252	0.024	0.288	-0.272	0.271	0.407*	0.502*	0.690**	0.471*	0.374	0.464*	-0.322	0.084	1

	PH	TEMP	EC	DO	BOD	COD	TDS	TSS	TS	TURB	ALK
PH	1										
TEMP	-0.056	1									
EC	0.116	0.768**	1								
DO	0.204	0.113	0.203	1							
BOD	0.622**	-0.440*	-0.629**	-0.081	1						
COD	0.532**	-0.342	-0.385	0.321	0.614**	1					
TDS	0.447*	-0.688**	-0.811**	-0.054	0.899**	0.719**	1				
TSS	0.657**	0.372	0.509**	0.407*	0.083	0.379	0.003	1			
TS	0.340	-0.110	-0.283	-0.419*	0.638**	-0.082	0.430*	-0.034	1		
TURB	0.093	0.480*	0.645**	0.562**	-0.520**	0.198	-0.453*	0.601**	-0.769**	1	
ALK	0.119	0.615**	0.608**	0.385	-0.348	0.091	-0.366	0.805**	-0.310	0.730**	
TH	0.315	-0.488*	-0.656**	0.270	0.644**	0.886**	0.825**	0.165	-0.065	0.041	-0.0
THC	-0.072	-0.252	-0.502*	-0.558**	0.497*	-0.256	0.358	-0.471*	0.861**	-0.953**	-0.54

****.** Correlation is significant at the 0.01 level (2-tailed).

.* Correlation is significant at the 0.05 level (2-tailed)

Table 6a: Pearson Correlation between Elemental Parameters of Papalanto Hand-Dug Wells

	Na ²⁺	K ⁺	Ca ²⁺	Mg ³⁺	Cl ⁻	NO ₃ ⁻	NO ₂ ⁻	SO ₄ ²⁻	NH ₄ ⁺	PO ₄ ³⁻	HCO ₃ ⁻	MgCO ₃ ⁻	Cu ²⁺
Na ²⁺	1												
K ⁺	0.884**	1											
Ca ²⁺	0.645**	0.311	1										
Mg ³⁺	-0.385	-0.690**	0.296	1									
Cl ⁻	-0.202	-0.555**	0.321	0.801**	1								
NO ₃ ⁻	-0.580**	-0.777**	0.106	0.771**	0.755**	1							
NO ₂ ⁻	-0.402*	-0.687**	0.345	0.748**	0.606**	0.862**	1						
SO ₄ ²⁻	0.818**	0.982**	0.201	-0.738**	-0.642**	-0.847**	-0.767**	1					
NH ₄ ⁺	0.837**	0.980**	0.229	-0.750**	-0.671**	-0.866**	-0.727**	0.984**	1				
PO ₄ ³⁻	0.009	-0.407*	-0.594**	0.664**	0.642**	0.613**	0.843**	-0.517**	-0.456*	1			
HCO ₃ ⁻	0.835**	0.980**	0.226	-0.751**	-0.671**	-0.867**	-0.730**	0.984**	1.000**	-0.460*	1		
MgCO ₃ ⁻	0.827**	0.985**	0.237	-0.701**	-0.585**	-0.801**	-0.752**	0.986**	0.974**	-0.515**	0.976**	1	
Cu ²⁺	-0.612**	-0.475*	-0.565**	0.142	0.073	0.300	0.115	-0.466*	-0.453*	-0.127	-0.445*	-0.443*	1
Pb ²⁺	0.271	0.245	0.303	0.076	0.130	0.044	0.022	0.171	0.169	0.025	0.168	0.218	-0.084
Cd ²⁺	0.101	0.001	0.131	-0.019	-0.142	-0.144	0.163	-0.040	0.109	0.322	0.112	-0.011	0.029
Mn ²⁺	-0.223	-0.539**	0.138	0.409*	0.476*	0.419*	0.606**	-0.588**	-0.517**	0.774**	-0.520**	-0.635**	0.133
Zn ²⁺	-0.569**	-0.350	-0.889**	-0.187	-0.188	-0.076	-0.230	-0.282	-0.253	-0.361	-0.248	-0.293	0.696**
Fe ³⁺	-0.474*	-0.564**	-0.103	0.598**	0.493*	0.429*	0.262	-0.526**	-0.595**	0.131	-0.592**	-0.520**	0.429*
Ni	0.299	0.207	0.083	-0.242	0.121	-0.223	-0.192	0.170	0.217	0.089	0.218	0.214	-0.295
S	-0.629**	-0.563**	-0.568**	-0.040	0.025	0.217	0.201	-0.540**	-0.465*	0.064	-0.462*	-0.537**	0.470*
Al ³⁺	-0.008	-0.182	0.351	0.147	0.219	0.346	0.514**	-0.235	-0.199	0.531**	-0.206	-0.231	-0.547**
I	-0.138	-0.249	-0.062	-0.011	-0.075	0.055	0.316	-0.230	-0.182	0.415*	-0.196	-0.333	-0.210
Si	-0.346	-0.303	-0.465*	0.014	0.185	0.109	-0.068	-0.292	-0.271	-0.058	-0.265	-0.248	0.549**

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 6b: Pearson Correlation of Physico-chemical Parameters of Papalanto Hand-Dug Wells

	PH	TEMP	EC	DO	BOD	COD	TDS	TSS	TS	TURB	ALK	TH	THC
PH	1												
TEMP	-0.085	1											
EC	0.810**	-0.093	1										
DO	-0.286	0.001	0.308	1									
BOD	-0.578**	-0.159	-0.111	0.733**	1								
COD	-0.043	-0.434*	0.408*	0.732**	0.788**	1							
TDS	-0.180	-0.407*	-0.600**	-0.740**	-0.211	-0.335	1						
TSS	-0.098	-0.675**	-0.066	-0.006	0.356	0.501*	0.514**	1					
TS	-0.099	0.641**	0.312	0.710**	0.322	0.228	-0.914**	-0.595**	1				
TURB	0.167	-0.817**	0.049	-0.236	0.077	0.347	0.608**	0.834**	-0.749**	1			
ALK	-0.307	0.895**	-0.448*	-0.195	-0.216	-0.631**	-0.124	-0.682**	0.429*	-0.740**	1		
TH	-0.026	-0.300	0.288	0.518**	0.393	0.491*	-0.301	0.173	0.197	0.152	-0.367	1	
THC	-0.307	0.897**	-0.444*	-0.188	-0.207	-0.623**	-0.129	-0.681**	0.435*	-0.740**	1.000**	-0.363	1

* . Correlation is significant at the 0.05 level (2-tailed).

** . Correlation is significant at the 0.01 level (2-tailed).

Table 7a: PCA for Elemental Parameters of Papalanto boreholes

Rotated Component Matrix ^a						
	Component					
	C1	C2	C3	C4	C5	C6
Na ²⁺	0.205	0.284	0.474	0.365	-0.094	-0.660
K ⁺	0.917	0.067	0.064	0.184	0.232	0.197
Ca ²⁺	0.925	0.258	-0.121	0.142	0.124	-0.095
Mg ²⁺	0.910	0.104	0.064	0.220	0.288	0.004
Cl ⁻	0.897	0.104	0.328	-0.070	-0.113	-0.105
NO ₃ ⁻	0.242	0.454	-0.073	0.782	0.095	-0.130
NO ₂ ⁻	0.640	0.493	0.035	0.384	0.253	0.078
SO ₄ ²⁻	0.208	0.032	0.901	-0.132	0.186	0.090
NH ₄ ⁺	0.925	0.117	0.164	0.169	0.198	0.147
PO ₄ ³⁻	0.502	0.101	-0.300	0.335	0.627	-0.219
HCO ₃ ²⁻	0.160	-0.147	-0.291	0.832	-0.150	-0.193
MgCO ₃ ⁻	0.576	0.404	-0.321	0.529	0.067	0.086
Cu ²⁺	-0.124	0.923	-0.266	0.160	0.024	-0.138
Pb ²⁺	0.009	0.422	0.383	-0.191	0.724	0.321
Cd ²⁺	0.406	0.768	0.240	-0.022	0.172	0.367
Mn ²⁺	0.498	0.419	0.384	0.388	-0.027	0.376
Zn ²⁺	0.586	-0.014	0.291	0.407	0.582	-0.056
Fe ³⁺	0.425	0.147	0.190	-0.205	0.771	-0.219
Cr	0.384	0.813	0.201	0.049	0.282	-0.165
Ni	0.290	0.397	0.317	0.505	0.144	0.550
S	-0.043	0.007	-0.692	0.105	-0.053	0.019
Al ³⁺	0.064	-0.033	0.084	-0.125	-0.184	0.962
I	0.717	-0.090	0.534	0.058	0.129	0.047
Eigenvalue	11.104	3.467	2.514	2.277	1.585	1.038
Variance (%)	46.267	14.447	10.474	9.489	6.604	4.325
Cumulative (%)	46.267	60.714	71.188	80.672	87.282	91.606

Component Plot in Rotated Space

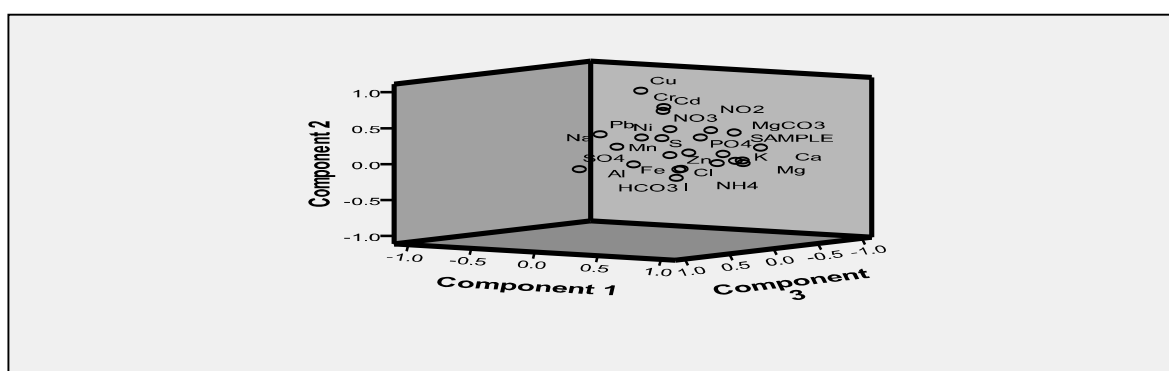


Figure 12a: Plot of Extracted Component 1, 2 and 3 of Elemental Parameters of Papalanto Boreholes in Rotated Space

Table 7b: PCA for Physico-Chemical Parameters of Papalanto Boreholes
Rotated Component Matrix^a

	Component		
	C1	C2	C3
PH	0.685	-0.104	0.502
TEMP	-0.414	0.036	0.753
EC	-0.522	0.216	0.786
DO	0.205	0.647	0.227
BOD	0.876	-0.430	-0.116
COD	0.876	0.364	-0.039
TDS	0.896	-0.199	-0.370
TSS	0.379	0.280	0.837
TS	0.309	-0.920	0.106
TURB	-0.111	0.841	0.504
ALK	-0.033	0.432	0.760
TH	0.869	0.324	-0.292
THC	0.077	-0.923	-0.287
Eigenvalue	5.944	4.067	2.074
Variance (%)	42.46	29.050	14.817
Cumulative (%)	42.455	71.505	86.322

Component Plot in Rotated Space

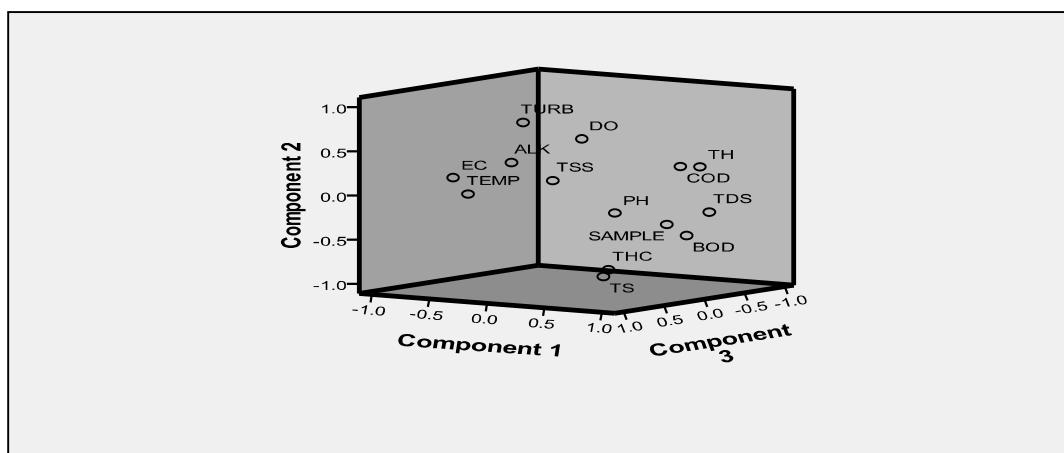


Figure 12b: Plot of Extracted Component 1, 2 and 3 of Physico-Chemical

Parameters of Papalanto Boreholes in Rotated Space

Table 8a: PCA for Elemental Parameters of Hand-Dug Wells

Rotated Component Matrix^a

	Component					
	C1	C2	C3	C4	C5	C6
Na ²⁺	-0.712	0.644	-0.013	0.128	0.148	0.102
K ⁺	-0.923	0.307	-0.008	-0.046	0.037	0.168
Ca ²⁺	-0.021	0.940	0.054	0.216	0.043	0.143
Mg ³⁺	0.842	0.341	-0.207	0.054	0.002	0.071
Cl ⁻	0.776	0.381	-0.127	-0.034	0.371	0.114
NO ₃ ⁻	0.937	0.108	0.060	-0.003	-0.035	0.126
NO ₂ ⁻	0.824	0.285	0.185	0.336	-0.168	-0.016
SO ₄ ²⁻	-0.957	0.215	-0.014	-0.122	0.011	0.097
NH ₄ ⁺	-0.973	0.200	0.009	0.027	0.010	0.098
PO ₄ ³⁻	0.587	0.554	0.141	0.534	0.048	-0.149
HCO ₃ ⁻	-0.973	0.195	0.001	0.027	0.014	0.104
MgCO ₃ ⁻	-0.934	0.227	-0.041	-0.124	0.081	0.198
Cu ²⁺	0.356	-0.624	-0.569	0.191	-0.148	0.129
Pb ²⁺	-0.042	0.215	0.147	0.071	-0.091	0.856
Cd ²⁺	-0.110	-0.127	0.127	0.862	0.256	0.059
Mn ²⁺	0.522	0.100	0.091	0.617	0.123	-0.418
Zn ²⁺	0.063	-0.908	-0.215	0.172	0.133	-0.131
Fe ³⁺	0.577	0.017	-0.613	-0.303	0.127	-0.280
Ni	-0.210	-0.025	0.295	0.259	0.887	-0.011
S	0.332	-0.724	0.222	0.404	0.316	-0.142
Al ³⁺	0.274	0.263	0.872	0.168	0.183	-0.020
I	0.134	-0.014	0.502	0.317	-0.149	-0.677
Si	0.180	-0.531	-0.331	0.213	0.664	-0.106
Eigenvalue	9.959	5.301	3.169	1.732	1.249	1.007
Variance (%)	41.497	22.086	13.204	7.217	5.203	4.195
Cumulative (%)	41.497	63.584	76.757	84.004	89.206	93.401

Component Plot in Rotated Space

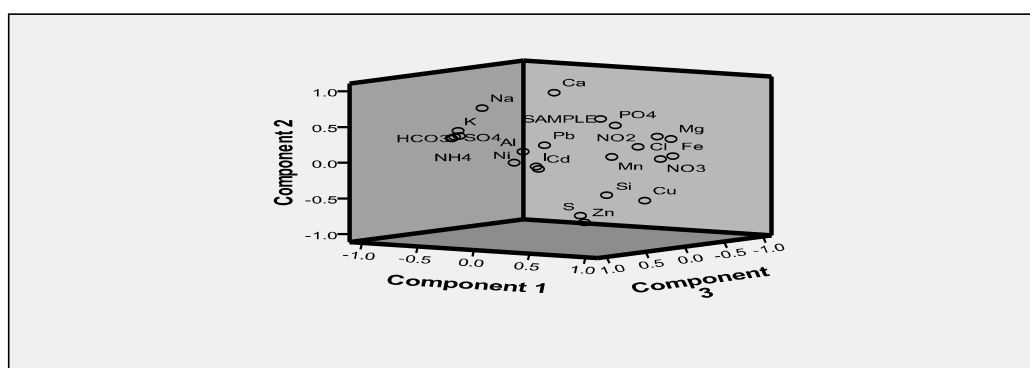


Figure 13a: Plot of extracted Component 1, 2 and 3 of Elemental Parameters of Papalanto Hand-Dug Wells in Rotated Space

Table 8b: PCA for Physico-chemical Parameters of Papalanto Hand-Dug Wells
Rotated Component Matrix^a

	Component		
	C1	C2	C3
PH	-0.129	-0.287	0.909
TEMP	0.902	-0.159	-0.103
EC	-0.009	0.280	0.943
DO	0.242	0.929	0.079
BOD	-0.082	0.877	-0.401
COD	-0.339	0.897	0.145
TDS	-0.645	-0.547	-0.499
TSS	-0.859	0.253	-0.197
TS	0.822	0.528	0.176
TURB	-0.950	0.014	0.017
ALK	0.823	-0.346	-0.386
TH	-0.143	0.599	0.191
THC	0.825	-0.337	-0.386
Eigenvalue	5.594	4.242	2.435
Variance (%)	39.959	30.298	17.392
Cumulative (%)	39.959	70.257	87.649

Component Plot in Rotated Space

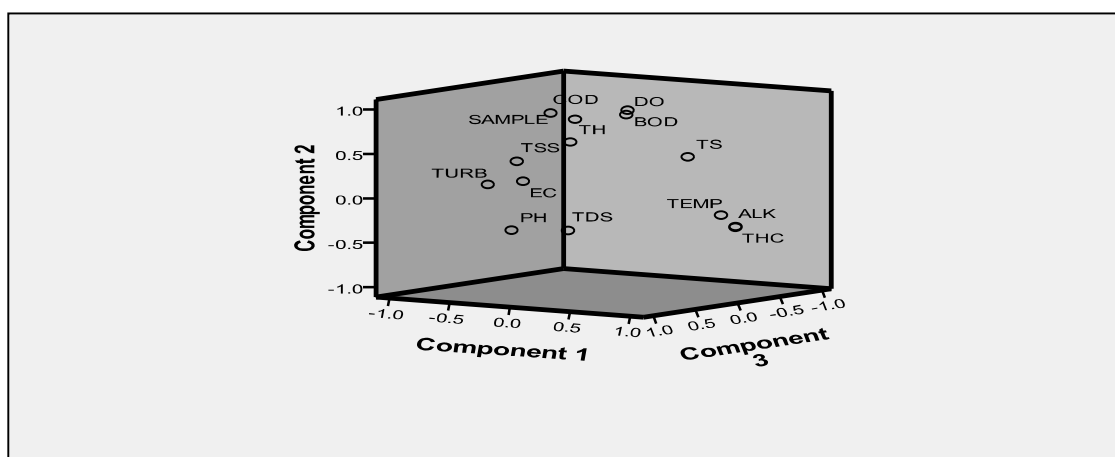


Figure 13b: Plot of Extracted Component 1, 2 and 3 of Physico-Chemical Parameters of Papalanto Hand-Dug Wells in Rotated Space

Also, there are three identifiable clusters in the sampled hand-dug wells of Papalanto, Cluster 1 consists of Cd^{2+} , Ni , Al^{3+} , Pb^{2+} , Si , NO_2^- , Mn^{2+} , I , Cu^{2+} , NO_3^- , NH_4^+ , Fe^{3+} , Zn^{2+} , S , SO_4^{2-} and MgCO_3^- and as the dominant constituents. Cluster two comprises of Ca^{2+} , PO_4^{3-} , Mg^{3+} , Na^+ , K^+ and Cl^- as the adjoining elements with few elements from cluster 1. Cluster 3 has HCO_3^- as its dominant elements linking Cl^- , K^+ , Na^+ , Mg^{3+} , PO_4^{3-} and Ca^{2+} . A significant subdivision which extracted Cluster 1 and 3 as clearly observed showing that their constituent elements are from different sources or origins (Fig. 14a) while for the Physico-chemical parameters, the dendrogram for descriptor shows 3 clusters that were identified. Cluster 1 consists of TSS, TURB, THC, TS, DO and TDS which are strongly associated with one another. Cluster 2 which linked cluster 1 and cluster 3 has pH, BOD, TH, TEMP, COD and EC as its adjoining constituent parameters. Cluster 3 consists of ALK as its dominant parameter. Cluster 3 is moderately associated with cluster 2 excluding its dominant EC parameter with little or no association with other parameter (Fig. 14b). According to the results (Fig. 14a, 14b, 15a and Fig. 13b) Cluster I, cluster II and cluster III of the sampled boreholes correspond to the low to moderate, moderate to high, and high to very

high chemical concentration and consequential vulnerability to pollution respectively. The physico-chemical parameters revealed cluster II to be of high to very, Cluster I as moderate to high and cluster III to be low to moderate Physico-chemical concentrations. The water analysis results also indicated that most of the samples classified as Cluster 3 have very low TDS values (<5000 mg/L) and concentration of other chemical parameters were far below or well within the permissible limit of drinking water as well as irrigational uses, indicating a low susceptibility to invasions. However, due to the continuous activities of industrial, irrigational, agricultural and biological population density, it is predictable that the study area may be vulnerable to invasions from different sources.

The concentrations of NO_3^- , PO_4^{3-} and SO_4^{2-} along with high Cl^- may be due to the use of fertilizers and pesticides in agricultural activities of the study area and has also resulted in localized enrichment of Nitrate in the groundwater. The source of Sulfate in water is from alkaline sedimentary rocks, chemical industrial wastewater and fertilizers whose compounds are constituents of Sulphate minerals (Atay *et al.*, 2005).

**Dendrogram using Average Linkage (Between Groups)
Rescaled Distance Cluster Combine**

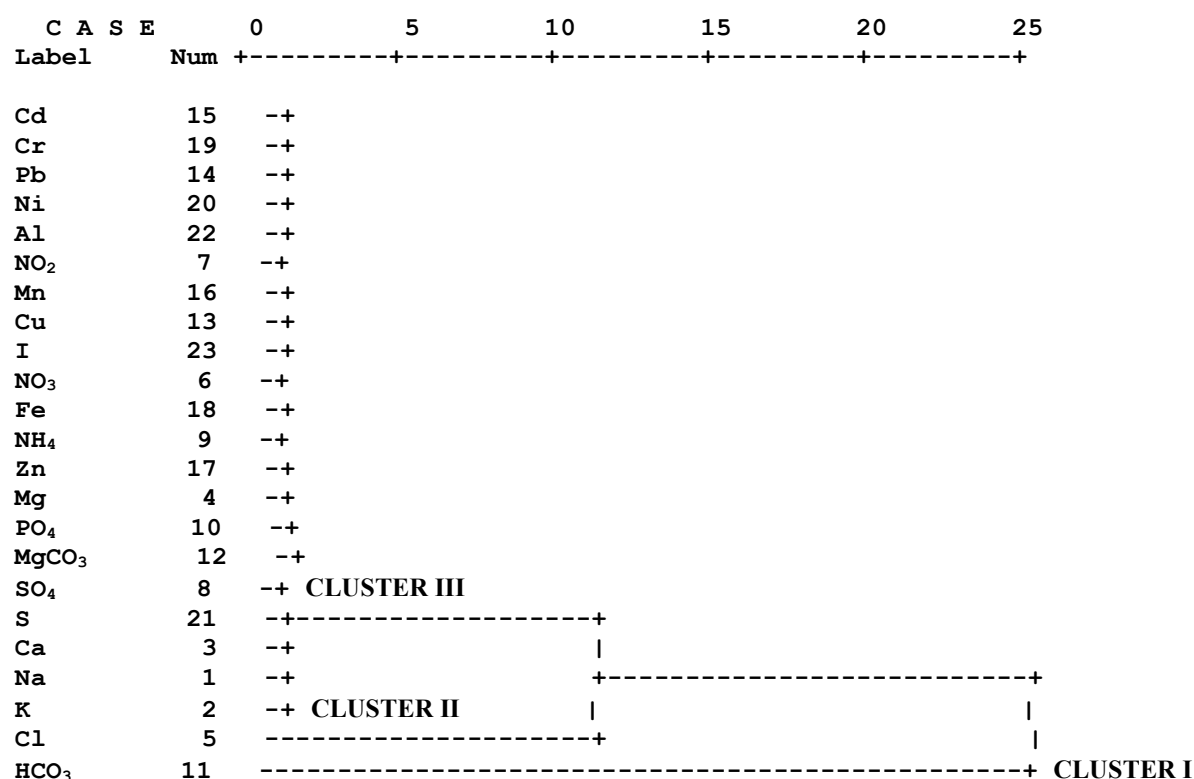


Figure 14a: Dendrogram for Elemental Parameters of Papalanto boreholes

**Dendrogram using Average Linkage (Between Groups)
Rescaled Distance Cluster Combine**

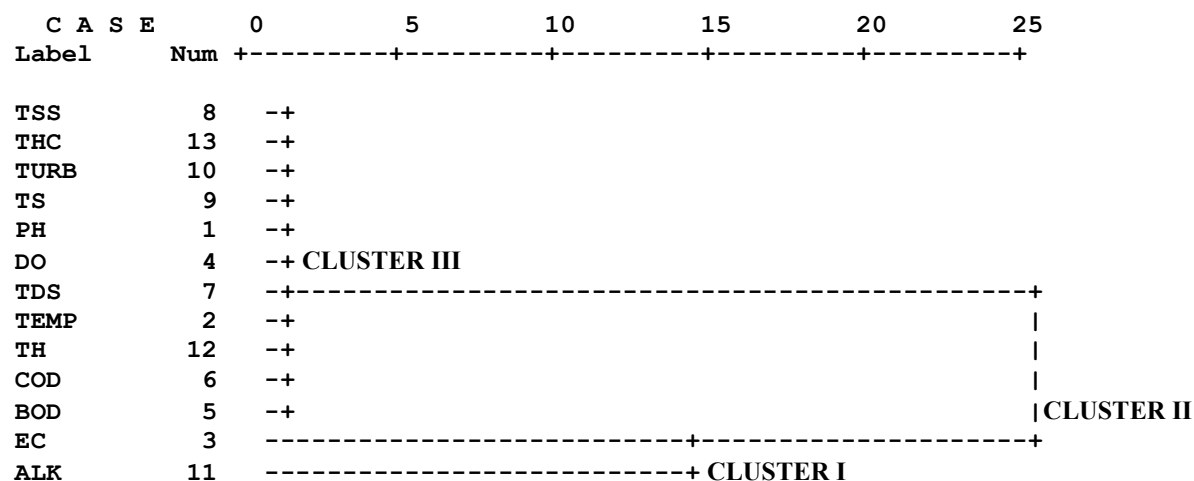


Figure 14b: Dendrogram for Physicochemical analysis of Papalanto Boreholes

**Dendrogram using Average Linkage (Between Groups)
Rescaled Distance Cluster Combine**

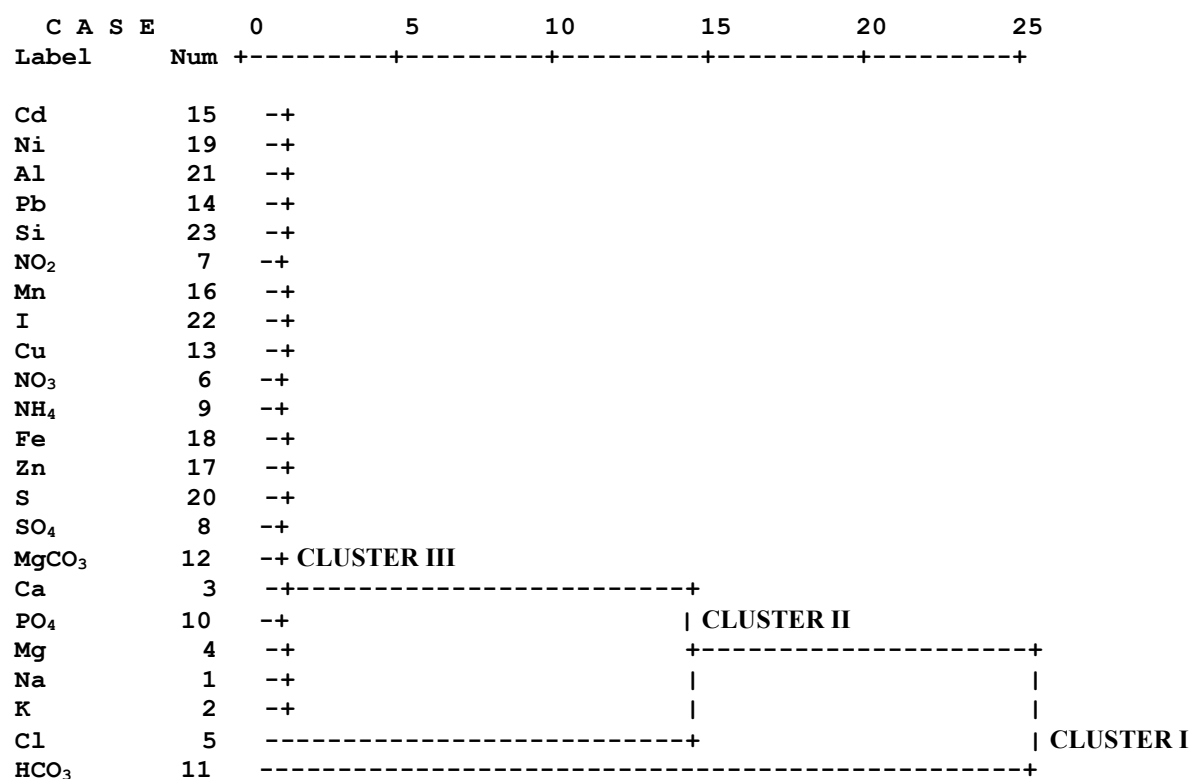


Figure 15a: Dendrogram for Elemental Analysis of Papalanto Hand-Dug Wells

**Dendrogram using Average Linkage (Between Groups)
Rescaled Distance Cluster Combine**

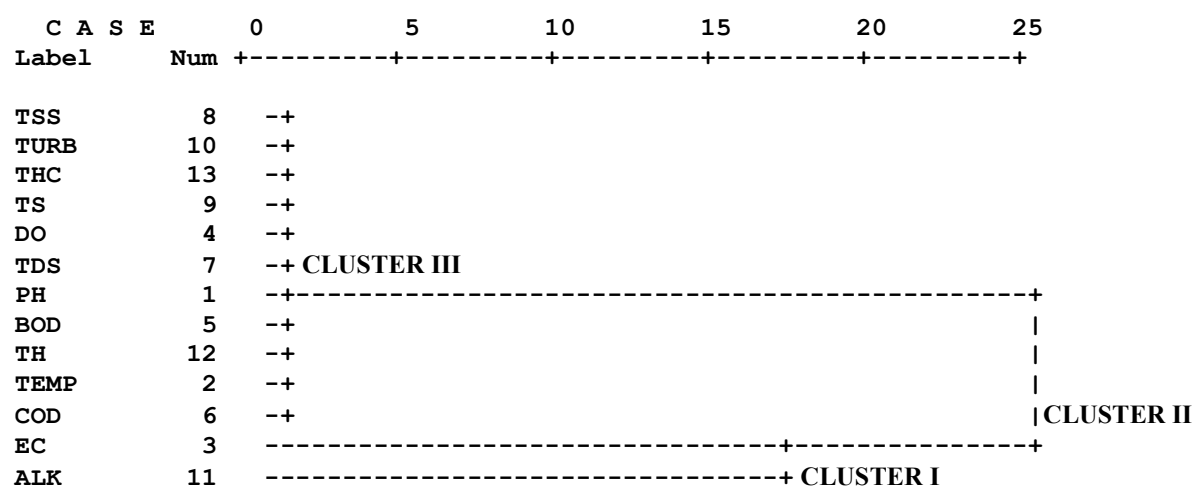


Figure 15b: Dendrogram for Physicochemical Analysis of Papalanto Hand-Dug Wells

CONCLUSIONS

This study carried out hydrogeochemical characterization using multivariate statistical techniques namely HCA, PCA, HCA, Correlation Analysis, Bubble plots alongside other descriptive statistics to classify and assess the groundwater quality status for the purpose of understanding pollution sources in Papalanto District. The result of the physicochemical parameters indicates that the groundwater in the study area is generally alkaline, fresh and very soft in nature. The abundance of major ions is in the following ordered pattern of cation abundance of $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$. Cationic concentrations revealed that about 70% of the groundwater samples have lower concentration value than the provisional permissible limits of 200, 150, 200 and 12 mg/L respectively of the approved national and international standards including WHO and NESREA. The outcomes of PCA and HCA analyses suggested that most of the variations are

consequently related to the anthropogenic pollutants and the set of natural soluble contents. The threatening environmental issues affecting the groundwater quality status in Papalanto; a rapid urban development in Ewekoro Local Government area of Ogun State, South-West Nigeria are the probable invasions from point and non-point source pollutants, especially surrounding industries and mining areas; it may lead to groundwater quality deterioration in the surrounding environment and the increasing population growth which has inadvertently encroached the land use pattern and has subsequently invaded the quality status of the water resources of the district. The results of the present study provide better and improved information that can be useful for the water resource management not only in Papalanto but also in the entire Ewekoro Local Government Area particularly with respect to anthropogenic stress.

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