Identification and Quantification of Heavy Metals, Anions and Coliforms in Water bodies using Enrichment Factors

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Abstract

Seven water samples collected from five surface waters and three deep wells in Ondo South were analyzed for the presence of heavy metals, anions and coliform bacteria. Five of the water samples gave MPN values ranging from 3 to 180 colony forming units (CFU)/per 100 mL, with presence of Escherichia coli and other coliforms. The mean of the results which was expressed in mg/l ranged from: Mg, 0.02-0.52; As, 0.01-0.02; Pb, 0.00-0.02; Cd, 0.00-0.05; Cu, 0.02-1.05; Fe, 0.01-0.46; Cr, 0.00-0.01; Zn, 0.01-0.3; Ni, 0.00-0.04; Mn, 0.00-0.08; Phosphate, 0.74; 2.97; Sulphate, 2.48-24.22; Chloride, 118.33-324.97; Nitrate, 0.5-2.23. Mg, As, Cu, Cr and Ni showed significant positive relationship with PO₄²⁻ and SO₄²⁻ at 0.01 level while Pb, Cd and Zn at 0.05 level. Heavy metal concentration showed weak positive relationship with Cl⁻ except Mn at 0.05 level. The trace metals had no relationship with NO₃⁻ except Mg, As, and Cr which showed positive weak correlation. Manganese, Chromium and Iron were used to as reference elements for the computation of enrichment factor. The enrichment factor values using iron as reference element in all the locations had a decreasing trend of: Cd>Cu>Zn>As>Cr>Pb>Mn>Ni>Mg. Two major components were obtained from the principal component analysis.

Keywords: Anions; Trace metal; Coliforms; Most probable number; Escherichia coli; Enrichment factor; Principal component analysis

Introduction

Water is very essential to plant, animal and human existence. Unfortunately, access to good quality water in Nigeria has been a mirage [1]. The major Sources of water in Ilaje and Okitipupa communities for cooking, drinking and other domestic purposes are streams, rivers, hand-dug wells as rain water harvest. Nigeria is blessed with numerous surface and groundwater resources, yet the provision of potable and safe water supply is still a mirage [2]. The need to assess the quality of water from these alternative sources has become pivotal because they have a direct effect on the health of the people in the communities [3]. Contaminants such as bacteria, viruses, heavy metal and anions have populated water supply as a result of non-treatment, disposal of waste from humans, livestock and leaching from farm land [4]. In public health studies, importance is placed on the analysis for chemical properties such as trace metal contents and anions in natural water. In addition, coliform enters water supply from direct disposal of waste into streams or lakes or from runoff from septic tank, feed lots into stream and also waste from animal like bird etc. [5]. The presence of Escherichia coli in drinking water denotes that the water has been faecally contaminated and therefore present a potential health risk to households that use them untreated [6].

In water, heavy metals are rapidly degrading the sediment in the form of hard soluble carbons, sulphate and sulphides on the bottom. At the time when the absorptive capacity of sediment is exhausted, the concentration of metal ions in water will increase. The toxicity level of metals significantly differs and depends on their physical-chemical form. According to the World Health Organization (WHO), about 400 million people in developing countries suffer from the diseases which are caused by use of contaminated drinking water [4]. In developing countries, access to both clean water and sanitation is not guaranteed to most people, and water-borne infections are common. According to UNICEF report, about 800 million people in Asia and Africa are living without access to safe drinking water. Inadequate quantity, poor quality of drinking water, and poor sanitation are the main reasons in incidence and prevalence of diseases in the world [7].

The pollution increase, caused by heavy metals and organometallic compounds is one of the today’s most serious problems. Heavy metals are incorporated in drinking water and in entire food chain. The heavy metals also includes number of physiologically significance elements such as Copper, Iron, Zinc; than the highly toxic Lead, Manganese, Cadmium, Arsenic, and less harmful as Chromium, etc [8].

Good water quality occurs when there are no bacteria of faecal origin present that may cause human diarrhoea and other life-threatening diseases (e.g. typhoid fever). There is no levels of chemicals (e.g. heavy metals) or chemical substances that would cause harm to human health, and water does not have a bad taste or smell. Most of the diseases and short life span in Nigeria can be adduced to lack of good water and report has it that each day about 25,000 people are said to die from the use of contaminated water [8]. Hundreds of thousand suffer from frequent and deadly water borne illnesses. Children under five, primarily in Asian and African countries, are the most affected by microbial diseases transmitted through water [8]. The objectives of this study include; assessing the level of trace metal and anions in the water bodies in both communities and compare with the regulatory limits, determine the micro-bacteriological quality of water from both Ilaje and Okitipupa communities, evaluate the relationship between the level of trace metals and anions in the water bodies and to determine the possible sources using enrichment factor and principal component analysis methods.

Materials and Methods

Geographical/social-culture/economic pattern of the water samples location areas

Okitipura, Igbokoda and the surrounding Araromi communities are located in the Ondo state south senatorial District of Nigeria. The samples used were taken from Ebute River near the Okitipupa oil palm mill and Idepe localities. Furthermore, the water samples were drawn from Araromi seaside, Araromi lagoon, River Olua glass Igbokoda,

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Igbokoda borehole, Ologodiji stream Igodan, and OSUTECH borehole. As regards the geographic location of the place, Okitipupa is in Ikale Local Government Area, while Igbokoda and Araromi are in Ilajeese-odo Local Government Area. Okitipupa, Araromi and Igbokoda people are rural dwellers. Their occupation includes crop farming and fish. The two major sources of water pollutant in the region are municipal wastes and trade wastes. Trade wastes are those are those arising from occupation such as metal works, welding, panel beating, battery charging, furniture making, wood construction work, soap making and sawmilling while municipal waste involves wastes from market stall, slaughter houses, street washing and flushing, drainage and sewage. Table 1 show the co-ordinates of the various sampling locations.

**Determination of heavy metal and anions in water samples**

The water samples were collected by standard methods using well-cleaned polythene sample bottles unanalyzed, after pre-concentration where necessary. Samples were digested and analyzed with Alpha 4, Atomic Absorption Spectrophotometric (Chem. Tech. Analytical) using standard methods established by APHA for metals determination. Exactly 2.5 mL of concentrated HNO₃ (Analar grade) was added to 25 mL of water sample in a clean Teflon beaker. The mixture was heated on a hot plate to concentrate the sample to about 10 mL. Heating of the sample continued with periodical addition of 1 mL portion of concentrated HNO₃ until a clear solution was obtained. The clear solution was then allowed to cool after which it was transferred into 25 mL standard flask and made up to the mark with distilled water. Blank samples were prepared for background correction using the method as described.

The analytical procedure described was quality controlled. Quality assurance study was carried out in terms of recoveries of metals from a spiked sample in order to ascertain the efficiency of the analytical procedures. This was done by spiking water with known amount of standard of the metals and recovered as described by AOAC [9]. The chloride was determined by argentometric method, phosphate by Vanadate-molybdate method, sulphate by turbidimetry method and nitrate (NO₃⁻) by UV spectrophotometric method, model Thermo scientific Helios Omega Uv-Vis (APHA, 1992).

**Determination of Most Probable Number (MPN) of coliforms**

The Most Probable Number (MPN) of coliforms was determined using the Multiple Tube Technique, including the presumptive and confirmatory tests according to established standards [10]. For the confirmatory tests, tubes from the presumptive test were re-incubated for an additional 24 hours at 37°C. After incubation, loop-fulls from positive tubes (tubes containing gas) were inoculated onto Eosin methylene blue (EMB) agar plates, using the streaking method. The plates were incubated in an inverted position at 37°C for 24 hours.

**Isolation of coliforms**

Each water sample (100 mL) was membrane filtered, and the membrane filter was removed with a pair of sterile forceps, placed on a plate of solid medium and incubated at 37°C for 24 hr. After incubation, colonies were collected aseptically from the membrane filters and streaked on plates of MacConkey agar and Eosin-methylene blue agar (EMB). The plates were incubated overnight at 37°C, and after incubation, cultures were examined for distinct colonies. These colonies were streaked on nutrient agar slant and incubated for 24 hours at 30°C, and kept as stock cultures. Conventional bacteriological methods and were used for identification of each isolate [11].

**Data analysis**

Data generated were subjected to statistical analysis using principal component analysis, Pearson correlation and enrichment factor method. During this study the enrichment factor was computed using Iron, Manganese and Chromium as reference element. In previous study iron, Chromium and Manganese were used as reference element [12,13]. The reference crustal ratio was taken from [14]. An enrichment factor less than one suggests no enrichment, enrichment factor less than three suggests minor enrichment, three to ten is moderate enrichment, ten to twenty-five severe enrichment, twenty-five to fifty is very severe enrichment and greater than fifty is extremely severe enrichment [15]. The enrichment factor was computed using this formula:

\[
\frac{Q_{\text{water sample}}}{Q_{\text{crust}}} = \frac{C_{\text{water sample}}}{C_{\text{crust}}}
\]

Where the concentration of the element is \( Q \) in the water and \( C \) is the concentration of the reference element (Fe).

**Results and Discussion**

Concentration of metals in water samples of the studied sites are given in Table 2. Metals concentrations in water were found in the following order: Cu>Mn>Zn >Fe>Cd>Mg>Ni>As>Pb.

Iron is one of the most abundant metals in the Earth’s crust. Its concentration window in natural fresh waters at levels ranging from 0.5 to 50 mg/litre [16]. From Table 1, the mean concentration for Iron (Fe) in this study varied from 0.01-0.48 mg/L; with the highest measured at River Oluwa glass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. Araromi seawater didn’t show any significant different (p<0.05) with Araromi lagoon water; also Araromi seawater didn’t show any significant difference (p<0.05) with Igbokoda borehole. Iron had concentrations below the WHO limit in all the locations except in River Oluwa glass and Ologodiji Stream which had higher concentration than the WHO limit (0.3 mg/L). The high concentration observed in River Oluwa glass and Ologodiji Stream could be attributed to metal recycling and batteries charging activities. The low level of trace metals in OSUSTECH borehole is as result of constant treatment of the water. The primary sources of Iron in drinking water are natural geologic sources and corroding distribution system and household pipes. Iron- based material such as cast iron and galvanized steel. Unlike lead and copper, ingesting iron from drinking water is not directly associated with adverse health effects. Although, trace impurities and microorganisms that are absorbed by iron solids may pose health concern. The effects associated with iron contamination can be grouped into two; aesthetic effect and physical effect. The aesthetic effects are the undesirable tastes or odors, iron in quantities greater than 0.3 mg/L in drinking water can cause unpleasant metallic taste and rust colour. Physical effects can lead to blockage or slowing down water flow [16]. However, the values in Table 2 show the concentration of iron (Fe) in the various sampling locations.

**Table 1:** Shows the co-ordinate of the various sampling locations.
Mean with different superscript are statistically significant @p<0.05

Table 2: Mean of heavy metal concentrations (mg/l) in the sampled locations.

| Location                | Mg     | As      | Pb      | Cd      | Cu      | Fe      | Cr      | Zn      | Ni      | Mn      |
|-------------------------|--------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| Araromi seawater        | 0.31 ± 0.01 | 0.01 ± 0.00 | 0.01 ± 0.00 | 0.02 ± 0.00 | 0.44 ± 0.00 | 0.14 ± 0.01 | 0.07 ± 0.00 | 0.10 ± 0.01 | 0.02 ± 0.00 | 0.34 ± 0.01 |
| Araromi lagoon water    | 0.24 ± 0.01 | 0.01 ± 0.00 | 0.02 ± 0.00 | 0.02 ± 0.00 | 0.43 ± 0.02 | 0.15 ± 0.01 | 0.08 ± 0.00 | 0.11 ± 0.01 | 0.02 ± 0.00 | 0.04 ± 0.00 |
| River oluwa glass       | 0.52 ± 0.02 | 0.02 ± 0.00 | 0.02 ± 0.00 | 0.06 ± 0.00 | 1.05 ± 0.06 | 0.48 ± 0.03 | 0.10 ± 0.01 | 0.30 ± 0.01 | 0.04 ± 0.00 | 0.10 ± 0.00 |
| Igbokoda borehole       | 0.04 ± 0.00 | 0.01 ± 0.00 | 0.01 ± 0.00 | 0.01 ± 0.00 | 0.07 ± 0.00 | 0.11 ± 0.00 | 0.06 ± 0.00 | 0.02 ± 0.00 | 0.01 ± 0.00 | 0.10 ± 0.00 |
| Oluwa river ebute       | 0.20 ± 0.00 | 0.02 ± 0.00 | 0.02 ± 0.00 | 0.03 ± 0.00 | 0.38 ± 0.01 | 0.22 ± 0.01 | 0.06 ± 0.00 | 0.13 ± 0.01 | 0.01 ± 0.00 | 0.03 ± 0.00 |
| Ologodi j stream        | 0.46 ± 0.01 | 0.02 ± 0.00 | 0.02 ± 0.00 | 0.05 ± 0.00 | 0.87 ± 0.01 | 0.33 ± 0.02 | 0.09 ± 0.00 | 0.16 ± 0.01 | 0.03 ± 0.00 | 0.08 ± 0.00 |
| OSUSTECH borehole       | NA     | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.02 ± 0.00 | 0.01 ± 0.00 | 0.00 ± 0.00 | 0.01 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |

Obtained in this study can be compared to other studies [13,15,17-19].

Magnesium is found in seawater (about 1300 ppm) rainwater and ocean, river contain approximately 4 ppm of magnesium. Health effect of magnesium in the water is well-known and applied in life and it has a dietary mineral for humans, one of the micro elements that are responsible for membrane function, nerve stimulant transmission, muscle contraction, also protein construction and DNA replication. It is an ingredient of many enzymes in our body. Large dose of it can get muscle slackening, nerve problems depression, personality change, vomiting and diarrhea [16]. The amount of magnesium in water varies by source and brand (ranging from 1 mg/L to more than 120 mg/L [20]. The mean concentration for magnesium (Mg) (Table 2) in this study varied from 0.02 - 0.52 mg/L; with the highest measured at River Oluwa glass and the lowest was at Ologodi River. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations; except for Igbokoda borehole and Osustech borehole which were statistically not significant (p>0.05). There is no WHO limit for magnesium, but according to the Nigeria standard, the values in all the locations exceeded the limit except in Osustech borehole and Oluwa river ebute that fell within the ambit of the limit. The high concentration of magnesium could be attributed to soil erosion, fertilizer application and cattle feeds, plastic production.

The concentration window of Arsenic in natural waters generally ranges between 1 and 2 mg/L although concentrations may be elevated (up to 12 mg/litre) in areas containing natural sources [16]. The mean concentration for Arsenic in Table 2 in this study varied from 0.00-0.02 mg/L; with the highest concentration measured at River Oluwa glass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. The mean concentrations of Arsenic was the same as the WHO limit in all the location except the River Oluwa glass and Ologodi River whose concentrations were higher than the WHO limits (0.01 mg/L) and the lowest mean concentration which fell below the WHO limit (0.01 mg/L). The high concentration of arsenic in those location could be attributed to sawmilling, selling of chemicals and animal rearing activates in the area. The value obtained in this study is also comparable to other studies [13,15,17-19]. Several studies have shown that ingestion of arsenic can increase the risk of skin cancer and cancer in the liver, bladder, and lungs [16].

The mean concentration for Lead (Pb) from Table 1 in this study varied from 0.00-0.02 mg/L; with the highest measured at River Oluwa glass and Ologodi River and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. Araromi seawater didn’t show any significant different (p<0.05) with Araromi lagoon water; also River Oluwa didn’t show any significant difference (p<0.05) with Araromi Lagoon water. The mean concentration of lead was the same as the WHO standard in all the locations except in River Oluwa glass and River Ologodi j which had higher concentration than the WHO standard. This high in concentration of lead could be attributable to direct release of domestic waste containing lead from human activities at the riverbank and vehicular exhausts and also the wearing of lead from metal pipes into the water. The lowest mean concentration was seen in Osustech borehole which was below the WHO limit (0.01 mg/L) and maximum contaminant level (MCL) of 0.015 mg/L for drinking water [21]. The mean value obtained is comparable to other done in other areas and countries [13,15,17-19]. Exposure to high lead levels can severely damage the brain and kidneys in adults or children and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. Highlevel exposition in men can damage the organs responsible for sperm production [16].

The mean concentration for Cadmium in this study varied from 0.00-0.06 mg/L; with the highest measured at River Oluwa glass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations; except for Araromi Seawater, Araromi Lagoon water and Oluwa River primarily Ebute Borehole which were statistically not significant (p>0.05). Cadmium concentration window in all the locations fell below the WHO limit (3 mg/L). However, the low concentration of all the trace metals in Osustech borehole was as a result of constant treatment the water is being subjected to. The mean value obtained is comparable to other done in other areas and countries [13,15,17-19]. The major source of Cadmium are decayed debris that had accumulated as rocks and undergone mineralization through bacterial processes which lead to accumulation of Cd in the soil and then later leach into water bodies [23]. Drinking water with very high levels severely irritates the stomach, leading to vomiting and diarrhea. Long-term exposure to lower levels of Cadmium in water leads to a buildup of Cadmium in the kidneys and possible kidney disease. Other long-term effects are lung damage and fragile bones [16].

Copper concentrations in drinking-water range from <0.005 to >30 mg/litre, as a result of the corrosion of interior copper plumbing. The mean concentration for Copper in Table 2 in this study varied from 0.02-1.05 mg/L; with the highest measured at River Oluwa glass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations; except for Araromi Seawater, Araromi Lagoon water and Oluwa River Ebute Borehole which were statistically not significant (p>0.05). The concentration window in Copper also fell within the ambit of the limit.
below the WHO limit (2 mg/l) in natural waters copper appears due to dissolution of minerals, at around of 1-10 μg/L [16]. The mean value obtained is comparable to other done in other part of countries [13,15,17-19].

The major sources of copper in water bodies are; agricultural activities and municipal solid wastes, pesticides, batteries charging and blue colour for consumer products [16]. Ingesting high levels of copper can cause nausea, vomiting, and diarrhea. Very-high doses of copper can cause damage to your liver and kidneys, and can even cause death [16].

Manganese (Mn) levels in water typically range from 1 to 200 mg/litre, although levels as high as 10 mg/litre in acidic groundwater have been measured; higher levels in aerobic waters usually associated with industrial pollution. The mean concentration for Manganese (Mn) from Table 2 in this study varied from 0.00-0.34 mg/L; with the highest measured at Aroromi seawater and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. Igbokoda borehole didn’t show any significant different (p>0.05) with Osustech borehole; also Araromi lagoon didn’t show any significant difference (p>0.05) with Oluwa River Ebute. Manganese had a window concentrations below the WHO limits in all the locations (Mn, 0.5 mg/litre). The major sources of manganese are fertilizer, steel production, pesticides and batteries charging. The values obtained in this study can be compared to other studies [13,15,17-19].

The concentration of nickel in drinking-water is usually less than 0.02 mg/litre, although nickel released from other sources may heighten the concentration up to 1 mg/litre [16]. The mean concentration for Nickel (Ni) from Table 2 in this study varied from 0.00-0.04 mg/L; with the highest measured at River Oluwaglass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. Araromi seawater didn’t show any significant different (p>0.05) with Aroromi lagoon water; also Igbokoda borehole didn’t show any significant difference (p>0.05) with Oluwa River Ebute. Nickel has concentrations below the WHO limit (0.02 mg/litre). The reason for the high concentrations in these two locations could be attributed to municipal incineration, combustion of fuel, waste water and metal production. The values obtained in this study can be compared to other studies [13,15,17-19]. The most common harmful health effect of nickel in human is an allergic reaction. Approximately 10-20% of thepopulation is sensitive to nickel. Workers who drank water containing high amounts of nickel had stomach ache and suffered adverse effects to their blood and kidneys. Damage to the lung and nasal cavity has been observed in rats and mice breathing nickel compounds. Eating or drinking large amounts of nickel has caused lung disease indigo and rats and has affected the stomach, blood, liver, kidneys, and immune system in rats and mice, as well as their reproduction and development [16].

The total Chromium concentrations in drinking-water are usually less than 2 mg/liter, although concentrations as high as 120 mg/litre have been measured [16]. From Table 2, the mean concentration for Chromium (Cr) in this study varied from 0.00-0.10 mg/l; with the highest concentration measured at River Oluwaglass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. Ighokode Borehole didn’t show any significant different (p>0.05) with Osustech borehole. The mean values of Chromium obtained from this study fell within ambit of the WHO limit (0.1 mg/L) and the values obtained in this study can be compared to other studies [13,15,17-19]. The major sources of Chromium are erosion from rocks and soils, discharge from steel and pulp mills. The main health problems seen in animals following ingestion of Chromium(VI) compounds are irritation and ulceration in the stomach and small intestine and anemia. Chromium(III) compounds are much less toxic and do not appear to cause these problems. Sperm damage and damage to the male reproductive system have also been seen in laboratory animals exposed to Chromium(VI) [16].

Zinc levels in surface water and groundwater normally do not exceed 0.01 and 0.05 mg/litre, respectively, concentrations in tap water can be much higher as a result of dissolution of zinc from pipes [16]. Zinc is found naturally at low concentrations in my rocks and soils principally as sulphide ores and to a lesser degree as carbonates. Most zinc is introduced into water by artificial pathways such as by-products of steel production or coal –fired power station or from burning of waste materials, from fertilizer that may leach into groundwater.

The mean concentration for Zinc (Zn) (Table 2) in this study varied from 0.01-0.30 mg/l; with the highest measured at River Oluwaglass and the lowest was at Osustech borehole. Analysis of variance (ANOVA) showed that there was significant differences (p<0.05) between the various sampling locations. Araromi seawater didn’t show any significant different (p>0.05) with Aroromi lagoon water; also Aroromi seawater didn’t show any significant difference (p>0.05) with Oluwa River Ebute. Zinc had a window concentrations below the WHO limits in all the locations (Zn, 3 mg/l). The values obtained in this study can be compared to other studies [13,15,17-19]. Zinc is an essential element in our diet. Too little zinc can cause problems, but too much zinc is also harmful. Harmful effects generally begin at levels 10-15 times higher than the amount needed for good health. Large doses taken by mouth even for a short time can cause stomach cramps, nausea, and vomiting. Taken longer, it can cause anemia and decrease the levels of your good cholesterol [16].

Table 3: shows mean concentrations of the anions and the spatial variation of the anions in the sampled locations. For PO₄ ³⁻, Cl and NO₂⁻ there was no significant spatial variation; while SO₄ ²⁻ showed significant spatial variation; with Araromi seawater having significant higher NO₃ than Ighokode Borehole and Oluwa River, Ebute respectively. The concentration window ranged from, Phosphate, 0.74-2.97; Sulphate, 2.46-24.22; Chloride, 118.33-324.97; Nitrate, 0.5-0.23. Phosphates enter waterways from human and animals waste, phosphorus rich bedrock, laundry, cleaning, industrial effluents, and fertilizer runoff. Phosphates become detrimental when they over fertilize aquatic plant and cause step up eutrophication. According to [18] a concentration window of 0.01-0.03 mg/l of phosphates in water signifies un-contamination, 0.025-0.1 mg/l stimulates plant growth while concentration greater than 1 mg/l of phosphate stimulates accelerated plant growth and consequent problem. There is no regulatory limit for phosphates in drinking water continentally and nationally. But certain criterion has recommended by US EPA, [24] for total phosphates, 0.025-0.1 mg/L of phosphate from stream should be discharged into reservoirs.

The concentration sulphate obtained in this analysis fell below the regulatory limits by WHO and the Nigerian Standard which are; 250 mg/l WHO and for Nigerian Standard is 100 mg/l in all the locations. Sulphates in water is primed to have an offensive taste with a concentration of above 500 mg/l [25]. The concentration of sulphate in water obtained in this analysis is comparable to other results obtained in other part of countries [24,26]. The health effect of the sulphate concentration in water in both animal and human ranges from...
1600-3000 mg/L [27,28]. Sulphates in water are the result of natural weathering of minerals, anthropogenic discharge and atmospheric deposition. The chloride ion is highly mobile. Chloride in groundwater and surface water emanates from both numerous sources, such as run-off containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation, drainage and seawater intrusion in coastal area [29]. The mean concentrations of chloride obtained in this work were higher than the WHO limit and the Nigerian Standards in some locations such as: Araromi seawater, Araromi lagoon water, River Oluwa glass and Ologediji river while Osustech borehole, Igokoa and Oluwa River Obute were within the WHO and Nigerian Standard limit, 250 mg/L.

The mean chloride concentrations obtained in this analysis are comparable to other studies [30,31]. Excessive intake of chloride concentration in water above 2500 mg/L has been reported to cause ill-health [32]. WHO International Standards for Drinking-water suggested that concentrations of chloride greater than 600 mg/L would markedly impair the portability of the water.

The nitrate values obtained from this analysis as shown in Table 3 are lower than the prescribed limit in drinking water. The US EPA maximum contaminated level (MCL) for nitrate in drinking water is 10 mg/L and the WHO guideline (2004) is 50 mg/L. In most countries, nitrate levels in drinking-water derived from surface water do not exceed 10 mg/litre, although nitrate levels in well water often exceed 50 mg/litre; nitrite levels are normally lower, than a few milligrams per liter [16].

Nitrate had been reported to have insidious effect on human and animal [22]. Unpolluted water generally have nitrate below 1 mg/L [33]. The major sources of nitrate in water are: Animal feed, municipal waste water and sludge, septic system and nitrogen fixation from atmosphere by legumes, bacteria and lightning. However nitrate also occurs naturally in groundwater. The values obtained in this analysis are also comparable to the values obtained in other studies [22].

Nitrates in water bodies using Enrichment Factors.

Table 4 shows the Most Probable Number (MPN) of coliforms per 100 mL of the water samples. Analysis of MPN of coliforms for the deep well water samples revealed the MPN values of OSUSTECH deep well was 0.00 CFU/100 mL, with no coliform isolated. This seems to satisfy the international hygienic standard for microbiological water quality.

| Araromi seawater | Araromi lagoon water | Oluwa river | Igokoha borehole | Oluwa river ebute | Ologediji river | OSUSTECH borehole | WHO limit | SON 2007 limit |
|------------------|----------------------|-------------|------------------|------------------|----------------|------------------|-----------|----------------|
| PO<sub>4</sub><sup>-</sup> | 2.97 ± 1.48<sup>a</sup> | 2.95 ± 1.78<sup>a</sup> | 0.81 ± 0.35<sup>b</sup> | 1.33 ± 0.15<sup>a</sup> | 2.43 ± 0.64<sup>a</sup> | 0.74 ± 0.17<sup>a</sup> | NA        | NA             |
| SO<sub>4</sub><sup>-</sup> | 22.70 ± 147.25<sup>a</sup> | 22.22 ± 9.73<sup>a</sup> | 2.46 ± 1.15<sup>b</sup> | 10.17 ± 2.97<sup>a</sup> | 13.04 ± 2.63<sup>a</sup> | 4.68 ± 1.88<sup>a</sup> | 250       | 100            |
| Cl<sup>-</sup> | 256.33 ± 162.39<sup>a</sup> | 324.97 ± 276.00<sup>a</sup> | 155.65 ± 5.55<sup>b</sup> | 249.43 ± 87.53<sup>a</sup> | 266.00 ± 77.25<sup>a</sup> | 118.33 ± 27.54<sup>a</sup> | 50        | 50             |

Mean with different superscript are statistically significant @p<0.05.

Table 3: Anion mean concentrations (mg/L) in the sampled locations.

Table 4: The Most Probable Number (MPN) of coliforms per 100 mL of the water samples.

| Water sample source | MPN 24 hr | Coliforms isolated |
|---------------------|-----------|--------------------|
| River Oluwa, Ebute  | 160       | Unidentified coliforms |
| Ologogidi stream, Igodan | 14       | Unidentified coliforms |
| Igbokoda deep well  | 160       | Unidentified coliforms |
| River Oluwaglass, Igokoha | 180   | Escherichia coli, Unidentified coliforms |
| Araromi beach (Sea water) | NT      | Escherichia coli   |
| Araromi lagoon (Brackish water) | NT     | Escherichia coli   |
| OSUSTECH deep well  | 000       | -                  |

Key: NT- Not tested
Mg, As and Cr showed a significant positive weak correlation with NO$_3$ while the other heavy metals didn’t show any significant relationship with it. The correlation values obtained in this analysis are also comparable to other studies [19,22]. However, the results obtained is not in agreement with other studies [34].

**Principal component analysis**

After x-raying the background relationship between the heavy metals, we now group these relationships into components and associate them with the anions to shows the relationship and predictive ability. This was achieved using principal component analysis. Principal component analysis revealed two components as shown in Table 6 using the criteria of Eigen value of 1; this accounted for 96.2% of the total variance. The rotated component matrix reveal that Mg, As, Pb, Cd, Cu, Fe, Cr, Zn and Ni loaded higher on Component 1; while only Mn loaded higher in component two.

Multiple linear regression of the factors scores of the two components on anions is shown below:

- $PO_4 = 2.014 + 0.67PC1 + 0.52PC2$; $R^2 = 0.438$; $R^2 = 0.375$; $p < 0.05$
- $SO_4 = 13.726 + 5.43PC1 + 4.88PC2$; $R^2 = 0.592$; $R^2 = 0.547$; $p < 0.05$
- $Cl^- = 224.469 + 59.93PC1 + 23.47PC2$; $R^2 = 0.438$; $R^2 = 0.375$; $p < 0.05$
- $NO_3 = 1.530 + 0.346PC1 + 0.351PC2$; $R^2 = 0.292$; $R^2 = 0.214$; $p < 0.05$

The result shows that the extracted components of the heavy metals have been able to explain 44% of the presence of PO$_4$ in water. This linear relationship is however statistically significant ($p<0.05$). For SO$_4$, the model was able to explain 59% which is statistically significant ($p<0.05$). The principal components were able to predict 44% of Cl; which not statistically significant ($p>0.05$). While the principal components were able to predict 29% of NO$_3$; which is statistically significant ($p<0.05$) Source apportionment of the contributory proportions of the components to the availability of PO$_4$ in Water is given below: From Figure 1, PC1 contributed 56.2% of PO$_4$; while PC2 (i.e. Mn) contributes 43.81% of PO$_4$. From Figure 2 PC1 contributed 53% of SO$_4$; while PC2 (i.e. Mn) contributes 47% of SO$_4$. From Figure 3 PC1 contributed 72% of Cl; while PC2 (i.e. Mn) contributes 28% of Cl. From Figure 4 PC1 contributed 49.6% of NO$_3$; while PC2 (i.e. Mn) contributes 50.4% of NO$_3$. This implies that Mn is a better predictor of NO$_3$ compared to other metals in PC1. The two principal components also suggest two major sources of pollutant; Trade waste and municipal waste [19,35]. Table 7 shows the enrichment factor values using Iron, Manganese and Chromium as reference elements in all the locations.

**Enrichment factors (EFs)** are widely used in environmental sciences to speculate on the origin of elements in air, atmospheric dust or precipitation [36,37]. Few studies had in water[13,15]. The most common reference elements in the literature are Aluminum (Al), Zirconium (Zr), Iron (Fe), Scandum (Sc) and Titanium (Ti) [20,38], although there are also attempts at using other elements (e.g., Manganese (Mn) [12,39], Chromium (Cr) [13]. From Table 7, the enrichment factor values using iron as reference element in all the locations had a decreasing trend of; Cd>Cu>Zn>As>Cr>Pb>Mn>Ni>Mg, except in Araromi and River oluwaglass in which Ni was greater than Mn. When Mn and Cr were used as reference elements in the computation of enrichment factor in all the locations, a decreasing trend Cd>Cu>Zn>As>Cr>Pb>Mn>Ni>Mg, except in Araromi and River oluwaglass where Cl and Pb were not enriched in all the locations. However, in Igbokoda borehole and River ebute where Mn was severely enriched. However, in River ebute Ni was severely enriched and Mg was moderately enriched except Igbokoda and River ebute, Mg had minor enrichment. However, when Mn was used as a reference element, Cd and Cu were extremely and severely enriched in all the locations and also Mg and iron were not enriched in all the locations as well. In Araromi, As, Pb, Fe and Zn had a minor enrichment, in River oluwa and Igbokoda, Zn was very severely enriched while Pb, Cr, and As were severely enriched and Ni was moderately enriched. In Igbokoda, Pb and As were very severely while Ni, Zn and Cr were severely enriched. River ebute, Zn was very severely enriched, As, Pb, and Cr severely

| Component | 1   | 2   |
|-----------|-----|-----|
| Mg        | .933|     |
| As        | .971|     |
| Pb        | .988|     |
| Cd        | .978|     |
| Cu        | .974|     |
| Fe        | .978|     |
| Cr        | .899|     |
| Zn        | .968|     |
| Ni        | .959|     |
| Mn        | .988|     |

**Table 6:** Rotated component matrix.
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Table 7: Enrichment factor using Iron, Manganese, and Chromium as a crustal value in all the locations.

| River Location | Mg | Mn | Cr | Mg | Mn | Cr | Mg | Mn | Cr |
|----------------|----|----|----|----|----|----|----|----|----|
| Araromi seawater | 7.05 | 0.05 | 0.03 | 5.19 | 0.37 | 0.02 | 3.42 | 0.31 | 0.03 | 1.15 | 0.24 | 0.02 |
| Araromi lagoon | 292.68 | 2.14 | 1.11 | 321.09 | 22.97 | 1.15 | 203.99 | 18.39 | 1.77 | 169.57 | 35.47 | 3.33 |
| Oluwaglass river | 161.1 | 1.18 | 0.61 | 178.2 | 12.75 | 0.64 | 112.81 | 10.17 | 0.98 | 136.15 | 28.48 | 2.67 |
| Igbohoda borehole | 27307.7 | 199.52 | 103.46 | 24830.8 | 1776.58 | 88.89 | 20516 | 1849.25 | 177.88 | 13975.6 | 2923.58 | 274.53 |

Fe was moderately enriched while Ni was moderately enriched, from Ologediji, As, Cr, and Zn were severely enriched while Ni and Pb were moderately enriched. In OSUSTECH borehole, Pb was very severely enriched. Zn, As and Cr were severely enriched while Ni was moderately enriched. When Cr was used as a reference element Cd was extremely and severely enriched in all the locations while Cu was severely enriched in all the locations except OSUSTECH borehole, whose Cu was moderately enriched. In Araromi seawater and Araromi lagoon, As and Zn had a minor enrichment, while Mg, Pb, Ni and Mn were not enriched. River Oluwaglass, As and Zn had minor enrichment while Mg, Pb, Ni, and Mn were not enriched, while in Igbohoda, As was moderately enriched, Ni, Zn and Pb had a minor enrichment, also Mg, Mn and Fe were not enriched, in River ebute, Zn had a minor enrichment while As, Mn, Mg, Fe, Ni, Pb where not enriched, in Ologediji, As was moderately enriched, Ni, Zn and Pb had a minor enrichment, also Mg, Mn and Fe were not enriched. In Osustech, Zn, As and Pb had a minor enrichment while Mg, Mn, Ni, and Fe were not enriched. The anthropogenic contribution is directly proportional to enrichment factor [40].

Conclusion

The quality Assessment of water sources in Ilajeand Okitipupain Ondo State, showed that the nitrate, phosphate and chloride contents were found mostly within the limits set by both National and International standard regulatory bodies for drinking and domestic waters. Also there was a direct relationship between anions and the trace metals in water of the samples. Similarly, apart from Pb, As and Mn which were higher than the limits in two locations, all the other elements were found within the limits recommended by Standard Organization of Nigeria [41] for drinking water quality and WHO. Cd

Figure 1: Source apportionment of contribution of PC1 and PC2 to the availability of $PO_4^-$. 
and Cu were extremely and severely enriched in the water samples. Two components were observed from the principal component analysis that suggested two major sources of pollutant. Results from this study indicate that people from the areas under study might be prone to water-borne diseases, which result in the large number of diarrheal cases that have been seen in patients attending nearby hospitals.

The authors recommend that Local Government Authorities in Ondo South should ensure adequate environmental sanitation, inclusion of water closet toilets in homes and work places, adequate treatment of deep well water, as well as incorporate laws regulating activities in and around water bodies, to protect the surface waters from contamination.

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