Total and Exchangeable Metals in Groundwater of Ile-Ife, Southwestern Nigeria

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Abstract

The groundwater samples of Ile-Ife obtained from ten different locations were analysed for their total and exchangeable heavy metals in order to determine their potability status. Water samples collected for two months were analyzed for pH, conductivity, temperature, total and exchangeable heavy metal values using standard methods. The ion exchange chromatographic extraction of the exchangeable metals was carried out with anionic trimethylhyroxyammonium resin. Atomic Absorption Spectrophotometer analysis for total and exchangeable Cu, Pb, Zn, Cd and Mn was performed. The mean pH, conductivity and temperature values, measured *insitu*, were 6.0 ± 0.5, 340 ± 244 µS/cm and 27.5 ± 0.3^{o}C respectively. Total mean levels (µg/mL) of Cu, Pb, Zn, Cd and Mn were 8.275 ± 0.912, 0.179 ± 0.041, 31.858 ± 3.635, 0.090 ± 0.010 and 76.789 ± 12.889 respectively while 1.484 ± 0.228, 0.040 ± 0.008, 5.911 ± 1.002, 0.017 ± 0.003 and 20.151 ± 5.845 (µg/mL) were detected as the respective mean values (µg/mL) of the exchangeable metal fraction in the samples. Comparing the levels of heavy metals in the samples to the WHO provision for drinking water, the groundwater was capable of constituting serious health hazards.

Key words: Groundwater, heavy metals, ion-exchange chromatography, Ile-Ife, Nigeria.

Introduction

Water has maintained a status of being one of the most essential commodities on earth owing to its indispensable roles for agricultural and household uses; industrial, tourism and cultural purposes; and as a medium for numerous biochemical and physicochemical reactions. However, there is a growing national, regional and seasonal water scarcity in much of the world such that severe challenges are posed for national governments, international development and environmental communities (Rosegrant *et al.*, 2002).

In 2004, the World Health Organization (WHO) reported that some 1.1billion people representing 17% of the global population were without safe drinking water. Substantial numbers of these people live in China, India, Africa and Middle East. The report further revealed that 42% of sub-Sahara Africa lacks drinking water. No less than one-third of the world population is currently living in regions experiencing acute water shortage in which case, emphasis is on the availability and not quality. Researchers reported a decline in water availability in Asia from 60% to 40% between the years 1955 and 1990 with a projection of an overly severe water shortage in the region by the year 2025 (www.globalchange.umich.edu/). This is synonymous with a forecast by other experts that more than 47% of the global population will face the hardship by year 2030 (Robert, 2008).

In the past, water shortage had led to major crises between nations. For example, General Ariel Sharon, Israeli Prime Minister, revealed that the six-day war between Israel and The Arabs which started on 5th June, 1967 was necessitated by the earlier plan of the Arabs, led by Colonel Nasser, to divert the water away from Jordan. After series of protracted dispute, the two governments settled with a sharing ratio of 4:1. Another example is the Egyptian Government, which in protecting her water resources, has vowed to go into war with any country illegally exploiting her water resources (www.news.bbc.co.uk/).

To ensure that desirable quality of drinking water is attained (WHO, 2008), there is the need for regular drinking water assessment to show the level of compliance with the World Health Organization guidelines at any given time in terms of levels of chemical and biological contaminants such as trace heavy metals, mineral compounds, pH, organic matters and compounds as well as pathogens which possess acute or chronic health implications (WHO, 2008).

Elevation in the trace metal contents of an aquatic system may arise from the daily human activities, various degrees of geochemical reactions occurring in the sub-surface of the earth, runoff addition, aerial deposition and percolation-related phenomena (Ibe and Duruike, 2005). Among the possible contaminants in water, heavy metals have attracted an unprecedented attention owing to their high toxicities even at low concentrations. Heavy metals are known to exhibit a wide range of oxidation states which determine their physico-chemical forms like simple hydrated, complexed and colloidal particles (Matthew, 1996; Tokalioğlu *et al*, 2000). The different oxidation states of trace metals have been discovered to possess varying degrees of toxicity hence, the need for speciation. Most transition metals are very toxic while some called micro-elements are very essential to the human biochemical systems in trace amounts. Speciation, which is the analytical study of heavy metal to determine their form of occurrence in any given sample, has wide applications in biological, geochemical, environmental, and water treatment processes. Speciation, in water analysis, is accomplished through the use of ion-exchange resin to selectively separate the exchangeable ions from the solid metals.

In Nigeria, water usage was estimated to be around 8 km^3/yr in the year 2000 (Kundel, 2008). According to the report, 5.5 km^3, representing 69%, was voted into agriculture while domestic and industrial uses consumed 1.7 km^3 (21%) and 0.8 km^3 (10%) respectively. Like many Nigerian towns and cities, over 90% of the Ile-Ife residents depend on groundwater, to a large extent, for their drinking and other water needs without prior knowledge of its compositions. Within the population of Ile-Ife residents, cases of water related ailments are still very much reported on regular basis. These diseases range from common cholera and typhoid fever to cases of cancers and failure of major internal organs. Some of these health problems have been associated with chemicals, including toxic heavy metals, which may be ingested into the human system in part through contaminated water. Based on this fact, health and medical practitioners can only logically identify causes of some illness and advise appropriately if there is scientific proof.

This study was carried out to assess the potability of drinking water sources available to the Ile-Ife people with respect to levels of some of the heavy metals (Cu, Zn, Cd, Pb and Mn) commonly encountered in the environment. This could be useful in proposing the kind of treatment most suitable for the available water sources.

Materials and Methods

Description and Suitability of the Study Area

Ile-Ife is an ancient town in Osun State within the southwestern geopolitical zone of Nigeria. It is located 64 km away eastward of Ibadan at an interception point between Ilesa, Ondo and Ibadan. The ancient town of Ile-Ife is relatively densely populated as a result of the presence of three institutions of higher learning - Obafemi Awolowo University, Ile-Ife; Oduduwa University, Ipetumodu; The Polytechnic, Ile-Ife; and several other primary and secondary schools and study centres. The predominant economic mainstay of the people of this area includes small-scale agricultural practices, timber processing and commercial transportation activities. Unarguably, these activities, in addition to waste from metal scraps and lead from internal combustion engines and other metal works, are capable of contributing noticeably to the environmental pollution sources that have the potential of elevating trace metal content of both surface water and groundwater in the area.

The topography of Ile-Ife is quite undulated with some rocky hills mostly made up of igneous rock surrounding the ancient town. The sampling sites (Figure 1) within the town lie approximately between Longitude 004^{o}29′ to 004^{o}35′ E and Latitude 007^{o}27′ to 007^{o}32′ N. The altitude of the studied sites varies from about 244 to 308 m making the depth of the unconfined aquifer layer unsteady and varying according to the land topography. Thus, the exploitation of deeper groundwater in the confined aquifers could be technically difficult without the availability of the advanced drilling technology to penetrate the rocky soil to the desired depth in many cases. Hence, a large number of the residents of the town, including those operating water packaging small-scale industries, rely on shallow hand-dug wells as their predominant potable water sources.

Reagents used and their Sources

All the reagents used, viz. nitric acid, HNO_3, (Riedel-deHaën, Germany), hydrochloric acid, HCl, (Sigma-Aldrich, Germany), sodium hydroxide (NaOH) pellets (British Drug House, BDH, Chemicals Ltd, Poole, England), sodium chloride, NaCl, (British Drug House, BDH, Chemicals Ltd, Poole, England), concentrated perchloric acid, $HClO_4$, (Sigma-Aldrich, Germany) and doubly distilled water , were of analytical grade. From the list above, reagent I (0.12mol/L of HCl containing 100g of NaCl made up to 500 mL) and reagent II (2 M NaOH and 0.34 M NaCl) were prepared.

Pre-treatment and Sterilization of Apparatus

Plastic bottles used for sampling and collection of worked-up samples were first washed with liquid detergent and rinsed with distilled water. They were then soaked in 10% trioxonitrate (V) acid for 48 hours. This was followed by vigorous three times rinsing with distilled water.

Sample Collection and Pre-treatment

Samples were collected once a month for two months (July and September, 2010) from ten different locations within Ile-Ife. The locations were Ajebandele, Arubidi, Eleyele, Ife-City, Oke-Ogbo, Ondo Road, Opa, Our Lady, Parakin and Sabo (Figure 1). The geographical locations of the sampling points (Table 1) were mapped out using a Magellian GPS 310. At the spots of sampling, the sampling bottles were rinsed with the water samples four times before being filled to the brim with the sample. The samples were preserved briefly at a temperature of 4^{o}C without adding nitric acid so as to avoid the dissolution of the insoluble metal components by the acid before total metal and speciation analyses commenced.

Determination of pH, Conductivity and Temperature

The pH, conductivity and temperature measurements were performed *in situ* as soon as the samples were collected using a handheld pH Meter (Eutech Instruments pH Testr 2) and Conductivity Meter/Thermometer (Eutech Instruments EC Testr 2) respectively. Each parameter was done in triplicates.

Sample Digestion for Total Metal Determination

A 20 mL aliquot of water sample was transferred into a Teflon beaker and 5 mL of concentrated HNO_3 was added. This was followed by gentle boiling on a thermostated hot plate in a fume cupboard for about 45 minutes. Replenishing with the acid was done as necessary to avoid total dryness. Then, 5mL of 1:1 (v/v) concentrated $HClO_4$ and concentrated HNO_3 mixture was added to the sample and allowed to gently boil further for 30 minutes (Christian, 2004) without going to total dryness. The digested sample was quantitatively transferred into a 25 mL volumetric flask and diluted to volume. From this, an aliquot was taken for AAS analysis.

Extraction of Dissolved Metals in Water Samples

A modified method of Tokalioğlu *et al*. (2000) employing Ion-Exchange Chromatography (IEC) was used for the extraction of heavy metals dissolved in the water samples. The method is schematically represented in Figure 2.

Data Analysis

The standard deviation for the metals from three replicate measurements was determined. Evaluation of the data was done using the mean values. Student's *t* -test was used to demonstrate the significant difference between the means of the heavy metal levels obtained. Coefficient of variation was adopted to evaluate the intra and inter site temporal variability of the metals.

Results and Discussion

Table 1 gives the geographical locations of the sampling sites. The study area precisely lies within longitudes 004^{o}29.859′ to 004^{o}34.709′ E and latitudes 07^{o}27.381′ to 07^{o}31.603′ N, while the land elevation is within 244 and 308m above sea level. Under the experimental conditions used, the standard calibration curves obtained showed high linearity level with r^2 values (Table 2) between 0.9856 for Zn^{2+} and 0.9987 for Cu^{2+}. Recoveries of heavy metals in water ranged from 83.78 % for Cd^{2+} to 98.02 % for Mn^{2+} (Table 2). These values are adjudged acceptable, and hence, the results obtained are reliable.

More than the total metals in the water, the exchangeable metal ions possess immediate health implications owing to their higher ease of absorption into the human body systems. The results of the analysis of the water samples for the mean total heavy metal levels (µg/mL) are presented in Table 3 while Table 4 contains the values for the mean levels (µg/mL) of heavy metals in the exchangeable fraction in the water samples for the two months. The total metal burden, in µg/mL, (Table 3) was of the order: Ajebandele (96.96) < Sabo (100.55) < Ife-City (103.02) < Ondo Road (104.59) < Oke-Ogbo (108.81) < Parakin (117.94) < Opa (120.51) < Arubidi (133.88) < Our Lady (139.22) < Eleyele (146.47). The high metal load observed at Eleyele area could be as a result of seepage from a close by refuse dump over the years, in addition to the geochemical composition of the underlying rocks around the well, which might possibly contain some of the metals assessed.

The two months mean total Zn levels in the water samples, with a mean of 31.86 ± 3.64 µg/mL, ranged from 27.56 ± 1.15 µg/mL at Ajebandele to 37.82 ± 1.01 µg/mL at Eleyele (Table 3). The Zn levels in this study were lower than the 147.3 ± 30.4µg/mL (hand-dug well) levels reported by Oluyemi *et al.* (2010) for Ife North Local Government Area of Osun State, but much higher than the respective 0.03mg/L and 0.045 - 0.35 mg/L Zn contents of boreholes and wells in Makurdi metropolis reported by Nsi and Ogori (2005). The Zn values obtained in the present study were also much higher compared to the 0.04 ± 0.06 µg/mL (range: 0 – 0.23µg/mL) of Ojota area in Lagos (Oyeku and Eludoyin, 2010). These discrepancies may have resulted from the geological differences, mainly. The exchangeable Zn fraction gave a mean value of 5.911 ± 1.002 µg/mL. The percentage of the exchangeable fraction was approximately 18.85%. The amounts of Zn detected in both the total and exchangeable fractions exceeded the WHO standard of 3.00 µg/mL and recommended daily in-take of 15 – 20 mg (WHO, 2008), considering an average of 2.5 L daily consumption of drinking water by an average adult (www.globalchange.umich.edu/).

Granted, Zn is an essential element required for life processes of various enzymes (Wordstron, 1982), and low serum zinc, for example, can lead to acrodermatitis enterohepatica, a familiar disease characterized by skin eruptions and gastrointestinal disorders (Cartledge, 1992). However, at elevated levels, Zn may be carcinogenic (Cartledge, 1992) and interfere, at different levels, with the endocrine system, lipids and carbohydrate metabolism. Excessive Zn symptoms include nausea, dizziness, gastric ulcers, lethargy, muscle pain, impairment of immune function, headaches, vomiting, dehydration, stomach-aches, poor muscle coordination, fatigue, possible renal failure and increased blood level of insulin-like growth factor and testosterone, both of which are related to prostate cancer (Jameson, 1976; Michael and Stanford, 2003).Those who solely rely on the underground waters from the study area may sooner or later suffer from some of the aforementioned ill-health cases.

Lead, which has no known health benefit, had a significant amount of it detected in all the groundwater samples of the studied area. The mean total Pb levels in the water samples ranged from 0.14 ± 0.01 µg/mL at Ajebandele to 0.25 ± 0.02 µg/mL at Our Lady. The overall mean total Pb levels of 0.18 ± 0.04 µg/mL obtained in the underground waters of Ile-Ife in the present study were considerably lower than the 4.01 ± 3.82 µg/mL, 4.9 ± 0.18 µg/L, and 2.4 ± 3.3 µg/mL (with a range of 0 – 14.8 µg/mL) Pb levels respectively reported for the groundwater resources from Ife North Local Government Area, Ibadan and Lagos by Oluyemi *et al.* (2010), Abiola (2010) and Oyeku and Eludoyin (2010).

However, the value was 18 times higher than the World Health Organisation (WHO, 2008) Guideline Limit of 0.01 µg/mL Pb for drinking water. Elevated Pb level of groundwater may be an indication of surface pollution resulting from the several years of automobile combustion of petrol containing organolead additives in the past, unguarded disposal of used lead-acid batteries, alloys, soldering metals and uninformed open air incineration of waste material at the dump sites. All these activities could increase the metal contents of the underground water resources through percolation related phenomena if the Pb or its compounds become soluble at lower pH levels. The Pb mean level of 0.04 ± 0.01µg/mL in the exchangeable fraction, with a range from 0.03 to 0.06 μg/mL accounted for a mean percentage of 23.56% exchangeable Pb in the water samples. The exchangeable Pb levels were also well above the 0.01μg/mL value of WHO (2008) guideline limit. Hence, from the perspective of their Pb content, the water samples were unfit for human consumption.

Unarguably, there must have been anthropogenic Pb inputs from contaminated sites leaching and sinking into the wells through crevices in between concrete cement rings used for well lining. The ubiquity of Pb and its toxicity even at low concentrations make it one of the most insidious of all environmental hazards. It has been argued that, for humans, there is no level below which exposure is harmless (Goyer, 1996). On human beings, Pb has both physiological and neurological effects (Fullmer, 1992); the major risk of Pb as an environmental contaminant is, however, its toxicity to the nervous system. Pb poisoning can cause: nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anemia, irritability, mood disturbance and coordination loss (Grandjean and Nielson, 1979); neurological effects such as restlessness, hyperactivity, confusion and memory impairment as well as convulsions, coma and sudden death of both adults and infants can result (Boeckx, 1986). Still births (Piotrowski and Coleman, 1980; Boeckx, 1986) and increased risk of hypertension and birth defects for pregnant women (Rabinowitz, 1988) are other health effects for which Pb has been implicated. According to Lanphear *et al*., (2000) and Wu *et al*. (2003), blood Pb concentrations of less than 10 μg /dL in children and adolescents can cause cognitive deficits. Chronic effects of Pb especially on the foetus and children may include behavioural changes and impaired performance in IQ tests (Needleman, 1989; Fatoki *et al*., 2002).

Cadmium is another very toxic environmental metallic pollutant. Its mean total levels measured in the underground water samples of Ile-Ife ranged from 0.08 ± 0.01 μg/mL at Ajebandele to 0.11 ± 0.00 μg/mL at Eleyele while levels in the exchangeable fraction varied from 0.01 ± 0.00 μg/mL at Arubidi and Ajebandele to 0.02 ± 0.01μg/mL at Oke-Ogbo and Sabo. The mean amount of Cd measured in water samples in terms of total and exchangeable fractions were 0.09 ± 0.01 μg/mL and 0.02 ± 0.00μm/mL respectively. By comparison, the values of mean total Cd in the present study were lower than the values (0.98 ± 0.67μg/mL) reported by Oluyemi *et al.* (2010) for Ife North Local Government Area. The percentage exchangeable Cd in this study was about 19.23%. Again, it is obvious that Cd content in the groundwater sources of the present study far exceeded the WHO permissible limit of 0.003 μg/mL (WHO, 2008) in folds of up to 30 and 6.7 for total and exchangeable Cd fractions, respectively.

The heightened levels of Cd in the water samples could be as a result of its long-term anthropogenic inputs from contaminated sites and corroded utensils used for water fetching in some instances. Cd toxicity symptoms include excessive salivation, nausea, vomiting, diarrhoea, abdominal pain, vertigo, and for large doses, loss of consciousness (Nordberg, 1972; 1988). Other effects of Cd in man include kidney damage (Herbert *et al*., 1988), pains in the bones-"itai-itai" disease (Kjellstroem, 1986) and endocrine disruption (Schantz and Widholm, 2001). The outcome of "itai-itai" disease is the softening of bones (osteomalacia) produced by vitamin D deficiency. The early signs of the disease are pains in the joints, lumbago pains and pseudo fracturing of the bones (Bryce-Smith, 1975). Cd also has mutagenic, carcinogenic and teratogenic effects (Heinrich, 1988; Goyer and Clarkson, 2001).

Cu is an essential trace metal to human life at moderate levels functioning as part of several enzymes e.g. tyrosinase (necessary for the formation of melanin pigments), cytochrome oxidase, super oxide dismutase, amine oxidases and uricase. It is essential for the utilization of iron in the formation of haemoglobin (Piscator, 1986; Andrew and Michael, 2000). In the present study, Cu occurred at a mean total level of 8.28 ± 0.91 µg/mL in the underground waters of Ile-Ife. Its mean total levels ranged between 7.19 ± 0.01 µg/mL at Ajebandele and 9.76 ± 0.04 µg/mL at Eleyele while the mean level of exchangeable Cu fraction was 1.48 ± 0.23 µg/mL (or 17.87% of the mean total Cu level) with a range between 1.21 and 1.98 µg/mL. While the exchangeable Cu level fell below the 2.0 µg/mL WHO (2008) permissible limit for drinking water, the total levels were much higher. Depending on the pH and redox conditions of the underground waters, more of the total Cu could go into exchangeable fraction especially under lower pH and anoxic conditions, thus becoming readily available and exceed the WHO Guideline Limit of Cu for drinking water. Hence, those who rely on the water may, in the long run, suffer such copper-induced health effects such as intestinal discomfort, dizziness, headaches, vomiting, diarrhoea with bleeding, circulatory collapse, liver and kidneys failure and severe haemolysis (Johnson and Kays, 1993). From its current underground water levels, anthropogenic inputs could not be considered to have seriously impacted the underground waters of the studied areas. By far, the geochemical environment might have been responsible for the levels of Cu detected in the water samples.

The mean total Mn levels ranged from 61.99 ± 0.56 µg/mL at Ajebandele to 98.57 ± 0.92 µg/mL at Eleyele while the mean Mn for the two months stood at 76.79 ± 12.89 µg/mL whereas the levels of exchangeable Mn ranged from13.87 to 33.99 µg/mL with a mean of 20.15 ± 5.85 µg/mL. The result obtained for total Mn levels was in good agreement with the 93.65 ± 0.16µg/mL for hand dug wells and 99.14 ± 0.23µg/mL for boreholes of Ife North Local Government Area reported by Oluyemi *et al.* (2010), much higher than the 0.005 - 0.0055 mg/L levels for well water and 0.14-0.15mg/L for borehole waters of Makurdi (Nsi and Ogori, 2005). In a situation where the World Health Organisation (WHO, 2008) Guideline Limit of Mn for drinking water is 0.4 µg/mL, the waters certainly contained excess Mn. Manganese is an essential element being a constituent of certain enzymes, an activator of many enzymes and a stimulator of the synthesis of chondroitin sulphate, an important constituent of cartilage and connective tissue (Keen and Ziderberg-Cherr, 1996). Symptoms of Mn deficiency include skeletal abnormalities and impaired growth (Underwood, 1977); malformation of inner ear of foetus (ataxia and defective otoliths) as a result of maternal manganese deficiency (Hurley, 1976); dermatitis, pigment changes of hair, retarded hair growth and hypocholesteromia (Doisy, 1973). However, in humans, excessive exposure to Mn and its compounds (especially oxides) has led to a variety of symptoms some of which are irreversible. According to Keen and Ziderberg-Cherr (1996), Mn toxicity presents a serious health hazard, resulting in severe pathological disorder of the central nervous system. The toxicity can be manifested by a permanent crippling neurological disorder of the extra pyramidal system similar to Parkinson's diseases. In its milder form, the toxicity is expressed by aggressiveness, hallucinations, disturbances of libido and improper coordination. These symptoms once established, tend to persist even after the Mn body burden returns to normal. Apart from neural damage, reproductive and immune system dysfunction, nephritis, testicular damage, pancreatitis, lung disease and hepatic damage can also occur with Mn toxicity. Hence, those regularly using the waters for drinking and cooking purposes need to be cautious in order to avert serious health problems.

The coefficient of variation (CV) is a useful statistical tool that can be employed to interpret the temporal and spatial distribution and variability patterns of pollutants in an environmental matrix. In the present study, the CV values with a mean value of 14.91, ranging from 10.34 in Cu to 16.79 in Mn (Table 3), were not markedly different from one another. This indicated, more or less, a steady rate of input of the metals into the underground waters either as a result of gradual dissolution of the metals from the underlying parent rocks or steady leaching from the sites of contamination. In other words, the factors responsible for the presence of these metals in the waters might not be sudden changes in the anthropogenic activities or weather elements.

Generally, the results (using t-test) revealed that the mean amounts of total Zn, Pb, Cd, Cu and Mn in the ground waters of Ile-Ife were significantly higher at $p \leq 0.05$ than the guideline limits stipulated by the World Health Organisation (WHO, 2008) for drinking water. The geochemical structure and mineral composition of the soil of Ile-Ife environment due mainly to igneous rock weathering may have a link to the trend, and most importantly, the high content of these metals in the groundwater may be as a result of the water serving as the main transporting medium of the dissolved minerals in secondary deposition process.

Table 5 contains the mean values of such physicochemical parameters as electrical conductivity (EC), pH and temperature of the groundwater samples for the two months. The EC of a water body is related to its concentration of dissolved mineral salts (Department of the Environment, 1972) and it is affected by the total concentration of ions and by other factors such as the mobility of the individual ions (Egborge, 1994). It is a useful indicator of the extent of mineralization in a water sample. The effects of high EC may include disturbances of salt and water balance and high salt concentrations in water and effluent samples. High salt concentrations may result in adverse ecological effects on the aquatic biota (Fried, 1991). Some of the adverse ecological effects of high salt concentrations include heart problem, high blood pressure and renal disease (DWAF, 1998). In the present study, the EC of the water samples ranged between 130 ± 3 µS/cm at Parakin and 865 ± 4 µS/cm at Sabo. With a mean of 350 ± 237 µS/cm and a coefficient of variation 67.71, the EC can be said to have a wide disparity among the locations generally.

In this study, an attempt has been made to propose a general descriptive and easy to classify environmental surface and underground water samples based on their EC values (µS/cm) as follows: EC ≤ 200, very low; 200 < EC ≤ 300, low; 300 < EC ≤ 500, moderately low; 500 < EC ≤ 700, minimally high; 700 < EC ≤ 1000, high; and EC > 1000, very high. On this basis, water samples from Parakin and Eleyele with respective EC values (µS/cm) of 130 ± 3 and 155 ± 1 had low EC values, and hence, low dissolved inorganic salt levels. Water samples from Ondo road (EC 220 ± 1 µS/cm), Opa (EC 240 ± 2 µS/cm), Our Lady (EC 250 ± 2 µS/cm), Ajebandele (EC 290 ± 3 µS/cm) and Oke-Ogbo (EC 295 ± 2 µS/cm) can be classified as having EC and dissolved inorganic salts values to be low while samples from Ife-City (EC 375 ± 4 µS/cm) and Arubidi (EC 680 ± 5 µS/cm) had moderately low and minimally high EC and dissolved inorganic salt values respectively. Only water samples from Sabo (EC 865 ± 4 µS/cm) could be said to have a high EC and possibly high dissolved inorganic salt levels. All the samples, however, had EC values less than the 1200 µS/cm set by the World Health Organization (WHO, 2008) or the 1000 µS/cm set by the Standard Organisation of Nigeria

(SON, 2007). Ions other than the ones determined appeared to have substantially contributed to the EC of the water samples from site to site since the total metal burdens do not appear to correspond to the measured EC values.

The pH values, which give the indication of acidity and alkalinity of the waters, had a mean of 6.02 and ranged from 5.04 at Ondo road to 6.46 at Parakin. With the World Health Organisation (WHO, 2008) acceptable pH range of 6.5 - 9.2 for drinking water, the water samples were generally slightly acidic. In part, this slight acidic nature of the waters could explain the relatively high levels of total and exchangeable metals detected in the water samples since lower pH values favour higher metallic dissolution in the environmental matrices. Based on their pH values, with some treatment, the underground waters in the area are particularly safe for agricultural, recreational and domestic purposes. The mean temperature measured was $27 \pm 0.3^{o}C$. Higher temperature may activate the dissolution of the metals and cause rapid deterioration of other physicochemical parameters of the underground water. In terms of the three physicochemical properties determined, the groundwater of the area under study is potable and safe for human consumption and other domestic applications.

Conclusion

The two month survey with respect to pH, electrical conductivity and temperature values revealed that the groundwater of the area under study is potable and safe for human consumption and other domestic applications. The same could not, however, be said of the total and exchangeable metal levels of the underground waters in which the amounts of Zn, Pb, Cd, Cu and Mn determined in the samples were significantly higher than the World Health Organisation Standard for drinking water. The consumption of the water, without any treatment geared towards its heavy metal level reduction, should be discouraged. Those who solely rely on the untreated underground waters from the study area may sooner or later suffer from several heavy metal-induced toxicity symptoms and repercussion ranging from mild ones such as excessive salivation, nausea, vomiting, diarrhoea with bleeding, abdominal pain, dizziness, headaches, dermatitis, aggressiveness, hallucinations and disturbances of libido to very serious ones such as lung disease; hepatic damage; liver and kidneys failure; “itai-itai” disease; endocrine disruption; mutagenic, carcinogenic and teratogenic effects; circulatory collapse; severe pathological disorder of the central nervous system; reproductive and immune system dysfunction; testicular damage; and pancreatitis.

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Table 1: Geographical locations of the sampling sites

Site	GPS Grid Coordinate		Altitude (m)
	Latitude (°N)	Longitude (°E)	
Arubidi	007°28.252′	004°33.449′	290
Eleyele	007° 29.800′	004°32.781′	275
Ajebandele	007°29.689′	004°29.859′	244
Oke-Ogbo	007°27.907′	004°34.353′	294
Our Lady	007°28.769′	004°32.198′	264
Ondo Road	007°27.318′	004°33.347′	308
Sabo	007°29.521′	004°33.337′	282
Parakin	007°29.545′	004°32.217′	273
Ife-City	007°30.544′	004°34.709′	279
Opa	007°31.603′	004°34.592′	277

Table 2: Values of recovery analysis and calibration curve

Metal species	Amount spiked	Amount measured*	% Recovery	Calibration curve, r^2
Zn^{2+}	50	42.36 ± 2.56	84.72	0.9856
Pb^{2+}	50	48.92 ± 3.01	97.84	0.9889
Cd^{2+}	50	41.89 ± 2.71	83.78	0.9975
Cu^{2+}	50	46.44 ± 1.53	92.88	0.9987
Mn^{2+}	50	49.01 ± 3.72	98.02	0.9931

*Values are mean of triplicate analysis ± s.d.

Table 3: Mean total metal levels (µg/mL) present in the water samples for two months

	Elements					
Sampling	**Zn**	**Pb**	**Cd**	**Cu**	**Mn**	**Total metal burden**
Arubidi	35.41±2.25	0.19±0.00	0.10±0.01	9.17±0.03	89.01±0.13	133.88
Eleyele	37.82±1.01	0.21±0.02	0.11±0.00	9.76±0.04	98.57±0.92	146.47
Ajebandele	27.56±1.15	0.14±0.01	0.08±0.02	7.19±0.01	61.99±0.56	96.96
Oke-Ogbo	30.18±2.07	0.16±0.00	0.09±0.01	7.86±0.09	70.52±0.21	108.81
Our Lady	36.43±2.11	0.25±0.02	0.10±0.00	9.42±0.11	93.02±1.07	139.22
Ondo Rd	29.25±1.92	0.15±0.01	0.08±0.01	7.62±0.12	67.49±0.35	104.59
Sabo	28.29±0.54	0.15±0.03	0.08±0.01	7.38±0.08	64.65±2.39	100.55
Parakin	32.14±0.87	0.17±0.01	0.09±0.02	8.35±0.06	77.19±0.42	117.94
Ife-City	28.95±1.46	0.15±0.00	0.08±0.00	7.55±0.13	66.29±0.53	103.02
Opa	32.56±2.10	0.24±0.02	0.09±0.01	8.45±0.05	79.17±1.71	120.51
Range	**27.56-37.82**	**0.14-0.25**	**0.08-0.11**	**7.19-9.76**	**61.99-98.57**	**96.96-146.47**
Mean ± s.d.	**31.86 ± 3.64**	**0.18 ± 0.04**	**0.09 ± 0.01**	**8.28 ± 0.91**	**76.79 ± 12.89**	**117.20 ± 17.48**
CV	**11.42**	**22.22**	**11.11**	**10.34**	**16.79**	**14.91**
WHO*	**3**	**0.01**	**0.003**	**2**	**0.4**	

*World Health Organisation (WHO, 2008) Guideline Limit for drinking water.

Table 4: Mean levels (µg/mL) of the exchangeable metals in the sample for two months

Sampling Site	Zn	Pb	Cd	Cu	Mn
Eleyele	5.11±0.06	0.04±0.01	0.02±0.00	1.30±0.01	15.65±0.21
Ajebandele	4.72±0.09	0.04±0.00	0.01±0.00	1.21±0.03	13.87±0.22
Oke-Ogbo	6.45±0.01	0.05±0.01	0.02±0.01	1.61±0.07	22.92±0.32
Our Lady	5.23±0.02	0.06±0.01	0.02±0.00	1.32±0.05	16.17±0.16
Ondo Rd	6.18±0.02	0.04±0.00	0.02±0.00	1.55±0.04	21.26±0.21
Sabo	6.12±0.09	0.03±0.00	0.02±0.01	1.53±0.12	21.08±0.42
Parakin	6.18±0.10	0.03±0.00	0.02±0.00	1.58±0.08	21.27±0.12
Ife-City	6.04±0.06	0.04±0.01	0.02±0.00	1.53±0.13	20.56±0.36
Opa	8.15±0.05	0.05±0.01	0.02±0.00	1.98±0.21	33.99±0.26
Range	**4.72-8.15**	**0.03-0.06**	**0.01-0.02**	**1.21-1.61**	**13.87-33.99**
Mean±s.d.	**5.91 ± 1.00**	**0.04 ± 0.01**	**0.02±0.00**	**1.48 ± 0.23**	**20.15 ± 5.85**
WHO*	**3.00**	**0.01**	**0.003**	**2.00**	**0.4**

*World Health Organisation (WHO, 2008) Guideline Limit for drinking water.

Table 5: Mean physicochemical properties of the groundwater samples for two months

Sampling Site	Conductivity (µS/cm)	pH	Temperature (^{0}C)
Arubidi	680±5	6.25±0.21	27.5±0.3
Eleyele	155±1	6.09±0.25	27.7±0.2
Ajebandele	290±3	6.35±0.51	27.0±0.1
Oke-Ogbo	295±2	6.43±0.23	28.0±0.0
Our Lady	250±2	5.89±0.15	27.5±0.1
Ondo Rd	220±1	5.04±0.78	27.5±0.1
Sabo	865±4	6.10±0.39	27.4±0.2
Parakin	130±3	6.46±0.58	27.3±0.1
Ife-City	375±4	5.12±0.29	27.7±0.3
Opa	240±2	6.44±0.59	27.3±0.1
Mean	**350±237**	**6.02 ± 0.53**	**27.5 ± 0.3**
Range	**130-865**	**5.04-6.46**	**27.0-28.0**
WHO*	**1200**	**6.5 – 9.2**	**–**

*World Health Organisation (WHO, 2008) Guideline Limit for drinking water.

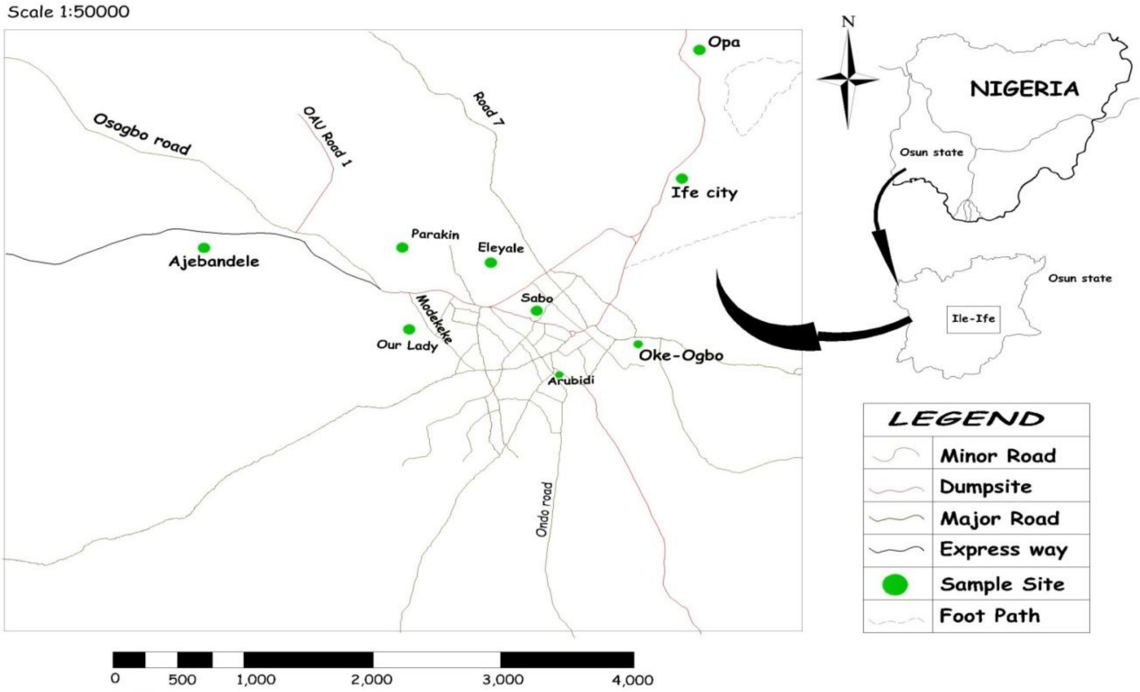

Figure 1: Map of the study area showing sample locations

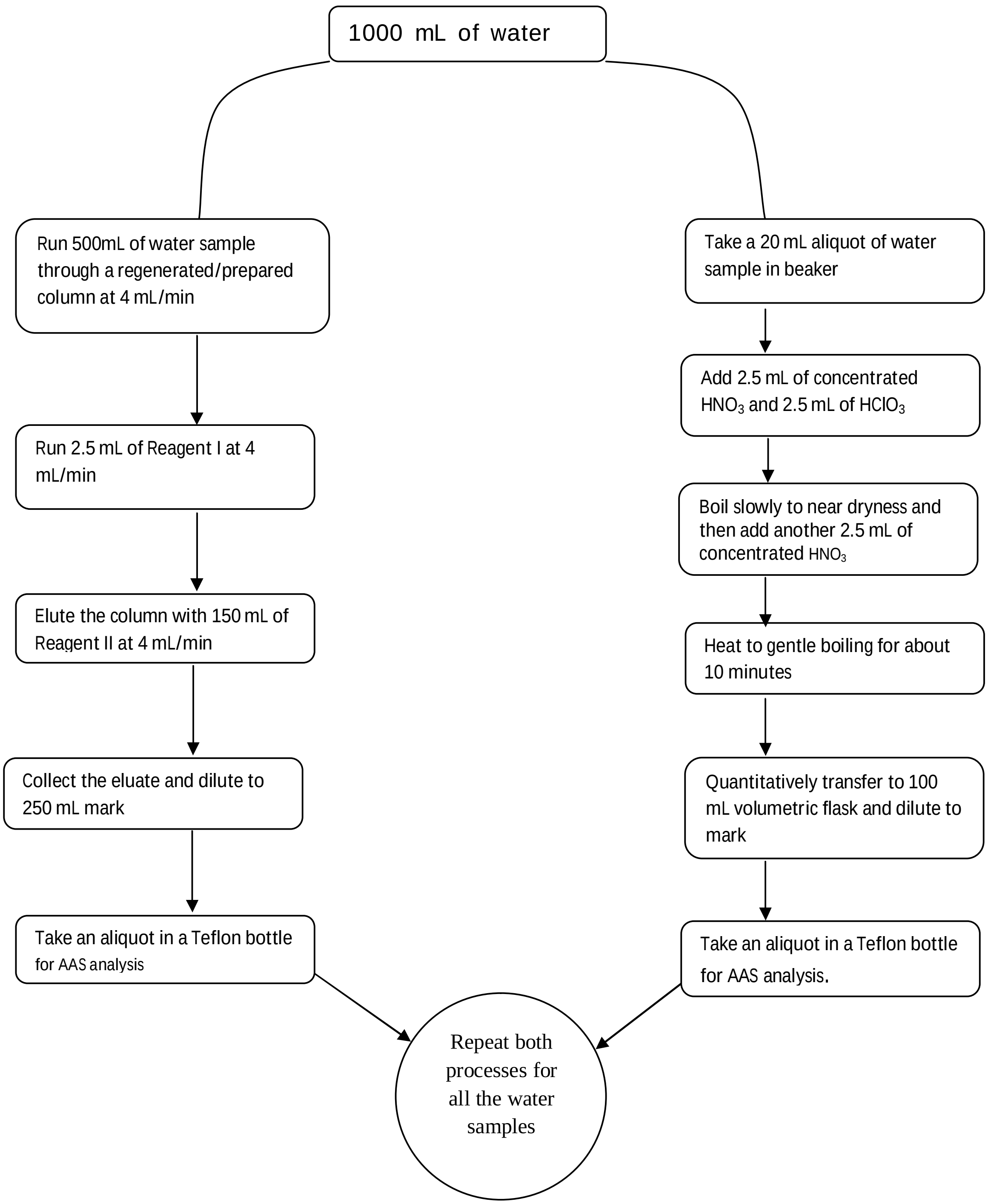

Figure 2: The flow scheme of ion-exchange extraction and digestion procedure (modified from Tokalioğlu *et al.*, 2000).