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ASSESSMENT OF HEAVY METALS IN GROUNDWATER IN APAPA AREA OF LAGOS STATE

OLAYEMI SOLADOYE
Department of Geography & Planning, Lagos State University,
P.M.B. 001, LASU, Ojo, Lagos, Nigeria
Email: soladoyeo@yahoo.com

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DOSUMU, ADEBIMPE SEYI
Centre for Environment Studies & Sustainable Development,
Lagos State University,
P.M.B. 001, LASU, Ojo, Lagos, Nigeria
Email: dosumuadebimpe@gmail.com

ABSTRACT
Assessment of heavy metals in groundwater located around petroleum depot in Apapa area has been done using Absorption Spectrophotometry (AAS) technique. Water samples collected were analyzed for copper (Cu), manganese (Mg), lead (Pb), chromium (Cr), nickel (Ni), zinc (Zn), and cadmium (Cd). The overall mean concentrations (range) of 0.058mg/l (0.002-0.169mg/l), 0.275mg/l (0.011-1.634mg/l), 0.050mg/l(0.005-0.134mg/l) were obtained for Cu, Mg, and Zn respectively in the study area and values of 0.082mg/l, 0.153mg/l and 0.181mg/l was recorded for Cu, Mg and Zn respectively from the control area. The levels of Cu and Zn in the water samples of both the study and the control area were observed to be below the prescribed limit set by regulatory bodies. Pb, Cr, Ni and Cd were absent in all the water samples from the study and the control area. It was observed that Manganese (Mn) concentrations in 18 water samples in the study area were significantly above the recommended limit. The source of Mn contamination could be from anthropogenic activities such as loading and offloading of petroleum products. This pollution of groundwater in this vicinity caused by Mg contamination is a potential threat to the people living in the area as groundwater is their major source of potable water. Therefore, treatment of water in the study locations prior to its use for drinking and domestic purposes is recommended. The outcome of this study suggests the need for further research in the area.

KEYWORDS: Heavy metals, Groundwater, petroleum products, contamination, water standards

1.1 INTRODUCTION
Heavy metals are metallic elements with high atomic weight and density. Such metals amount to over 20 metals which exist in a positively charged form and binds to negatively-charged organic molecules. They are not degradable nor can they be destroyed. Heavy metals are toxic and can be found in the air, soil and water. Examples of these metals include Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, Nickel and Silver.

The presence of heavy metal in water is an indication of global industrialization attributed to large scale of inappropriate disposal and untreated of wastewater containing heavy metal from anthropogenic sources (United Nations Commission on Sustainable Development, 2010). As heavy metals bio-accumulate over a period of time, the concentration become apparent and measureable. Through food chains and trophic levels, heavy metal bioaccumulation within target organ or tissue of organisms can ultimately threaten human health. Humans are exposed to these metals by ingestion or inhalation (Martin and Griswold, 2009). The source of the metals may natural since it can be leached from rocks and soils. It can also come from anthropogenic sources, as a result of human domestic and industrial activities. The increasing trend in industrial activities has intensified environmental pollution problems and led to the deterioration of several aquatic ecosystems wich consequently lead to the accumulation of metals in biota and flora.

Groundwater being an important source of drinking water by man makes up a larger percentage of the available fresh water resources and it is an important reserve of good quality water. However, it is extensively exploited through the construction of boreholes and hand dug wells in urban and semi urban areas for domestic, agricultural and industrial usage. In many areas, such boreholes and hand-dug wells are situated in environments that permit the inflow of pollutants and contaminants into groundwater aquifers. Thus, groundwater can be prone to heavy metal contamination.

As explained by Akhilesh *et al* (2009) and Musa *et al*, (2013), groundwater pollution is a gradual degradation in water quality through the addition of chemicals, heat or bacteria to a level that constitute public health hazards, and affects it adversely in terms of domestic, agricultural and industrial utilization. The quality of the water is the concern of the world as there is tendency of pollution of groundwater as a result of leaching of heavy metals generated due to rapid industrialization and urbanization. Heavy metal pollution has become a concern of both the general public and the scientific community in the light of the evidence of their toxicity to human and biological systems (Anazwa *et* al 2004). The gradual increase in the concentration of heavy metals such as copper, cadmium, lead, mercury, nickel, chromium, etc. is detrimental to humans and animals. They tend to accumulate, bio-accumulate and bio-magnify in body systems.

Studies have shown that industrial and agricultural activities are the major anthropogenic sources of pollutants in the environments through effluent discharge without prior treatment. Included as one of the anthropogenic sources of heavy metals are facilities where fossil fuels such as petroleum, diesel and kerosene are exploited, stored and dispensed for wider use. Various potentially toxic elements such as heavy metals are present in crude oil and elevated concentrations of these compounds are known to affect groundwater (Mac Grath 1994). Pollution from these sources emanates from two major routes, releases of the hydrocarbons into the atmosphere from combustion processes and direct spill of the hydrocarbon into the environment.

One of the major anthropogenic sources of heavy metal enrichment in Nigeria is the frequent spills of crude oil on land and gas flaring (Idodo-Umeh and Ogbeibu 2010). Major crude oil spillage has adversely affected inorganic levels of soils and underground water. Nigeria is one of the major crude oil producing countries in the world where petroleum products are transported via pipe lines to oil depots in different parts of the country from where it is further distributed by motor tankers to end users (Ogoko, 2014). While oil has accounted for over 90 per cent of Nigeria's foreign exchange earnings over the years, local consumption in Lagos accounts for about 60 percent of total gasoline consumption in the country.

An oil depot has been defined by Babatunde and Oyewale (2014) as an industrial facility for storing oil and/or petrochemical products where these products are transported to end users or for further storage. The environment is contaminated with heavy metals through blowouts, accidental spills and leakages from tanks and tanker trucks during loading and offloading in the depots, as well as washing of oil storage tanks (Majolagbe, 2011) and deliberate discharge of effluents by refineries. All these discharge arising from activities in depot significantly contaminate soils and pollute both surface and groundwater through leaching or infiltration. As a result, it constitutes serious health and environmental hazards to humans and aquatic resources living in the area. Also heavy metals are emitted through the abrasion of tires (Cu, Zn, Cd) and brake pads (Sb, Cu), corrosion (V, Fe, Ni, Cu, Zn, Cd), lubricating oils (V, Cu, Zn, Cd, Pb) (Pacyna and Pacyna, 2001) which occur on a daily basis in these petroleum depots.

The aim of the study is to examine the level of heavy metals in the groundwater around petroleum depots in the Apapa area of Lagos State. The study was focused on Apapa being an area where many oil pipelines and tanks are concentrated within a relatively small area of Lagos. The physico-chemical parameters of groundwater were considered and compared with acceptable international standards. The result of this research work would be useful in determining whether there should be concerns of heavy metal poisoning in other areas outside the oil-producing Niger delta zone. The study attempts to investigate the vulnerability of areas of heavy storage and consumption of crude oil products as is the case of Lagos where there are ageing tanks and pipelines.

2.0 MATERIALS AND METHODS

2.1 Study Area

Lagos is a coastal city which lies on the Atlantic coast of the Gulf of Guinea. It is located west of the Niger River delta on longitude 3° 24' E and latitude 6° 27' N. As a result of its coastal location, the area is an extensive low-lying area which serves as an outlet to the sea for many rivers and streams. The area is thus characterized by massive surface water bodies including lagoons, creeks and swamps. The rivers flowing to the sea form swampy lagoons like the Lagos Lagoon behind long coastal sand spits or sand bars. The Badagry Creek flows parallel to the coast for some distance before finding an exit through the sand bars to the sea. Featuring also are two islands which are separated from the mainland by a channel draining the lagoon into the Atlantic Ocean. It is on this unique physical landscape that the Lagos megacity lies. A fast growing city with a population of 9,113,605 in 2006 with a 2016 projection of 12,550,600 (NPC, 2016), Lagos is characterized by extensive urban development. The city serves as an administrative, commercial and industrial center with a population growth rate of 600,000 per annum and density of 4,193 persons per sq. km.

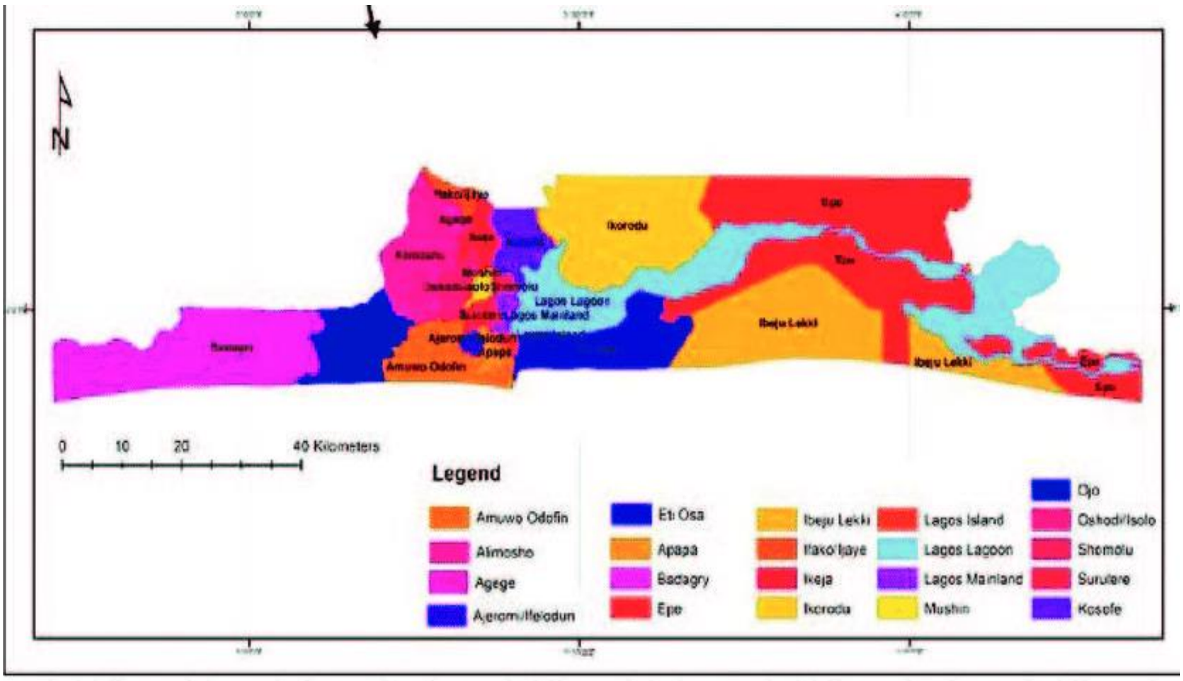

Figure 1: Map of the study area

The study area, Apapa Local Government Area (LGA) is one of the 20 LGAs into which Lagos state is divided for administrative purposes. It lies between latitude $6^0$22'N and $6^0$24'N and longitude $3^0$20'E and $3^0$40'E. It is bounded to the north by Lagos Mainland and to the west by Ajeromi-Ifelodun Local Government Areas. It is surrounded in the east and south by the Lagos lagoon and Atlantic Ocean. According to the Lagos Bureau of Statistics (2011), Apapa LGA has a total area of 38.5km^2 but 13km^2 is water. The area is a hub of socio-economic activities because of the large number of industries and population.

2.2 Sampling Procedure

A total of 60 water samples were collected from 30 sampling points (2 samples from each sampling points for precision purpose) around different petroleum depots and major filling stations in Apapa area. Samples were collected from both boreholes and hand dug wells, out of the 30 locations, 29 was done at the vicinity of the study area. A control sample was collected at the last location (location 30) (a residential area) in Surulere area of Lagos state far from the study area. All water samples were collected in fresh sample containers (polyethylene plastic bottles). The sample containers were first washed three times with each water sample before collection and container were tightly covered immediately and labelled appropriately for laboratory analysis. A GPS GARMIN etrex10 devise was used to get the coordinates of the sampling points while a Bluelab combo meter was used to determine physicochemical parameters. Sampling was carried out in October, 2020.

2.3 Water analysis

Collected water samples were analyzed and parameters such as the pH, Conductivity, temperature and Total dissolved solid (TDS) were measured in-situ using potable (handheld) Blue-lab combo meter. All the samples were kept in the refrigerator at 4^0c and packed in ice inside a cooler the next day while being transported to SMO Laboratory Services in Ibadan for the heavy metal analysis. The water extracts were analysed for heavy metals (Copper, Manganese, Lead, Chromium, Nickel, Zinc and Cadmium) by Atomic Absorption Spectrophotometry (AAS). Duplicate samples were also analysed and the mean values recorded.

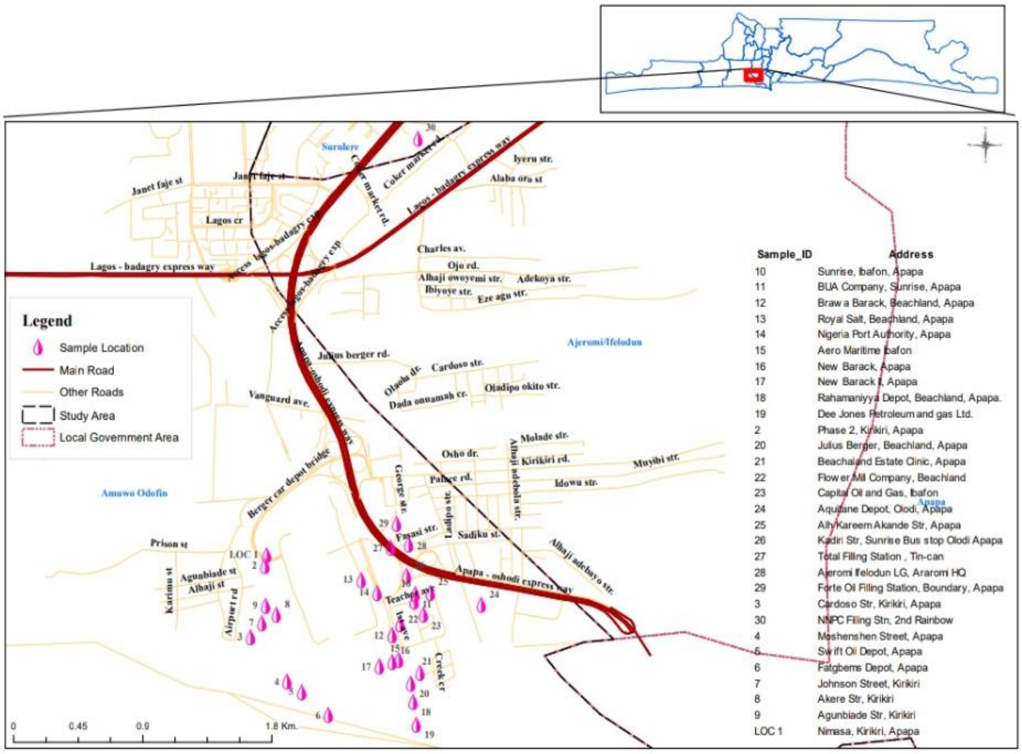

Figure 2: Map of the study area showing the sampling points

3.0 RESULTS AND DISCUSSION

The study assessed the concentration of Copper (Cu), Manganese (Mn) , Lead (Pb), Chromium (Cr), Nickel (Ni), Zinc (Zn), and Cadmium (Cd) from boreholes and hand dug wells used for drinking and other domestic chores around Petroleum Depots. Physical parameters were also assessed and recorded. Table 1 shows that the pH of the samples ranges from 6.01-7.75. This range is slightly higher compared to 3.84-7.72 and 5.8-6.9 reported for groundwater in the eastern parts of Niger Delta in Nigeria (Nwankwoala and Udom, 2011) and some areas of Bayelsa State in Nigeria (Okingbo and Douglas, 2013) respectively. However, not all the samples were within the WHO and NIS permissible limit of 6.5-8.5. The pH of water samples at location 6 (Fatgbems Depot), location 10 (Sunrise, Ibafon, Apapa), location18 (Rahamaniyya Depot, Beachland, Apapa) and location.

TABLE 1: Results of physicochemical parameter

LOCATION	ELEVATION (m)	pH	TEMP (^{0}C)	TDS (ppm)	CONDUCTIVITY
1	28	6.89	31	70	0.1
2	19	6.66	30	200	0.0
3	7	6.90	30.1	60	0.1
4	1	7.08	30	50	0.0
5	1	6.75	31	180	0.0
6	8	6.31	30.2	80	0.2
7	9	6.88	29	182	0.0
8	10	7.75	28	110	0.2
9	7	7.33	29	100	0.1
10	5	6.01	30	35	0.2
11	7	6.79	31	60	0.1
12	10	6.75	31	55	0.0
13	9	6.92	30	50	0.0
14	5	6.98	30.1	78	0.0
15	2	7.72	30.1	140	0.1
16	7	7.07	31	115	0.3
17	4	6.89	29	100	0.0
18	12	6.23	31	68	0.0
19	9	7.11	29	95	0.1
20	7	6.68	30	70	0.2
21	4	7.32	30	80	0.4
22	10	6.48	30	105	0.1
23	4	6.95	31	140	0.0
24	8	7.12	31.1	270	0.3
25	14	6.76	29	180	0.2
26	9	6.73	29.1	184	0.1
27	4	7.21	30.1	90	0.0
28	9	6.88	30	200	0.1
29	13	6.73	30	110	0.0
30 (CONTROL)	18	6.98	31	170	0.0

22 (Flower Mill Company, Beachland, Apapa) were slightly (weakly) acidic, which is attributed to the discharge of acidic material into the groundwater through effluent discharge from the depots and domestic activities. The temperature of the water ranged from 28^{o}c to 31.1^{0}c (Table 1) and average of 30^{0}C was recorded which falls within the recommended standard (30-32^{o}C) for drinking water quality by WHO (2011). The values of TDS recorded from the water samples in this study ranges from 35-200ppm while conductivity measure ranged from 0.0-0.4.

The mean concentration of heavy metals detected in groundwater in the vicinity of the oil depots are presented in Table 2 and shown graphically in Figure 3. Mean Cu contents in the water samples ranged between 0.002 and 0.169mg/l, the highest value was recorded at location 16 (New Barrack Kirikiri) with an overall mean of 0.058mg/l while that of control area (location 30) (NNPC Filling station 2nd Rainbow, Apapa Express) is 0.082mg/l. Mean Zn contents ranged from 0.005 to 0.134mg/l with an overall mean of 0.05mg/l whereas, 0.181mg/l was recorded at the control area. Pb, Cr, Ni and Cd were not detected from all the water samples analyzed including that of the control area (location 30). The mean concentration of Mg in the water samples has minimum concentration of 0.011mg/l and maximum concentration of 1.634mg/l (recorded at Fatgbems Depot) with an overall mean of 0.275mg/l. These values obtained for Cu and Zn in this study locations and the control area were far below the prescribed limits set by World Health Organization (WHO, 2011) and Nigeria Industrial Standards (NIS, 2007) (Table 3). This observation suggests no anthropogenic input of these metals (Cu and Zn) from the activities in the depot.

Manganese was found to be above 0.5mg/l recommended limits set by WHO (2011) for drinking water in three (3) of the water samples analyzed (locations 6, 10, 27), and fifteen (15) of the water collected (locations 2, 3, 4, 5, 6, 7, 8, 10, 11, 13, 14, 19, 20, 27, and 28) exceeds 0.2mg/l acceptable limit by NIS (2007) for potable water, this suggest that the water is contaminated with manganese metal, This high manganese level in this study area may be attributed to spillage of petroleum products arising from day-to-day activities taking place in this vicinity.

The overall mean value of 0.058mg/l of Cu obtained in this study is far below the overall mean of 3.11mg/l of Cu obtained in groundwater sample by Adewuyi and Olowu (2012) in similar study carried out in Nigeria while their overall mean of 0.052mg/l for Zn is the same as the overall mean obtained for this study. Overall mean of 0.003mg/l was recorded for cadmium in groundwater around battery factory in Ibadan by Dawodu and Ipeaiyeda (2007) while overall mean of 0.00635, 0.0014, 0.45 and 0.042 was recorded for Cu, Cr, Pb and Zn respectively in a work carried out by Peter and Okparaocha (2016) on the assessment of some heavy metals in groundwater in the vicinity of an oil depot. Like in this study, Cadmium was also not detected.
Copper is essential for good health, it deficiency can result into anemia, osteoporosis in infants and children (Fitzgerald, 1989; Dahunsi *et al*. 2014) However, exposure to higher doses can be

TABLE 2: RESULTS SHOWING THE MEAN CONCENTRATION OF HEAVY METALS

S/N	Longitude	Latitude	Elevation (m)	Copper (Mg/L)	Manganese (Mg/L)	Lead (Mg/L)	Chromium (Mg/L)	Nickel (Mg/L)	Zinc (Mg/L)	Cadmium (Mg/L)
1	$6^0$26’42”	$3^0$18’47”	28	0.032	0.187	ND	ND	ND	0.010	ND
2	$6^0$26’39”	$3^0$18’46”	19	0.095	0.211	ND	ND	ND	0.019	ND
3	$6^0$26’24”	$3^0$18’43”	7	0.129	0.241	ND	ND	ND	0.007	ND
4	$6^0$26’14”	$3^0$18’37”	1	0.016	0.286	ND	ND	ND	0.016	ND
5	$6^0$26’12”	$3^0$18’56”	1	0.002	0.340	ND	ND	ND	0.010	ND
6	$6^0$26’05”	$3^0$18’59”	8	0.049	1.634	ND	ND	ND	0.017	ND
7	$6^0$26’27”	$3^0$18’45”	9	0.033	0.316	ND	ND	ND	0.010	ND
8	$6^0$26’29”	$3^0$18’46”	10	0.047	0.324	ND	ND	ND	0.005	ND
9	$6^0$26’31”	$3^0$18’47”	7	0.036	0.036	ND	ND	ND	0.011	ND
10	$6^0$26’33”	$3^0$19’20”	5	0.105	0.823	ND	ND	ND	0.052	ND

11	**6^{0}26’32”**	**3^{0}19’21”**	**7**	**0.056**	**0.202**	**ND**	**ND**	**ND**	**0.050**	**ND**
12	**6^{0}26’24”**	**3^{0}19’15”**	**10**	**0.075**	**0.011**	**ND**	**ND**	**ND**	**0.023**	**ND**
13	**6^{0}26’36”**	**3^{0}19’8”**	**9**	**0.075**	**0.345**	**ND**	**ND**	**ND**	**0.080**	**ND**
14	**6^{0}26’33”**	**3^{0}19’12”**	**5**	**0.087**	**0.277**	**ND**	**ND**	**ND**	**0.030**	**ND**
15	**6^{0}26’19”**	**3^{0}19’17”**	**2**	**0.115**	**0.081**	**ND**	**ND**	**ND**	**0.019**	**ND**
16	**6^{0}26’12”**	**3^{0}19’18”**	**7**	**0.169**	**0.085**	**ND**	**ND**	**ND**	**0.119**	**ND**
17	**6^{0}26’18”**	**3^{0}19’12”**	**4**	**0.063**	**0.074**	**ND**	**ND**	**ND**	**0.134**	**ND**
18	**6^{0}26’10”**	**3^{0}19’20”**	**12**	**0.026**	**0.196**	**ND**	**ND**	**ND**	**0.019**	**ND**
19	**6^{0}26’5”**	**3^{0}19’21”**	**9**	**0.010**	**0.266**	**ND**	**ND**	**ND**	**0.008**	**ND**
20	**6^{0}26’14’**	**3^{0}19’19”**	**7**	**0.029**	**0.227**	**ND**	**ND**	**ND**	**0.010**	**ND**
21	**6^{0}26’16”**	**3^{0}19’21”**	**4**	**0.030**	**0.111**	**ND**	**ND**	**ND**	**0.032**	**ND**
22	**6^{0}26’27”**	**3^{0}19’17’**	**10**	**0.030**	**0.186**	**ND**	**ND**	**ND**	**0.018**	**ND**
23	**6^{0}26’22”**	**3^{0}19’25”**	**4**	**0.033**	**0.134**	**ND**	**ND**	**ND**	**0.116**	**ND**
24	**6^{0}26’24”**	**3^{0}19’38”**	**8**	**0.031**	**0.027**	**ND**	**ND**	**ND**	**0.018**	**ND**
25	**6^{0}26’27”**	**3^{0}19’26”**	**14**	**0.034**	**0.128**	**ND**	**ND**	**ND**	**0.123**	**ND**
26	**6^{0}26’30”**	**3^{0}19’21”**	**9**	**0.066**	**0.136**	**ND**	**ND**	**ND**	**0.129**	**ND**
27	**6^{0}26’43”**	**3^{0}19’15”**	**4**	**0.074**	**0.513**	**ND**	**ND**	**ND**	**0.118**	**ND**
28	**6^{0}26’44”**	**3^{0}19’19”**	**9**	**0.067**	**0.384**	**ND**	**ND**	**ND**	**0.132**	**ND**
29	**6^{0}26’42”**	**3^{0}19’19”**	**13**	**0.068**	**0.187**	**ND**	**ND**	**ND**	**0.115**	**ND**
30	**6^{0}28’13”**	**3^{0}19’20”**	**18**	**0.082**	**0.153**	**ND**	**ND**	**ND**	**0.181**	**ND**

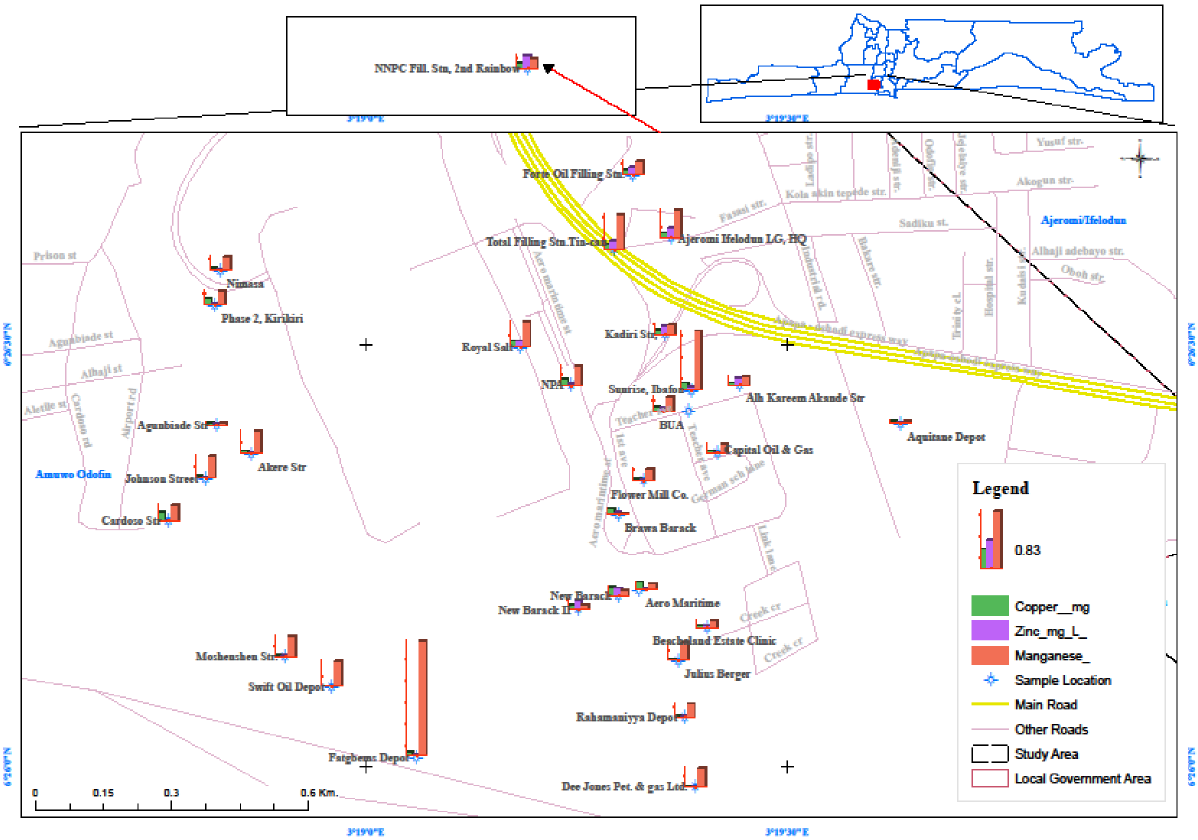

Figure 3: Map showing the concentration of heavy metals detected in each sampling locations

harmful. If drinking water that contain higher than normal levels of copper is ingested, adverse effects like nausea, vomiting, stomach cramps or diarrhea may occur. Manganese deficiency in humans seems to be rare because manganese is present in many common foods (USEPA, 1984, Hurley and Keen, 1987). However, many studies have shown that at high concentration, manganese can be toxic. Exposure to elevated concentration may, however, result in the syndrome known as manganism (Caito and Aschner, 2015).

TABLE 3: Comparison of overall mean heavy metal concentrations with WHO (2011) NIS (2007) acceptable limit for drinking water

	Cu	**Mn**	**Pb**	**Cr**	**Ni**	**Zn**	**Cd**
Mean	0.058	0.275	ND	ND	ND	0.05	ND
Min	0.002	0.011	ND	ND	ND	0.005	ND
Max	0.169	1.634	ND	ND	ND	0.134	ND
SD	0.03363	0.31171	ND	ND	ND	0.05398	ND
WHO	2.00	0.5	0.01	0.05	0.02	3.00	0.03
NIS	1.00	0.2	0.01	0.05	0.02	3.00	0.03

ND = NOT DETECTED. WHO = WORLD HEALTH ORGANISATION. NIS = NIGERIAN INDUSTRIAL STANDARD. SD = STANDARD DEVIATION

Lead is highly toxic and injurious even at a very low concentration, it has no biological importance in the body system. Lead reduces intelligence quotient in children and Lead poisoning in adults can affect the central and peripheral nervous system, the kidney, liver failure, headache, brain damage, loss of memory, gastrointestinal tract, and blood pressure. Zn is required in human system at low level. However, toxicity in human may occur if zinc concentration ingested is high above the recommended standard which can cause fatigue, dizziness, and neutropenia, vomiting, diarrhea, icterus (yellow mucus membrane), bloody urine, anemia, liver and kidney failure, impairment of growth and reproduction (Duruibe and Ogwuegbu, 2007). Cadmium is highly toxic when consumed at low level. It causes adverse health effects such as kidney damage, bronchitis and Osteomalacia (soft bones). It affects the nervous system, causes damage to DNA and immune system and enhances the development of cancer.

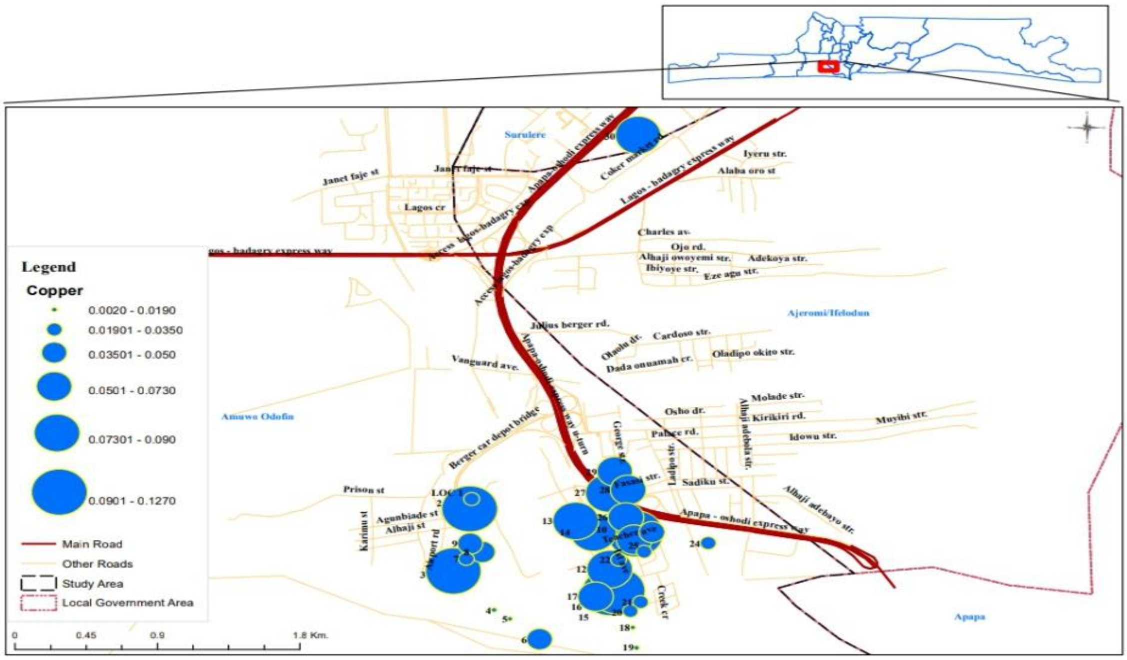

Figure 4: Concentration of Copper in water samples in the study area

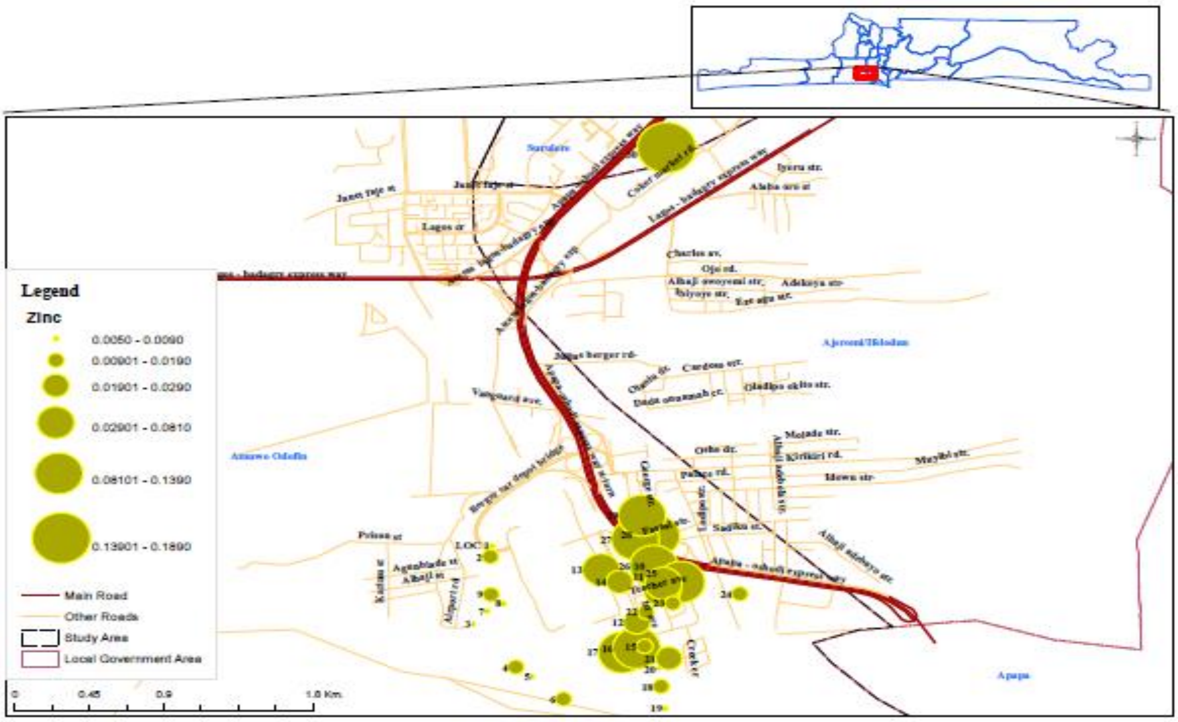

Figure 5: Concentration of Zinc in water samples in the study area

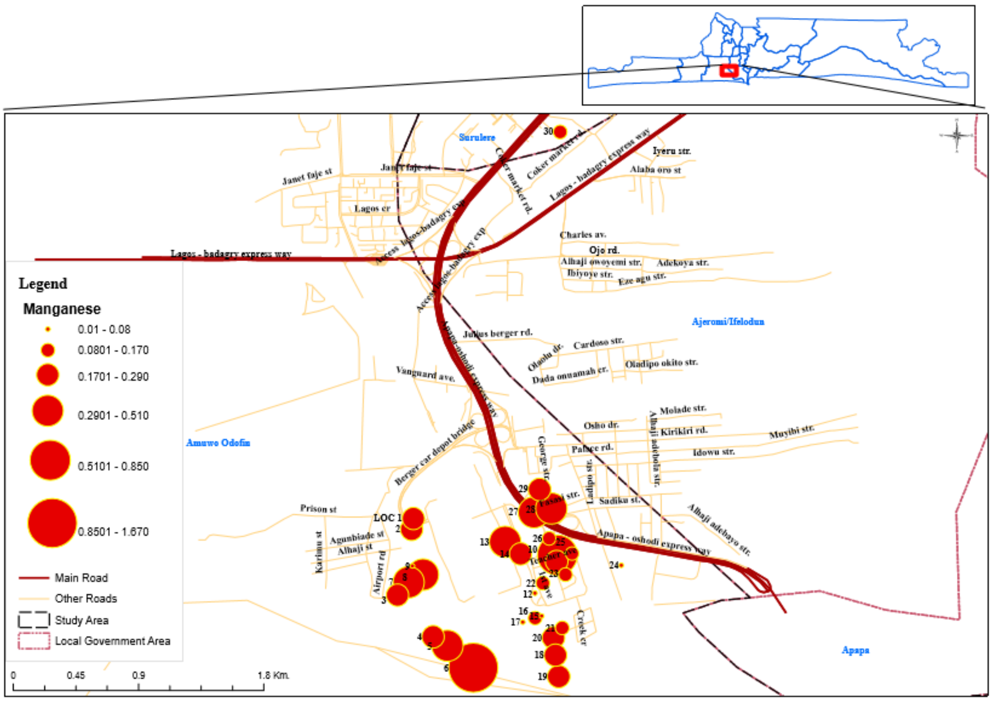

Figure 6: Concentration of Manganese in water samples in the study area

4.0 CONCLUSION AND RECOMMENDATIONS

Toxic heavy metal Pb, Cr, Ni, and Cd were not detected in all water analyzed while Cu and Zn metals investigated were far below the permissible limits of the regulatory bodies. Acidic concentrations of pH along some sampling points also indicated heavy discharge of effluent from various depots activities. The effluents discharged by these petroleum depots and leaking of petroleum products are deposited into the outer drainage/culvert of the depots without being treated. This, in turn, gets into the land and sinks in. It eventually gets into their boreholes and wells. These results show increased concentration of Manganese in almost all the borehole and hand dug well sampled which were above the WHO and NIS maximum limits for potable water which implies that the underground water in the study location is contaminated with manganese metal. The outcome of this study suggests the need for further research in the investigation of heavy metals in the study area. Prior treatment of water in this vicinity before consumption is advised. Also, monitoring, environmental safety and management of these depots are suggested due to the high concentration of this metal pollutants which could be very hazardous to human health when too much doses are bio accumulated.

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