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Assesment of heavy metals contamination in groundwater: A case study of central industrial district in Ilorin, Kwara State, Nigeria

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Heavy metals were investigated in groundwater in the central industrial district of Ilorin, Kwara State, Nigeria. Water and sediment samples from 8 wells in the district and 2 away from the district (control) were analysed to assess the suitability of the water for human consumption and domestication purposes. The measured heavy metals concentrations exceeded the World Heaith Organization (WHO) standard guideline for potable water usage. The result reflects probable pollution from the industrial effluent which are often released into storm water runways without further treatment. Analysis of variance (ANOVA), Pearson correlation and principal component (PCA) analysis were used to describe the data.

Key words: Heavy metals, groundwater, pollution, sediments, x-ray fluorescence (XRF), atomic absorption spectrometer (AAS).

INTRODUCTION

The accumulation of metals in groundwater has direct consequences to man and to the ecosystem. Interest in metals like zinc (Zn) and copper (Cu), which are required for metabolic activity in organisms lies in the narrow "window" between their essentiality and toxicity. Others like aluminium (Al), cadmium (Cd) and lead (Pb) exhibit extreme toxicity even at trace levels (Vanloon and Duffy, 2005). Water is one of the most essentials that supports all forms of plant and animal life (Vanloon and Duffy, 2005) and is obtained generally from two principal natural sources; surface water such as freshwater, lakes, streams, rivers etc and groundwater such as borehole water and well water (Bachmat, 1994; Carter and Fernando, 1979). Only a small fraction (about 2.5%) of earth's water is fresh and suitable for human consumption. About 13% of this fraction is groundwater; an important source of drinking water for many people worldwide (Mandie, 2005). In rural and small communities groundwater serves as the only source of drinking water. In fact, more than 50% of the world population depend on groundwater for domestic use (Marcovecchio et al., 2007).

Heavy metals are priority toxic pollutants that severely limit the beneficial use of water for domestic or industrial applications (Nouri et al., 2006). Groundwater pollution over the years due to contaminant leaking from the disposal sites is a big problem in many countries. Industries such as ceramic, painting, glass, mining and battery and manufacturing are considered the main sources of heavy metals in local water streams, which eventually contaminate groundwater with heavy metals. Landfill leachate site is another source of heavy metal contamination in groundwater (Sang et al., 2008). Increase in human activities such as industrialisation coupled with over population and increase in ambient temperature amongst other factors have become major environmental issues in recent years. Exposure to very low levels of elements such as lead, cadmium and mercury have been shown to have a cumulative effects

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on humans since there is no homeostatic mechanism that can operate to regulate the levels of these toxic substances (Carter and Fernando, 1979).

The quality of water has now become an important topic in all the countries, especially with respect to drinking water. Though water plays an essential role in human life, it has a great potential for transmitting a wide variety of diseases and illnesses. Contaminated water related conditions are cholera, dysentery, typhoid fever, ring worms, skin irritation, and any other illnesses associated with the consumption and use of poor water supplies. This study reports the levels of dissolved trace elements and heavy metals in the ground water system. The catchment area supports a rapidly growing population and there are concerns regarding the water quality of the ground water system. The main uses of water in the catchment area are domestic and agricultural (livestock watering) (Carter and Fernando, 1979). Therefore, the presence of high concentration levels of heavy metals in the environment presents a potential danger to human health due to their extreme toxicity (Fatoki et al., 2012). The objective of this study was to assess the heavy metal concentration in the sediment and selected groundwater samples of Ilorin and its relation to the highly developed industrial activities. The results obtained will establish a baseline data for future reference.

MATERIALS AND METHODS

Description of the study area

Ilorin is situated approximately between latitudes 8.5 (8 30°N) and longitude 4.6 (4 33°E). Ilorin was built as a residential, industrial and agriculture city. The ground water from the wells also serves as a source of drinking water in the study area. The terrain in the study area is generally flat, low lying and riddled with an intricate system of ground water channels. This area is located mainly within wooded savannah and characterized by an average temperature ranges between 30 and 36°C and generally the area is marked by two climatic seasons, the dry and wet seasons with an intervening cold and harmattan from December to January and an annual rainfall range between 1,000 and 1,500 mm. This area is marked by high industrial activities. Figures 1 to 3 show the locations where samples were collected. The sampling sources generally are shallow wells ranging about 3.35 to 5.79 m and not very far from each; other about 100 m and above. There are 10 locations altogether. The depth, well water features for each location are summarised in Table 1.

The objective of sampling is to collect a portion of material, small enough to be transported conveniently and handled in the laboratory while still accurately representing the material being sampled. This implies that the relative proportions or concentrations of all pertinent components will be the same in the samples as in the materials being sampled, and that the sample will be handled in such a way that no significant changes in composition occur before the analysis is carried out (Adeniyi, 2009). Sample labels were used to prevent sample misidentification. These labels carried such information as date and time of collection, place of collection and preservation method. A field logbook was kept in which all information pertinent to a field survey or sampling is recorded. The logbook contains information such as location of sampling point, the purpose of sampling, and method of sample preservation if applicable (Adeniyi, 2009).

The type of container used is of utmost importance. Containers are basically made of plastic or glass, but one material may be preferred over the other; for example, silica and sodium may be leached from glass but not plastic and trace levels of metals sorbs onto the wall of glass containers. For these reasons, samples containing organic compounds were collected in glass bottles, while samples for heavy metal determination were collected in plastic containers.

Preservation of water samples

The sampling bottles (1 L capacity) were washed and rinsed in dilute nitric acid prior to use. The bottles were further pre-treated by rinsing them two or three times with the water being collected. Dilute nitric acid was poured into the sample bottles and the bottles were shaken properly so that the acid will react with the metals and some other particles and the bottles were left over night. They were then poured away the next day and washed with detergent and hot water and rinsed with distilled water so as to get well purified or neutral sample bottles. The bottles were normally filled up. Special precaution were taken for sample containing organic compounds and trace metals because many constituents may be present at microgram per litre (μg/L) concentration levels and these may be partially or totally lost when proper sampling and preservation procedures are not followed. Sample were preserved immediately after sampling by acidifying with concentrated nitric acid (HNO_3) to pH <2 using a few drops of concentrated HNO_3 per litre of sample.

The acidified sample was stored in a refrigerator at approximately 4°C in order to prevent a change in volume due to evaporation, and to make sure that samples with metal concentration of several milligrams per litre are stable for up to 6 months. However, for microgram per litre metal levels, samples were analyzed as soon as possible after sample collection. The water samples for trace metal determination were digested to remove all that could interfere with the analysis by ensuring that the ions are in solution by using a combination of nitric acid and hydrochloric acid, after which they are subjected to atomic absorption spectrophotometry (AAS) analysis. Concentration of manganese, iron, lead, chromium, zinc and copper at the various locations were determined using the atomic absorption spectrophotometer (Model No. 210 VGP).

Reagent and instrumentation

All reagents used were of analytical grade and they were purchased from Sigma Aldrich. pH meter, conductivity meter, atomic absorption spectrophotometer (AAS), and X-Ray fluorescence technique (XRF) were used respectively for the sample analysis.

Pre-treatment of sample bottles

Sample bottles used to collect samples are made up of various materials such as glass, polyethylene and rubber. It was thus necessary to clean them thoroughly so that they do not contaminate water samples. All sample bottles were cleaned before use because they could be made of various materials such as glass, polyethylene, rubber, etc. and therefore care must be taken so that the sample containers does not contaminate the water sample. The following steps were taken in cleaning the sample bottles: hydrochloric acid was poured into the bottle and the bottles were shaken properly so that the acid will react with the metals and some other particles in the bottle, the bottles were left over the night. They were then poured away the next day, washed with detergent
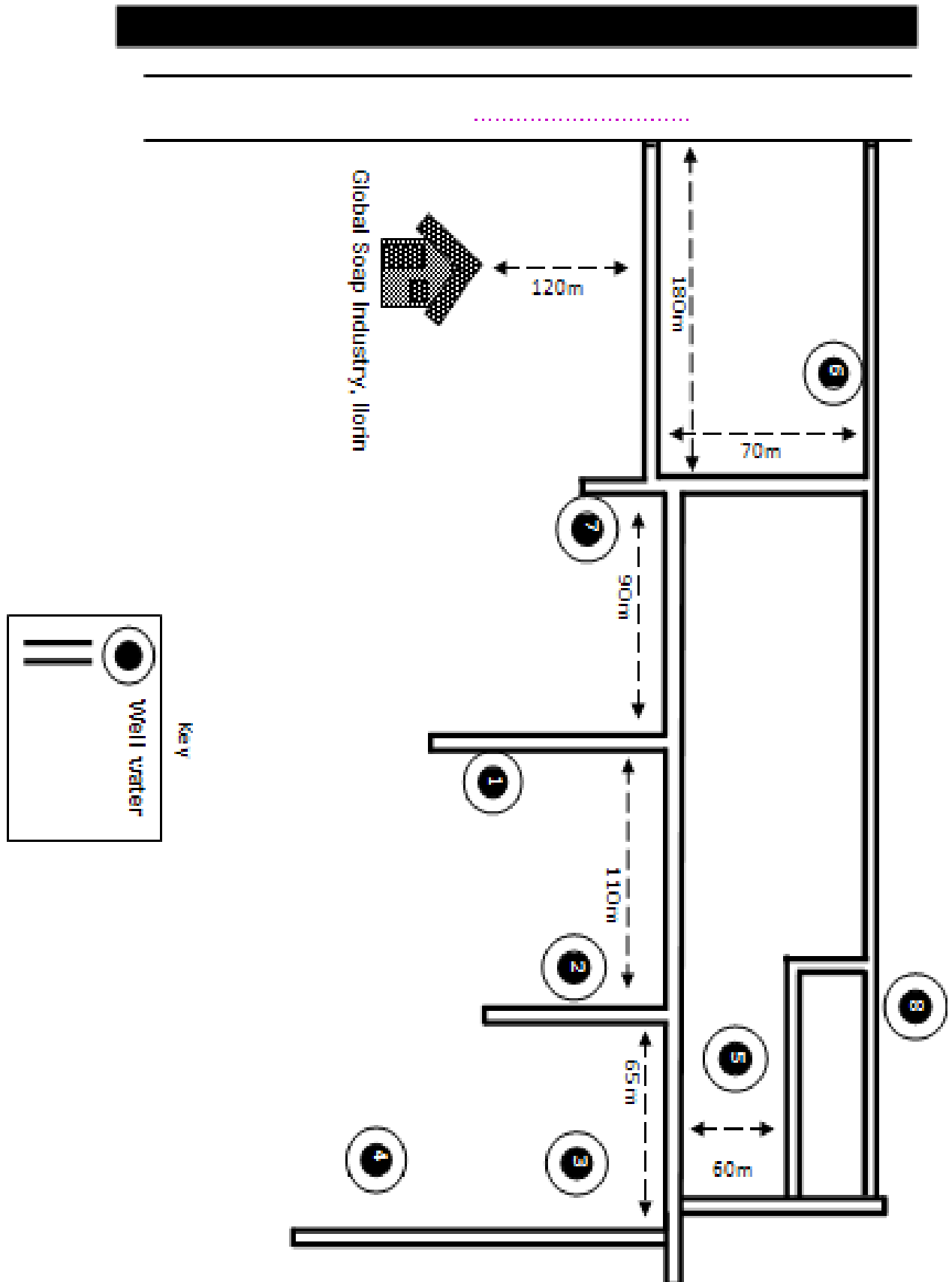
Figure 1. Map indicating the layout of sampling points (Industrial area, Ilorin).
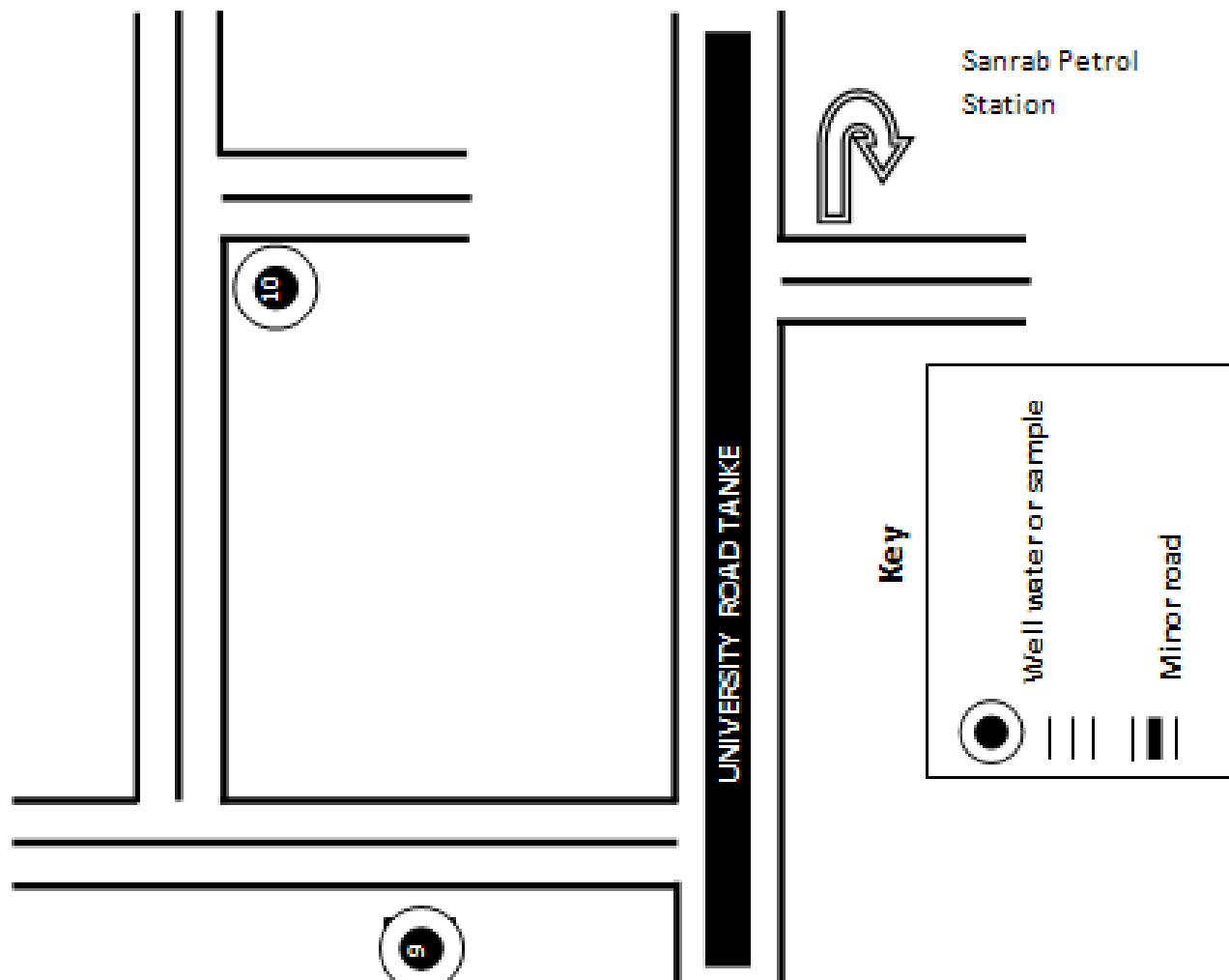
Figure 2. Map indicating the layout of control site (non- industrial area).

thoroughly and rinsed with distilled water. When the sample bottles are ready for use, they are boldly and clearly labelled so that wrong sample will not be poured into the sample bottle.

Collection of water and sediment samples

Each sample container was first rinsed with a small amount of water sample before the sample was collected. Great care was taken in taking water samples for analysis purposes. It is also of great importance that the sample collected for analysis must be representative of the water source and be free of any foreign matter that may be introduced. The different water samples were collected into their appropriate containers and concentrated nitric acid was added to each water sample taken to preserve them till when they are needed. In removing a small portion of the water sample from the sample bottle, it is important that the original bottle must be shaken to ensure that any suspected or precipitated materials are properly represented in the small sample being tested (Nouri et al., 2006).

For the trace metal determination, the sediments were collected using a grab sampler and air-dried in the laboratory to prevent the loss of some volatile component, after which they were sieved to remove stones and other debris prior to digestion for the total metal determination. Composite sampling was employed to have adequate representation of the samples at the locations. The sediment samples were collected from the industrial area of Ilorin. A total of 6 sampling sites not affected by anthropogenic activities were chosen for sampling. The sampling procedure was intended to obtain a representative average sample collected at each site. A total of ten (10) ground water samples were collected from ten groundwater wells twice. Eight of the ten water sample were from the eight sampling point of the industrial area of Ilorin. The other two (2) water samples are taken as control and were sample from non-industrial area of Ilorin a week interval as shown in Figures 1 and 2. The samples were collected from the ground well in washed and rinsed plastic containers. About 1 L of the sample was taken for the analysis.

Digestion of water samples

Briefly, 100 ml of well mixed acid preserved water sample was transferred into a beaker and 5 ml of concentrated nitric acid was added. The beaker was placed on a heater and allowed to evaporate to about 5 ml without boiling. This took about 35 min,
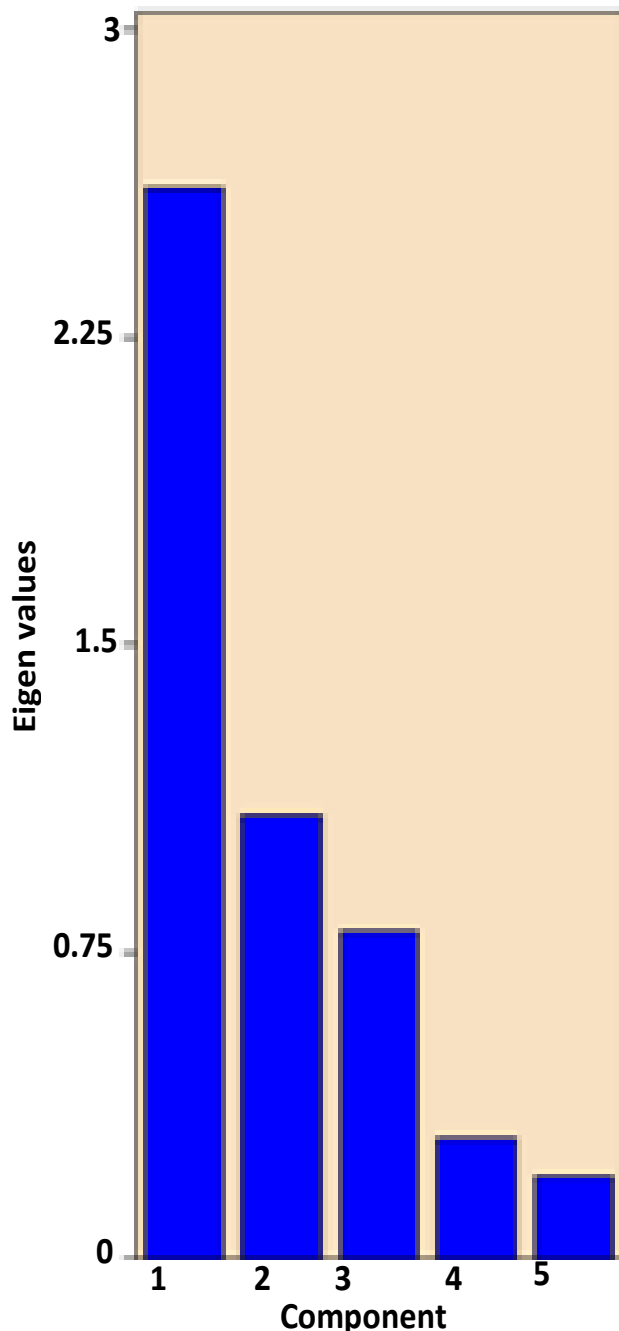
Figure 3. Scree plot showing variation in heavy metals in ground water. Component variations in the heavy metals Eigenvalues are shown in the order Ca > Mg > Fe > Mn >Zn.

after which the beaker was removed from the heater and allowed to cool, and another 5 ml of nitric acid was added to the remaining 5 ml in the beaker and the beaker was covered with a watch glass and place on the heater. The temperature was increased until a gentle reflux action occurs. Heating was continued and more acid was added as necessary until digestion was complete. This was indicated by a light colored residue. Ten milliliter (10 ml) of 1 M HCl and 15 ml of distilled water were added to the residue. The water sample was then filtered in order to remove silicates and other insoluble materials that could clog the atomizer. The filtrate was diluted to 100 ml in a volumetric flask and was ready for analysis. This procedure was conducted for all water samples (Nouri et al., 2006).

Sample preparation for various analyses

All the analytical techniques used in this study had different methods of sample preparation. This is because they all required that the samples be available in such a way that the equipment used could detect. Metals in water were analyzed using AAS, while the sediment samples were analyzed using XRF techniques, respectively. Requirements for determining metals by AAS vary with metal in sediment and water samples. For both XRF and AAS analysis, the sediment and water was digested prior to analysis (Adeniyi, 2009).

Preparation of sample for AAS

Preparation of standard solutions

Standard solutions of metals (100 ppm) were prepared from either the metal or soluble salt of the metal of highest purity (analytical grade reagent available). Metals were dissolved in concentrated HNO_3 and made up to 1 L in a volumetric flask. Different concentrations were prepared from this stock solution for plotting calibration graph for AAS analysis (Adeniyi, 2009).

Preparation of samples for XRF analysis

0.1 g of dried powdered sample was weighed within a range of 0.0995 0.1005 g. This sample was digested in a Teflon digestion bomb using ultra pure HNO_3 and HF. Then 5 ml of the filtered solution was put on a quartz sample carrier and dried under infrared lamp. This was irradiated on carrier with X-rays from a secondary target using Mo-tube excited source 5 part per million (ppm) gas internal standard. Each sample powder was mixed with a flux and transferred into a crucible. Lithium bromide (LiBr) as wetting agent was added at 1050°C for 10 to 12 min. The solidified fused sample was dissolved in 50 ml of 10% ultrapure HNO_3 and shaken. Dissolution was done in a sonicator and a wrist-action shaker.

After complete dissolution, 20 ml of this solution was aspirated into a syringe and filtered through an acrodisc into a clean scintillation vial. The remaining unfiltered solution was saved for additional analysis. The final analyte solution was prepared by pipetting 5 ml aliquot of the filtered solution and diluting it with 35 ml of 10% ultrapure HNO_3. This solution was diluted enough for analysis. A blank solution was prepared using the same procedure.

Statistical analyses

The results were statistically analysed using SAS 9 software (2002). The posteriori ANOVA procedure was performed to determine the variation and significance variations in the dependent variables due to sites with a $P \leq 0.05$ were considered significant. A post-hoc test was then conducted using Scheffe's test for mean comparison. Pearson's correlation was applied to evaluate the relationships between the variables. A correlation with $P \leq 0.05$ was regarded as significant and principal component analysis (PCA) was used to sort sampling sites into groups with similar responses.

RESULTS AND DISCUSSION

For the protection of human health, guidelines for the

Table 1. Description of sampling points.

Location	Sampling depth (m)	Water type	Water feature
Locations 1	5.79	Open well	Slightly muddy and unclear
Locations 2	4.88	Open well	Dirty, bad odour, not muddy and not clear
Locations 3	4.27	Open well	Odourless, little clean, not muddy and slightly clear
Locations 4	4.57	Open well	Unclear water, very muddy
Locations 5	3.35	Open well	Very shallow well, very clean and clear and odourless
Locations 6	3.96	Open well	Very shallow well, very clean and clear and odourless
Locations 7	5.18	Open well	Little foamy well water, slight soapy odour and not clean and clear
Locations 8	5.48	Open well	Odourless, very close to tide road, not very clean and clear

Table 2. Concentration of heavy metals in groundwater collected from eight industrial areas in Ilorin town in Nigeria.

Sites	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Mn (mg/L)	Zn (mg/L)
S1	6.33	0.61	0.05	0.13	0.09
S2	6.21	0.58	0.05	0.11	0.05
S3	14.21	0.62	0.03	0.08	0.33
S4	6.92	0.41	0.06	0.18	0.33
S5	30.45	0.36	0.02	0.18	0.33
S6	30.09	0.20	0.02	0.09	0.23
S7	31.11	0.51	0.06	0.23	0.32
S8	20.65	0.37	0.03	0.48	0.27
Control 1	7.28	0.86	0.99	0.40	0.63
Control 2	5.31	0.73	0.49	0.13	0.37
Mean	6.40	0.52	0.18	0.20	0.26
SD	5.46	0.42	0.47	0.20	0.31
MSD	31.36	2.66	2.58	1.15	2.11
$P \leq 0.05$	NS	NS	NS	NS	NS

****Significance at 95% confidence level; NS, not significant at 95% confidence level; MSD, minimum significant difference.

presence of heavy metals in water have been set by different International Organisations such as United States Environmental Protection Agency (US EPA), World Health Organization (WHO), and the European Union Commission (Marcovecchio et al., 2007). Thus, heavy metals have permissible limits in water as specified by these organisations. The heavy metals in ground water for eight industrial areas in Ilorin town in Nigeria are presented in Table 2. Ca, Mg, Fe, Mn and Zn did not vary significantly in all the sites.

The correlation coefficients for heavy metals in ground water are presented in Table 3. All the heavy metals analysed showed weak correlation of $r < 0.7$, with the correlations between Mg and Ca, Mn and Mg, Zn and Mg and Zn and Fe showing significance at ($P \leq 0.05$). Inverse correlation existed between Fe and Ca and Fe and Mg with $r = -0.1265$ and -0.2107, respectively. Standard two dimension PCA for five heavy metals (Ca, Mg, Fe, Mn and Zn), sites 1 to 8 and two control sites for ground water in Asadam industrial estates of Ilorin city in Nigeria (Figure 4) are plotted on the axes. The distribution of the component concentrations are highly concentrated in site (S3, S8 and Control) in both dimensions and the sites with similar response concentrations are clustered together for are from sites; S1, S2, S4, S5, S6 and S7 respectively.

Calcium

The value of calcium ranged from 5.31 to 31.11 mg/L. This values do not constitute any health hazard as they are within the (WHO, 1998) permissible level of 75 mg/L. Sample site 10 (control) had the lowest mean value of 5.31 mg/L, while sample site 3 had the highest mean value of 31.11 mg/L.

The hardness of water relates to its reaction with soap and to the scale and encrustations which form in boilers and pipes where water is heated and transported. It is attributed to the presence of divalent metallic ions, Ca^{2+} and Mg^{2+} being the most abundant in groundwater. The highest value recorded in location 3 might be due to industrial activities like soap and cement industries located in the area.

Table 3. Correlation coefficient matrix for heavy metals in ground water.

Metal	Ca	Mg	Fe	Mn	Zn
Ca	1.00				
Mg	0.6634	1.00			
	0.0014				
Fe	-0.1265	-0.2107	1.00		
	0.5950	0.3725			
Mn	0.0598	0.4675	0.2753	1.00	
	0.8021	0.0377	0.2401		
Zn	0.4408	0.6157	0.5685	0.4360	1.00
	0.0518	0.003	0.0089	0.0547	

The upper value denotes the correlation coefficient r; the lower value denotes significance level at 95% confidence limit.
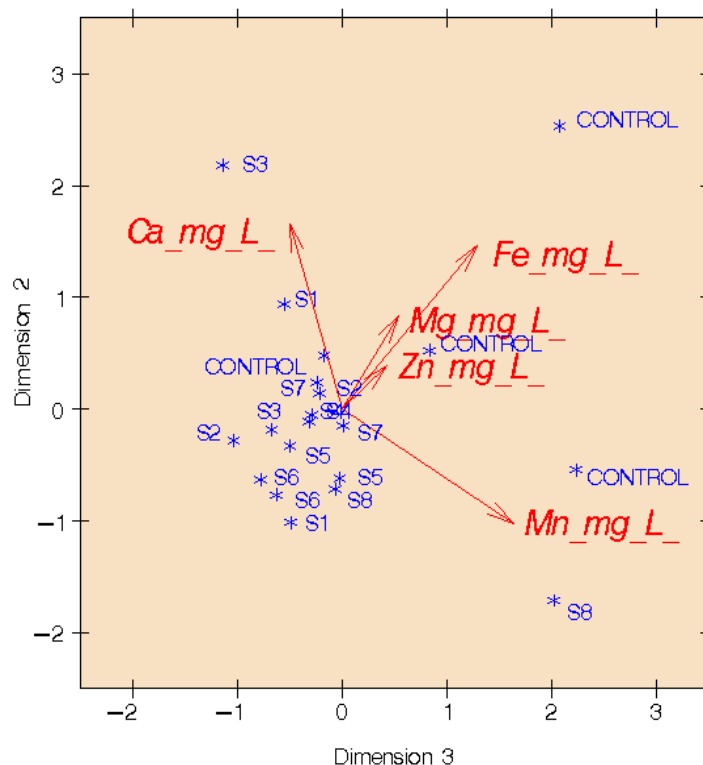

Figure 4. Principal component analysis (PCA) for heavy metals in ground water.

Magnesium

The concentration of magnesium ranged from 0.20 to 0.86 mg/L. Sample site 6 had the lowest mean value and sample site 9 had the highest mean value. Values obtained for magnesium content are within the WHO (1998) acceptable limit of 30 mg/L.

Iron

The value of iron recorded in the study ranged from 0.02 to 0.99 mg/L. Sample sites 9 and 10 had the highest mean value, which was above the permissible value of 0.3 mg/L. Values obtained for other sample sites were below the recommended value. Hence, water of this area

Table 4. Concentration of all the elements in site 1.

Element	Concentration (ppm)	RSD (%)
Ca	8.09	2.35
Fe	9.03	0.44
K	1.98	2.53
Ti	1.25	2.21
Cu	286.00	3.15
Mn	2593.00	2.12
Zn	844.00	2.84
Zr	4605.00	2.17

Table 5. Concentration of all the elements in site 3.

Element	Concentration (ppm)	RSD (%)
Ca	15.78	0.48
Fe	3.37	0.38
Ti	4627.00	1.99
0S	2397.00	6.93
Cu	46.00	8.70
Mn	493.00	2.64
Sr	1096.00	2.37
Zn	192.00	2.60
Zr	580.00	4.83
Cr	2.00	0.00

is safe for drinking. Iron values are objectionable for other domestic purposes and plumbing fixtures. Iron value greater than 0.3 mg/L can damage fabric, paper and corrode the inner walls of high pressure boilers.

Manganese

Manganese level of concentration ranged from 0.08 to 0.48 mg/L, with sample site 8 having the highest mean value and sample site 1 having the lowest mean value. Values obtained were within the WHO (1998) acceptable limit of 0.5 mg/L. Values above the acceptable limit may cause objectionable and tenacious stain to laundry and plumbing fixtures.

Zinc

Zinc mean concentration was within the range of 0.05 to 0.63 mg/L. Sample site 9 had the highest mean value of 0.63 mg/L and sample site 2 had the lowest mean value of 0.05 mg/L.

Values obtained were within the acceptable limit of 15 mg/L, and the presence of zinc could be due to the industrial waste from the industries.

Concentration of heavy metals in sediment samples using XRF techniques

Tables 4 to 9 gave the summary of the results obtained in this study for Ca, Fe, K, Ti, Ni, Cu, Mn, Sr, Zn, Zr and Cr at sites 1, 3, 4, 5, 7 and 9, respectively.

Site 1

The result for sample site 1 shows the presence of eight metals. Ca, Fe, Mn and Zn were found in both the water and sediment sample. Mg, Pb, Cr detected in water sample were absent in the sediment samples. Zn has the highest concentration of 4605 ppm and Ti had the lowest concentration of 124.59 ppm. Ca, Fe, Mn, and Zn exceeded the acceptable limit of (WHO, 1998).

Site 2

The result for sample 2 shows the presence of ten metals. Ca, Fe, Mn, and Zn were found both in water and sediment samples. Zn had the highest concentration of 2.5 ppm and Ti had the lowest concentration of 2 ppm. All available metals detected exceeded the acceptable limit.

Table 6. Concentration of all the elements in site 5.

Element	Concentration (ppm)	RSD (%)
Ca	15.87	0.41
Fe	2.55	0.38
K	2.30	1.38
Ti	3136.00	2.17
Cu	48.00	6.25
Mn	1285.00	1.95
Sr	46.00	6.52
Zn	178.00	3.37
Zr	53.00	7.54

Table 7. Concentration of all the elements in site 7.

Element	Concentration (ppm)	RSD (%)
Ca	13.59	0.71
Fe	2.75	0.57
Ti	4156.00	2.91
S	2.17	0.83
Ni	375.00	4.00
Cu	136.00	5.88
Mn	2201.00	2.32
Sr	573.00	2.79
Zn	591.00	2.70
Zr	212.00	5.66
Cr	172.00	9.30

Table 8. Concentration of all the elements in site 9 (control A).

Element	Concentration (ppm)	RSD (%)
Ca	6669.00	3.48
Fe	14.45	0.25
K	4.23	1.26
Ti	133.00	0.00
Cu	1749.00	0.29
Mn	544.00	5.70
Sr	504.00	6.15
Zn	406.00	3.20
Zr	3265.00	3.06

This may due to the bioaccumulation of toxic heavy metals in the sediment.

Site 3

The result shows the presence of nine metals. Ca, Fe, Mn, and Zn were found in both the water and sediment samples, while Cu, K, Ti, and Sr were found only in sediment. Ti had the highest concentration of 3136 ppm and K had the lowest concentration of 230 ppm.

Site 4

The result shows the highest available heavy metals. Ca, Fe, Zn were found in both the water and sediment sample. Ti had the highest concentration of 4156 ppm

Table 9. Concentration of all the elements in site 10 (control A).

Element	Concentration (ppm)	RSD (%)
Ca	21.73	1.86
Fe	43.75	0.52
K	12.97	2.05
Ti	6.98	2.16
Ni	3320.00	3.01
Cu	1100.00	4.73
Mn	9930.00	1.01
Sr	4222.00	2.37
Zn	4153.00	2.41
Zr	4.23	0.24
Cr	64.00	6.25

and Ca had the lowest concentration of 135 ppm. These did not exceed the acceptable limit.

Site 5

The result of sample 5 shows the presence of nine metals. Ca, Fe, Mn and Zn were present in both the water and sediment samples. The high concentration of Ca (6669 ppm) was due to the nature of the sediment and bioaccumulation of the Ca metal.

Site 6

The result shows the presence of eleven metals. Ca, Fe, Mn, and Zn were found in both water and sediment sample. Mn had the highest concentration of 9930 ppm and Cr had the lowest value of 64 ppm.

Conclusion

In light of the world Health Organization Standard, it can be inferred from the results that the values of different parameters showed pollution of the ground water. The result of the heavy metals and trace elements in the ground water and sediment samples shared the effects of the industrial activities in the area studied. All chemical pollutants in the ground water were within the WHO guide lines except for iron in sample 9 and 10 and also Manganese in sample 8. The use of water obtained from these wells must therefore undergo some measures to limit the possible chemical hazards.

This study highlighted the need for further research, in order to determine the permitted levels of metals in water and sediment samples, as well as to identify areas of potential toxicity and the drinking water quality. The results of values obtained for industrial areas were above the non industrial areas, showing the effects of industrial activities on pollution of environments. Although well regulated in some areas, industry has been the source of many pollutants and contaminants in water. Major industrial activities have the potential of generating air emission, waste water effluents and solid wastes which enter the water body. In view of these findings, there is need to monitor more closely the environment under review and put in place appropriate checks and balances to preserve the health of communities within the vicinity of the industrial areas, particularly as the effects of heavy metals are bio-accumulative and pose great dangers to the health of humans, animals and plants.

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