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Multivariate Analysis of Under Ground Water Pollution Sources in Agbabu Bitumen Belt

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Authors' contributions

This work was carried out in collaboration between all authors. Author ATM designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors IA, OC and AA managed the analyses of the study. Authors YJ and AS managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Multivariate data analysis is used to analyse underground water samples from ten (10) different water sources in Agbabu bituminous belt of Nigeria. Principal component analysis (PCA) showed Component one (PC1) to be the most significant Component accounting for 54.09% of the pollution, with high loadings for Cd, Pb and Mn suggesting them to be the most significant pollutants for the study area. Mean concentrations of heavy metals indicated high pollutions with Cr, Cd and Mn to have highest concentrations and a relatively fairly concentrated Pb. Physicochemical properties were analysed for Alkalinity, dissolved oxygen, biochemical oxygen demand, and phosphates. Using Hierarchical clustering analysis (HCA), similarities in the pollution patterns of the various wells was observed, with Cluster one (CL1) showing similar clustering for

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wells highly polluted with Pb and Cd but low in Fe. Wells in cluster two (CL2) indicate wells highly polluted with Cd. Low polluted wells for Pb, Fe and Cd pollutants are found in Cluster three (CL3). All clusters agree with ANOVA and Pearson's correlation result indicating variation among the various water sources. The cause of underground water pollution showed to be anthropogenic and geogenic in the study area and suggests the underlying bitumen deposit and its mining activity to be majorly responsible for the pollution.

Keywords: Multivariate; heavy metals; bituminous belt; Agbabu.

1. INTRODUCTION

One of the most urgent problems facing us today is the environmental pollution resulting from human activities. The development of industry and agriculture created a number of environmental problems including air and water pollution with their serious effects on human health [1,2]. In general, a strong relationship between contaminated drinking water with heavy metals and the incidence of chronic diseases such as renal failure, liver cirrhosis, hair loss and chronic anemia has been documented [3,4] Ground water occurs almost everywhere beneath the earth surface not only in a single widespread aquifer, but also in thousands of local aquifer systems [5]. Several factors such as climate, characteristics of soil, circulation of ground water through rock types, topography of the area, intrusion of saline water in coastal areas, human activities on the ground etc. posses several effects on the quality of water [6]. Some heavy metals such as Cu, Fe, Mn, Ni and Zn are compulsory micronutrients for flora –fauna and microbes. Besides metal like Cd, Cr and Pb are harmful beyond a certain limit [7]. Therefore the heavy metal concentration in drinking water should be kept in low ppb range. In most resource cities in developing countries such as Agbabu bitumen deposit area in Ondo state, Nigeria, several factors account for the underground water pollution, some which include: some tons of garbage left uncollected on the streets each day, acting as a feeding ground for pests that spread disease, clogging drains and creating a myriad of related health and infrastructural problems [8,9]. Recently Olabemiwo et al*.* [10] reported the statistical analysis of biochemical parameters of study rats fed with simulated bitumen leachates of Agbabu bitumen to have a significant difference of ($p>0.05$) indicating the leachates to be toxic to the health of the rats and in turn humans. It became necessary to assess the water from various well sources to ascertain the levels of pollution. This research intends to carefully study the geo-spacial location of the underground water sources mainly wells, around agbabu community and using multivariate analysis, identify major pollutants and suggest a heavy metal pollution cause based on relationship among well sources.

2. MATERIALS AND METHODS

2.1 Study Area

Agbabu is located on latitude 6° 35' 19" N and longitttude 4° 50' 03" E in Ondo State of Nigeria. Agbabu bitumen belt is made of the main Agbabu, inhabited by about 400 people and other smaller farm settlements such as Mulekangbo, Ilu-binrin and Mile 2 Agbabu village made up of about 300 people. Agbabu bituminous belt sand deposits in south western Nigeria is naturally occurring in a sticky tar-like form. Its geology suggests a large deposit of bitumen and Cretaceous tar sand formations. Agbabu's climate is classified as tropical. This location is classified as Aw by Köppen and Geiger. The average annual temperature is 27.1℃ in Agbabu. The rainfall here averages 1837 mm. The bitumen deposit, put at an estimated 42.74 billion metric tons, is the second largest in the world and was first discovered in 1900 [11]. This is where bitumen was first spotted in Nigeria in 1910 and the first bitumen well MBC-7 was drilled there.

2.2 Sample Collection and Preparation

The water samples were collected in triplicates from thirty (30) different sampling locations cumulated into ten (10) to give a representative sampling at weekly interval for 6 weeks while control samples were collected from non bituminous site in triplicate. All sampling points were fairly distanced apart to give a representative sampling of the entire study area. The underground water sample (500 ml) was collected from each of the sampling points and transported to the laboratory within two hours of collection while samples for physicochemical analysis were collected in clean sterile containers. Samples for dissolved oxygen (DO), biochemical oxygen demand (BOD) were collected in 250 ml bottles and sealed with stoppers. One millimetre each of Winkler's solutions A and B were added to the samples on site to fix the oxygen [12].

2.3 Physicochemical Analysis

2.3.1 Determination of alkalinity

Alkalinity would be measured by test for the presence /absence of Phenolphthalein alkalinity at pH 10. Adding about 25 to 50 ml sample in a conical flask, add 2 to 3 drops of phenolphthalein indicator if it turns pink (pH > 8.3), titrate with 0.02 N H_2SO_4 to disappearance of the colour. Record ml of titrant used.

Phenolphthalein alkalinity,

$$CaCO_3 \text{ mg/l} = \frac{A \, x \, B \times 1000}{ml \ sample} \quad (1)$$

Where:

A = ml titrant used to phenolphthalein end point
N = normality of titrant

2.3.2 Determination of phosphates

This was determined following a method used by taking the 50 ml sample into a 125 ml conical flask, add 1 drop of phenolphthalein indicator. Discharge any red colour by adding 5N H_2SO_4. Add 8 ml combined reagent and mix. Wait for 10 minutes, but no more than 30 minutes and measure absorbance of each sample at 880 nm. Use reagent blank as reference.

Phosphates are then calculated as:

$$PO_4 \text{ in mg/l} = \frac{\text{mg P from the calibration x 1000}}{\text{ml sample}} \quad (2)$$

2.3.3 Determination of Dissolved Oxygen (D.O)

The Dissolved Oxygen (DO) content of the underground water samples was measured using the Winker Method, Prescribed by (AOAC, 1998) this method involves the reaction

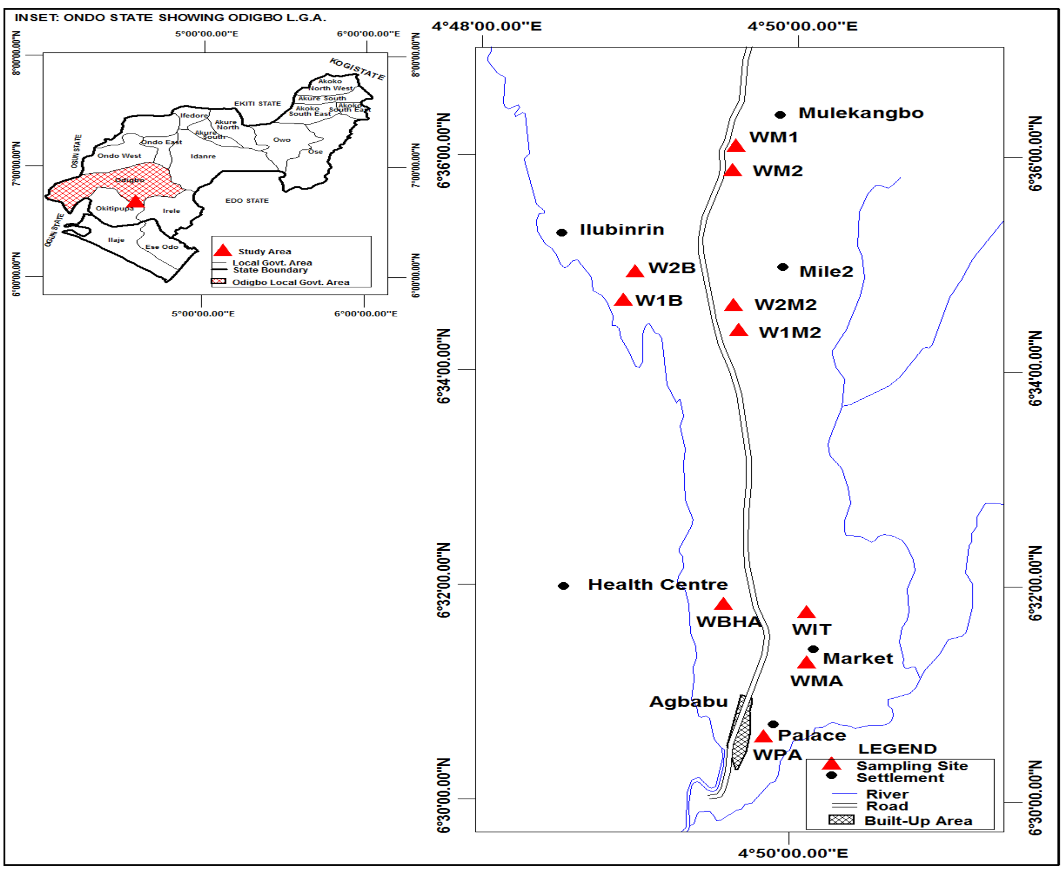

Fig. 1. Map of Agbabu community showing sampling sites

of Manganase sulphate ($MnSO_4$) with Potassium hydroxide (KOH) in alkaline potassium iodide solution to produce manganese precipitate. Dissolved Oxygen is then calculated as:

$$\text{Dissolved Oxygen (mg/l)} = \frac{V \times M}{0.025} \quad (3)$$

Where

V = ml of thiosuphate solution used.
M = molarity of thiosuphate titrant

2.3.4 Determination of Biological Oxygen Demand (B.O.D)

The BOD determination of the underground water samples was carried out using standard methods described by Ademoroti [13]. Samples were incubated for five days at 20℃ in BOD bottles. The dissolved oxygen (DO) content of the samples was determined before and after the incubation. BOD was calculated after the incubation period [13,8].

BOD_5= Dissolved oxygen after incubation period (5 days) - Dissolved oxygen of the first day. (4)

2.4 Preparation of Sample and Metal Analysis

The entire samples for the analysis were acidified at the time of collection with nitric acid in other to bring the pH below 2. Exactly 100 ml of water sample was then transferred into a 200 ml beaker, 5ml of concentrated HNO_3 will be added and digested on a hot plate at 90℃ to 95° C until the volume has been reduced to 15-20 ml [13,14]. The digested samples were transferred to a 50 ml volumetric flask. Distilled water was then added to required mark. Elements of Fe, Cd, Mn, Cr, Ni and Pb were then analysed by direct aspiration via Atomic Absorption Spectrophotometer (AAS).

2.5 Statistical Data Analysis

Statistical analyses were performed with SPSS for windows 7.0 software. Descriptive statistical analysis gave the mean, range and standard deviation of metal concentrations, correlation and analysis of variance (ANOVA) established a relationship among heavy metals and sampled points(wells).in attempt to extract the most important factors responsible for a most of the pollution in the study area. Using Multivariate analysis Data were log-transformed prior to Principal component Analysis (PCA) to reduce the influence of high data [15]. Principal Component Analysis was done using factor extraction with an Eigen value larger than one (1) after varimax rotation.

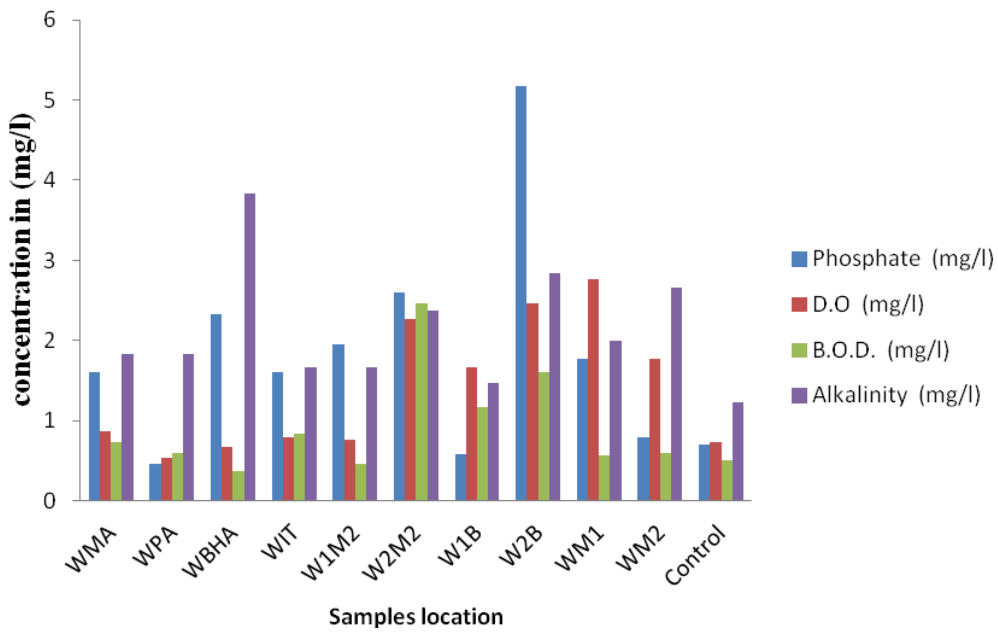

Fig. 2. Physicochemical properties across sites and control

3. RESULTS AND DISCUSSION

The physicochemical properties of the water samples were determined. Water with low alkalinity has little capacity to buffer acidic inputs and is susceptible to acidification (low pH). High amount of Alkalinity also enhance hardness of water. The value of alkalinity in water provides an idea of natural salts present in water. Alkalinity values of the studied wells were within permissible limits. Phosphate, borate and organic acids etc. contribute to water alkalinity; these factors are characteristics of the source of water and natural processes taking place at any given time [16]. The physicochemical of Agbabu bitumen belt could be said to be within acceptable limits hence may not pose a health risk to life and ecosystem. Dissolved Oxygen (DO) is considered the most important parameter for assessing water quality [17]. It regulates the distribution of flora and fauna. Its deficiency has an adverse effect on groundwater as the health of water largely depends on it [16]. Higher values than the control sample were observed for most sample points except for locations WHBA and W2B which recorded low values. The low value of dissolved oxygen is probably due to pollution emanating from underlying hydrocarbon bitumen belt and the mining activities in the area [18,19]. BOD measures the quantity of oxygen consumption by microorganisms during decomposition of organic matter [20]. Though it is not a precise quantitative test, it is widely used as an indicator of organic quality of water. The high BOD may indicate fecal and organic waste contamination from human and animal sources and restricts the use of water for drinking and domestic use. the mean values of BOD were low in all the samples compare with WHO standard of 50.0 mg/l. control sample was however lower than most sample points except for sample W1M2 and WHBA. An increase BOD asserts a potential health threat to the people those who are using the water with high BOD for drinking.

Phosphate ($P0_4^{2-)}$) contents in the samples are on all within the WHO acceptable limits for the drinking water even though higher than the control samples from distant wells. Similar report was observed by Kola et al. (2007) in Latosa of Ondo state, Nigeria. An increase in phosphate levels contribute to algal blooms that deprive fish and other aquatic organisms of oxygen [21]. The accumulation of excess nutrients over a period of time could also lead to eutrophication and the loss of aquatic and other microorganisms in the river.

3.1 Statistical Analysis

Presented in Table 1 are mean metal concentrations in the sampled wells of the study area. Lead (Pb) concentrations in the water sources were in the range of (0.49-0.70 mg/l) giving the results of the concentration at 10 sampled points. The mean concentration of lead was found to be (0.58 mg/l), while the highest value of 0.70 mg/l was recorded in the water samples; this concentration was found in well W_1M_2 located 50 m away from a major road. Cadmium (Cd) and manganese (Mn) also demonstrated fairly high concentrations in the sampled wells, concentration ranges for Cd and Mn were (0.82-1.46 mg/l) and (0.02-1.17 mg/l) respectively, mean concentrations were found as 1.18 mg/l for Cd and 0.75 mg/l for Mn. both Cadmium l and manganese mean concentration were higher than permissible limits for drinking water but lower than those reported by Fagbote and Olanipekun [22]. Chromium (Cr) had its mean concentration at 1.89 mg/l Iron (Fe) had its mean concentration as 0.14 mg/l. Most of the metals exceeded acceptable limits except for Fe indicating its low risk of ever polluting this environment, these high concentrations of all other metals could be worrisome due to their health implications. Lead concentrations were higher than 12ppb reported by Adefemi and Awokunmi [14] for heavy metal assessment in groundwater in Itaogbolu, Ondo State, Nigeria. High lead concentrations could cause serious nervous related ailments or even death due to lead poisoning [23]. Manganese and Iron though essential in body nutrition, is intolerable beyond acceptable limits, Cadmium does not exist in nature as native metal but as Ores, Pollutant cadmium in water may arise from industrial discharges and mining wastes [20]. Its low concentrations in the study area indicates its geogenic source of pollution. High concentrations of Cadmium can cause Kidney disease. Chromium concentrations were higher than 0.4 mg/l reported by Adefemi and Awokunmi [14] for water samples from River Ona and selected hand dug wells in Ita ogbolu area of Ondo State, Nigeria. High concentrations of Cr and its compounds can cause cancers of the stomach and larynx (ATSDR, 2008). Adebiyi et al. [24] carried out an elemental characterization of the Nigerian bitumen by total reflection X-ray fluorescence which showed Fe, Cr and Mn to be part of its components. Trace elements such as transition metals get into bitumen in form of porphyrin complexes in its early stages of formation. Therefore, the only likely lithogenic source of heavy metals at Agbabu environment is its large deposit of bitumen.

Correlation studies indicated a relationship between metals as shown in Table 3. High positive correlation is observed between Mn and Fe showing their pollution may have been from the same source, similar correlations were seen between Pb and Cr, and Pb and Mn. Low positive correlation was observed in the interaction between Cd and Mn. The analysis of variance (ANOVA) carried out is shown in Table 4. And showed no significant difference in concentration of each metal among the sample points but had a significant variation in metal concentrations among the various metals in the sample points. Indicating that the wells have relatively the same concentrations of each metal but the different metals have varying concentrations. This could mean that the wells of the study area had fairly similar concentration of metals and are said to be highly polluted.

3.2 Multivariate Analysis

By using the extraction method of principal component analysis (PCA) to get associations of metals. Principal component analysis was performed by computing the eigenvalues. The loadings having a greater than 0.70 are marked bold in the Table 5. With Component 1(PC1) accounting for 54.09% of the total variance while having high loadings of 0.91, 0.91 and -8.21 for the elements Mn, Cd and Pb respectively. This is shown in Fig. 3. Where Cd and Mn are far to the positive end of component one (PC1) and Pb to the far negative side. These high loadings indicate the metals to be responsible for most of the pollution in the wells of the study area. On the other hand, component 2(PC2) explains about 24.50% of the variance with high loadings of 0.85 for Cd and Fe.

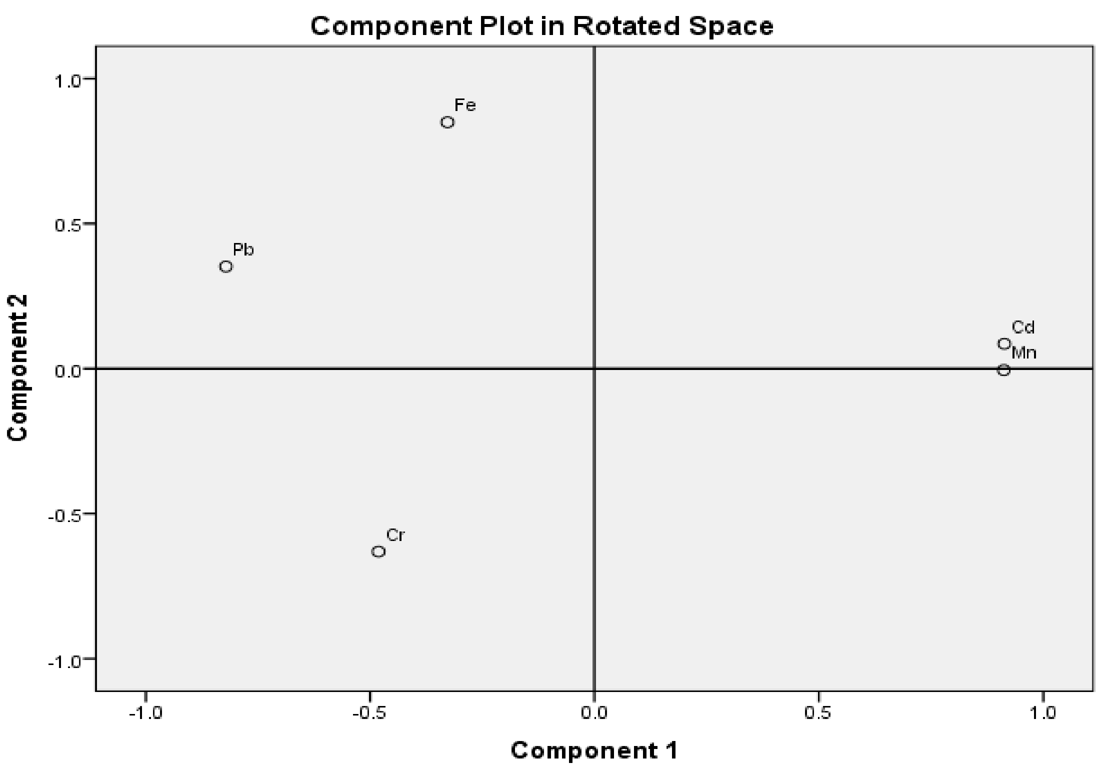

Fig. 3. Component plot for heavy metals

Table 1. Mean concentrations and descriptive statistics of physicochemical parameters for the sampled points

Heavy metals	WMA	WPA	WBHA	WIT	W1M2	W2M2	W1B	W2B	WM1	WM2	Min (mg/l)	Max (mg/l)	Mean (mg/l)	Std. dev	Limits (mg/l)
Alkalinity	1.83	1.83	3.83	1.67	1.67	2.37	1.47	2.83	2.00	2.67	1.47	3.83	2.21	0.72	200
DO	0.87	0.54	0.67	0.80	0.77	2.27	1.67	2.47	2.77	1.77	0.54	2.77	1.46	0.83	5.00
BOD	0.73	0.60	0.37	0.83	0.47	2.47	1.17	1.60	0.57	0.60	0.37	2.47	0.94	0.64	50.0
$PO4^{2-}$	1.60	0.47	2.33	1.61	1.95	2.60	0.58	5.17	1.77	0.80	0.47	5.17	1.89	1.35	0.10

Table 2. Mean concentrations and descriptive statistics of heavy metals for the sampled points

Heavy metals	WMA	WPA	WBHA	WIT	W1M2	W2M2	W1B	W2B	WM1	WM2	Min (mg/l)	Max (mg/l)	Mean (mg/l)	Std. dev	Limits (mg/l)
Pb	0.54	0.55	0.49	0.68	0.70	0.61	0.58	0.54	0.55	0.53	0.49	0.70	0.58	0.07	0.01
Mn	0.51	0.89	0.63	0.02	0.51	0.34	1.12	1.17	1.16	1.13	0.02	1.17	0.75	0.41	0.50
Cr	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.80	1.80	1.90	1.89	0.03	0.05
Cd	1.18	1.16	1.23	0.96	0.91	0.82	1.37	1.38	1.46	1.35	0.82	1.46	1.18	0.22	0.05
Fe	0.02	0.07	0.04	0.49	0.16	0.01	0.08	0.12	0.21	0.20	0.01	0.49	0.14	0.14	0.30

Based on correlation coefficient, relationship between wells given as distances of the variables are given in Fig. 4. A ward linkage dendrogram cluster analysis based on Squared Euclidean distance confirms previous findings, showing great similarities among the various wells based on their location. Three clusters are observed among the wells indicating the different pollutant groups. The individual clusters however showed variations, these are seen for wells in cluster one (CL1) which shows equal clustering for all the wells, W1B and W2B, WM1 and WM2. These wells are highly polluted with Cd and Mn. Both metals were found in component one (PC1) of principal component analysis constituting 54.09% of the pollution. The highest concentrations of Cd and Mn were found in wells; WM1 and W2B respectively and may be the most polluted wells in the study area. Generally the wells in CL1 have average concentrations of Pb and Fe. Cluster two (CL2) has the wells W1M2, W2M2 the wells of this cluster are highly polluted with Pb with the highest concentration found in W1M2. Moderate concentrations of all other metals can be found in these wells. Equal clustering was observed in cluster three (CL3) for the wells W1MA, WBHA and WIT and WPA. These wells have low concentrations of most of the metals except for well WIT which showed a high concentration of Fe. Fair concentrations of Cr are observed for all the wells. This observed clustering of the wells confirm the (P<0.005) Analysis of variance (ANOVA) result which indicated a variation in metal concentrations among the wells stating also that certain wells were more polluted with some metals than others. Generally the wells can be classified as high >moderate > least polluted for the CL1>CL2>CL3 respectively.

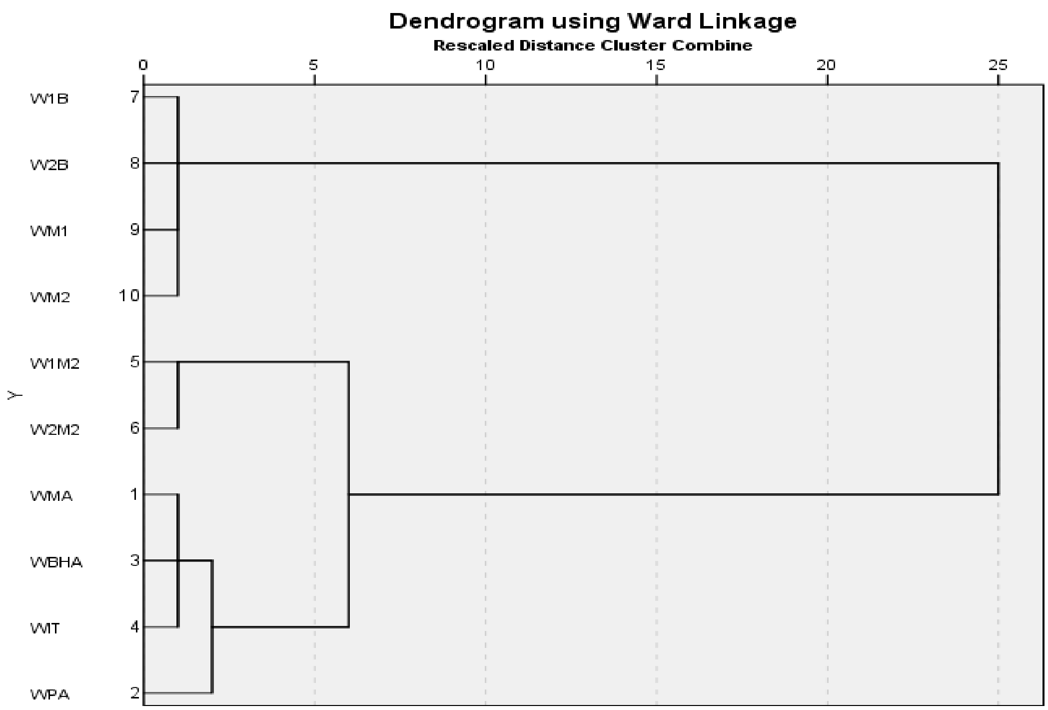

Fig. 4. Hierarchical cluster analysis for wells in Agbabu community

Table 3. Pearson's correlation for heavy metals

	Pb	Cd	Mn	Cr	Fe
Pb	1				
Cd	-.229	1			
Mn	.534*	.436*	1		
Cr	.783**	-.235	-.394	1	
Fe	-.456	-.184	.623**	.340	1

**Correlation is significant at 0.05 levels (2 tailed), ** Correlation is significant at 0.01 levels (2 tailed)*

Table 4. Analysis of variance (ANOVA)

Source of variation	SS	df	MS	F	P-value	F crit
Rows	7.861768	9	0.87353	1.154902	0.352113	2.152607
Columns	20.12295	4	5.030737	6.651185	0.000409	2.633532
Error	27.22921	36	0.756367			
Total	55.21393	49				

Table 5. Principal Component Analysis (PCA) matrix

Factors	PC1	PC2
Cr	-4.81	-0.63
Cd	0.91	0.85
Pb	-8.21	0.35
Mn	0.91	-0.05
Fe	-3.28	0.85
Eigen value	2.70	1.23
% variance	54.09	24.50

4. CONCLUSION

The above results reflect the concentration and location of the major pollutants as found in the various sample sources (Wells) of Agbabu bituminous belt of Nigeria. Physicochemical properties varied with control sites, however, routine monitoring is required especially for the phosphate. Heavy metals however were all above the WHO permissible limits except for Fe. No significant difference could be deduced in each metal concentration among the various sample points but they tend to vary among themselves. Multivariate analysis and classification of sampled water sources (wells) showed certain wells to be more polluted than others especially for the more worrisome high Cd and Mn concentrations which constitute 54.09% of the pollution in the wells of the study area. All the metals were highly polluted in the wells except for Fe. In view of these, the underground water of Agbabu bituminous belt could be said to be highly polluted with heavy metals especially Cd and Mn due to its underlying bitumen deposit and its industrial mining activities. Pollution in the study area is basically geogenic and anthropogenic. Further studies would endeavour to look critically at the wells of Cluster one (CL1) with specific interest on metals of high loadings in Principal Component one (PC1). Perennial Monitoring of water sources in Agbabu Bituminous belt should be carried out to prevent risk of an endemic.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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