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Multivariate Statistical Appraisal of Trace Elements in Shallow Groundwater of Keana Nigeria

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Abstract

The objective of this study was to determine the influence of trace elements in groundwater using multivariate statistical techniques, principal component analysis (PCA) and cluster analysis. Thirteen variables of fifteen shallow groundwater samples were analysed using Inductive Coupled Plasma Mass Spectroscopy (ICP-MS). Five principal components were extracted that accounted for 88.52% of the total variance in the data set. Principal component 1 was responsible for 31.58% of the total variance, which was represented by copper, zinc, chromium, nickel and iron. Principal component 2 explained 49.76% of the total variance and was represented by nickel, arsenic, manganese and selenium. Principal component 3 was participated by cadmium and beryllium, while PC 4 has molybdenum and cobalt, respectively. Principal component 5 was represented by lead and selenium. The cluster analysis revealed two distinct groups of groundwater that are distinguished by different trace elements constituents. These trace elements were mainly from anthropogenic sources and parent rock materials in the area of study.

Keywords: Anthropogenic sources; Keana; Parent rock; Principal component analysis; Trace elements

1. Introduction

Trace elements are inorganic constituents of water whose concentrations are less than 0.1% of total rock's composition. Natural geochemical processes and several factors could influence the spatial distribution of trace elements in groundwater (UNICEF, 2008). These processes are reductive dissolution, alkali desorption and sulphide oxidation, while the factors could be the lithology of the aquifer, the quality of recharge waters, the types of interaction between water and aquifer and human activities (Chen *et al*., 2007).

Groundwater contains trace elements that are leached from rocks and soils and these elements could impair the quality of groundwater. There is so much concern about the effects of trace elements in groundwater on the health of man and animals. In humans, trace elements have been associated with various diseases; wide spread arsenicosis caused by high arsenic levels in groundwaters in Bangladesh and west Bengal, India (Appelo and Postma, 1993; Khan, 2011). Lead poisoning in Dareta, Nigeria, where over four hundred children between the ages of 3 – 12 years died as a result of ingesting soils that were contaminated with lead from artisanal processing of lead-rich gold ores in the area (Plumlee, 2011). High cases of dental fluorosis are recorded amongst residents of Langtang-Kaltungo areas in northern Nigeria due to excess of fluoride in their potable water (Lar and Tejan, 2008).

Lar and Sallau, (2005) investigated the extent to which lead-zinc and barite mineralizations have affected the quality of groundwaters in Keana-Awe brine fields. They showed that, vanadium, chromium, arsenic, lead, copper, cobalt, nickel, titanium, cadmium and iron were in appreciable amounts in the groundwater. The chemistry of groundwater is characterized by complex interactions of variables and as such complex statistical data analytical techniques are needed to interpret the spatial distribution of trace elements in ground water. Multivariate statistical techniques such as principal component analysis (PCA), factor analysis (FA) and cluster analysis (CA) could lead to a better understanding of these interactions as well as spatial distributions of trace elements (Chen *et al*., 2007). They also identify the most important variables that influence the quality of the groundwater (Singh *et al*., 2012).

Singh *et al*. (2012) from their work on groundwater quality in Imphal West District, Manipur, India showed the influence of agriculture and agriculture-related land use changes on shallow groundwater quality and the efficacy of multivariate statistical techniques in understanding the complex interactions among large number of variables. Zhang *et al*. (2014) assessed groundwater chemistry and its status in a heavily used semi-arid region with multivariate statistical analysis. The quality of groundwater in the area was controlled by evaporation effect of the dry climate, dissolution of carbonate minerals and human activities, whi ch includes the treatment of industrial and municipal waste water, the discharge of domestic sewage and utilization of chemical fertilizer.

Keana and environs are mainly agrarian communities; these areas support an important agricultural industry that accounts for 30% of natural food production (Sallau, 2017). In recent times, these communities have developed artisanal mining settlement and they have the largest lead-zinc, baryte and copper mining district in Nigeria. Several mining companies were involved in the exploitation and processing of these mineral resources in the area. Mining of these minerals, exposure of the elemental constituents of these deposits, leaching and redistribution of the elements contained in them could impair the quality of the groundwater systems.

Multivariate statistical approach has been used to study the factors that influence the quality of groundwater in other parts of the world, no such assessment has so far been made in Keana and its environs. The focus of this study were (1) to determine the associations between groundwater and the variables that influence its trace element constituents; (2) to explore the importance of multivariate statistical techniques in our understanding of groundwater features.

2. Materials and Methods

2.1 Study area

Keana is situated in the Middle Benue Trough of Nigeria. It lies between latitudes 8º 05′ 00′′N and 8º 25′ 00′′N and longitudes 8º 45′ 00′′E and 9º 15′ 00′′E (Fig. 1). It has a geographical area of 1850 km^2 and a population of about 85,000 in the 2006 census (NPC, 2006). The area is generally smooth to gentle with ridges at Aloshi and Keana ranging from 230 to 280m. Major rivers in the area are Ome flowing through Keana and river Okpobi at Obi. The geology is made up of six sedimentary formations; the oldest is Asu River Group, it consists of olive-green to grey dark and pinkish micaceous siltstones, shales, mudstones and clays (Sallau, 2017). Overlying the Asu River Group is Awe Formation, the formation consists of flaggy, whitish, medium to coarse grained calcareous sandstones, carbonaceous shales from which brine issues out (Nwajide, 2013). The thickness of Awe Formation is made up of coarse grained arkosic sandstones (Sallau, 2015). These rocks were exposed at Keana, Jangerigeri and Azara areas respectively. The age of Keana Formation is Cenomanian and it is deposited under continental conditions (Offodile, 1976). Preceeding the Keana Formation is the Ezeaku Formation, the formation consists of calcareous shales, fine to medium grained friable sandstones and siltstones (Nwajide, 2013). The fifth formation is the Awgu Formation, which is mainly black shales and limestones with seams of coking coal at Obi, Agwatashi and Jangwa (Sallau, 2015). The sixth formation is the Lafia Formation, it is the youngest lithological unit and it is of continental ferruginous sandstones, loose sands with some flaggy mudstones and clays (Nwajide, 2013).

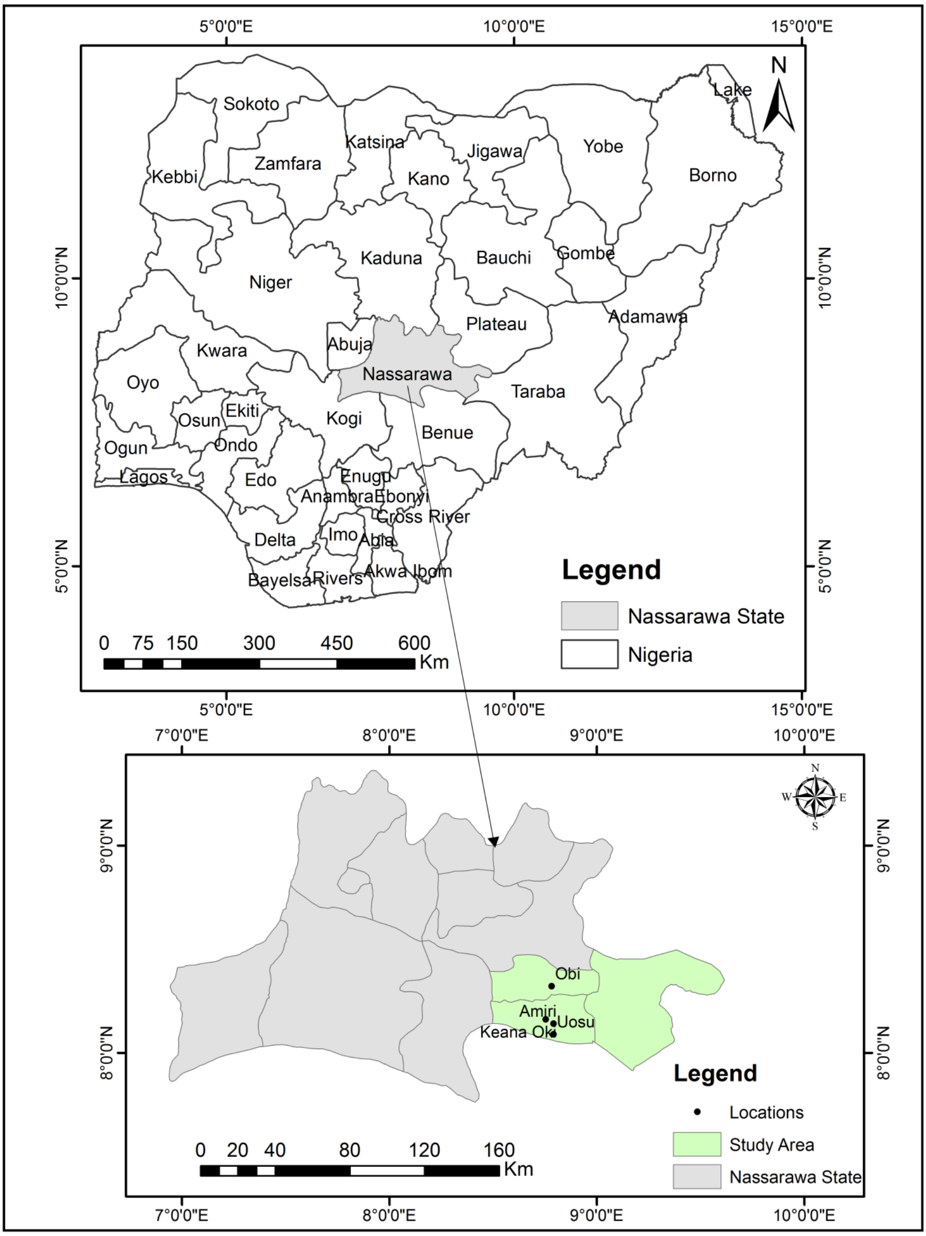

Figure 1: Map of the Study Area

Hydro-geologically, groundwater mostly occurs within unconfined to semiconfined aquifer systems with a depth of about 30m. The lithology is sand, gravelly sand, silt and clay. The aquiferous sandstone sequence is located at a higher stratigraphic level than the salty Awe Formation.

2.2 Sample collection and analyses

Fifteen water samples were collected from shallow hand dug wells in the locality (Table 1). Most of the hand dug wells were dry because the fieldwork was conducted in April 2016 at the peak of dry season. Each water sample was filtered through 0.45 µm membrane filter in 250 ml polyethylene bottles and the bottles were rinsed repeatedly with distilled water before sample collection. The samples were acidified with two drops of nitric acid to fix all the trace elements in the groundwater. The samples were kept in ice-chested coolers at a temperature of 4ºC to minimize the chemical reactions which could result in precipitation of dissolved elements.

The accuracy of estimation was verified by using standard reference materials. The groundwater samples were analysed at the Central Analytical Facilities, University of Stellenbosch, South Africa, and all the trace elements were determined by Inductive Coupled Plasma Mass Spectrometer (ICP-MS). The detection limit of the analytical tool was 0.01 mg/L.

2.3 Statistical analyses

Multivariate statistical techniques are tools that organize large data sets in order to provide meaningful insight (Chen *et al*., 2007). Principal component analysis will reduce large number of correlated variables by diagonalization of the correlation matrix of the data to a few uncorrelated principal components. The eigen values of the principal component are proportionate to the variance they account for (Helena *et al*., 2000; Chen *et al*., 2007). The raw data matrix can be reduced to two or three principal component loadings that account for the majority of the variance.

2.4 Cluster analysis (CA)

These are series of multivariate methods which are used to find true groups of data. It classifies objects by initially putting each object in a separate cluster, and then joins the clusters together, until a single cluster remains (Zhou *et al*., 2007; Singh, 2012). In clustering, objects are grouped in such a way that similar objects fall into same class (Danielsson, *et al.,* 1999). In this study, Ward's method of hierarchical agglomerative CA using squared Euclidean distance as a measure of similarity was used because it has a little space distorting effect compared to other hierarchical methods (Zhang *et al*., 2014).

3. Results and Discussion

Results of trace elements analyses in the shallow groundwater samples are presented in Table 2. Iron concentrations ranged from 0.02 to 66.76 mg/L, its concentrations in most of the groundwater samples were in excess of the WHO (2003) permissible limit of 0.03 mg/L. Concentrations of lead varied from 0.01 to 0.08 mg/L. The concentrations of chromium, cobalt, zinc, molybdenum, copper and cadmium were within WHO (2003) allowable limit for drinking water. Arsenic values in groundwater ranged from 0.01 to 0.06 mg/L with an average value of 0.03 mg/L. The PCA results are summarized in Table 3. Five principal components were extracted that accounted for 88.52% of the total variance in the original data set. The first component was responsible for 31.58% of the total variance, which was represented by copper, zinc, chromium, nickel and iron. Principal component 2 explained 49.76% of the total variance and was represented

Table 1: Water Sample locations at Keana and environs

SAMPLE LOCATION	LOCATION	SAMPLE DESCRIPTION	LAT (N)	LONG (E)
SW-1	Uosu village	Crystal clear water	08º 05′ 24.0″	008º 47′ 24.7″
SW-2	Tachia 1 hamlet	Light brownish water	08º 11′ 45.9″	008º 47′ 50.6″
SW-3	Tachia 2 hamlet	Clean water	08º 12′ 32.7″	008º 47′ 58.3″
SW-4	Akinwa village	Brownish water	08º 15′ 17.5″	008º 48′ 39.5″
SW-5	Obi town	Clean water	08 º 19′ 15.5″	008º 46′ 54.8″
SW-6	Gidan Joseph Obi	Clear water	08 º 22′ 41.7″	008º 47′ 32.1″
SW-7	Gidan Alice Obi	Clean water	08º 22′ 47.5″	008º 47′ 07.8″
SW-8	Obi hospital	Clean water	08º 22′ 53.8″	008º 47′ 02.0″
SW-9	Pastors college	Brownish water	08º 23′ 05.2″	008º 47′ 15.0″
SW-10	Maraba obi	Clear water	08º 23′ 13.9″	008º 45′ 40.0″
SW-11	Keana– Oki	Light brownish water	08º 09′ 11.9″	008º 47′ 52.9″
SW-12	Efribo–Agwatashi	Clear water	08º 19′ 10.8″	008º 51′ 28.8″
SW-13	Obi Health Centre	Clean water	08º 19′ 15.3″	008º 50′ 59.1″
SW-14	Amiri	Light brownish water	08º 08′ 50.2″	008º 47′ 50.0″
SW-15	Keana–Iwuga	Clean water	08º 08′ 40.6″	008º 47′ 33.9″

by nickel, iron, arsenic, manganese and selenium. Principal component 3 and 4 explained 66.12% and 78.39%. Principal component 3 was represented by cadmium and beryllium, while principal component 4 have molybdenum and cobalt, respectively. Principal component 5 explained 88.52% of the variance and it was represented by selenium and lead. Principal component 1 has strong loadings for copper, zinc, chromium, nickel and iron. Principal component 2 has strong loadings for manganese and negative loadings for arsenic and selenium. Principal component 3 to PC 5 showed moderate to strong loadings for the following trace elements selenium, cobalt, molybdenum, beryllium and cadmium, while PC 5 showed a very high negative loading for lead.

Table 2: Trace elements concentration in shallow groundwater of Keana and environs

	Cu	As	Zn	Mo	Co	Cr	Ni	Se	Pb	Cd	Be	Mn	Fe
SW 1	<	0.04	0.03	0.02	0.03	<	<	0.07	0.08	<	<	<	0.13
SW 2	<	0.01	<	<	0.02	0.01	0.06	<	0.02	<	<	0.04	7.61
SW 3	0.07	0.02	0.13	0.02	0.03	0.31	0.55	0.01	0.03	<	<	0.95	66.76
SW 4	<	<	<	0.03	0.05	0.06	0.22	<	0.01	<	<	2.51	45.59
SW 5	<	0.02	0.02	<	0.03	<	0.10	0.04	0.06	<	<	0.01	2.55
SW 6	0.01	0.04	0.03	0.02	0.03	<	0.06	0.03	0.01	<	<	0.01	0.06
SW 7	<	0.06	0.02	0.03	0.02	0.03	0.02	0.06	0.03	0.01	<	0.01	0.06
SW 8	<	0.02	0.03	0.04	0.04	0.02	0.06	0.02	0.02	<	<	0.04	1.18
SW 9	0.02	0.04	0.03	0.04	0.04	<	0.12	0.03	0.02	<	<	0.15	0.61
SW 10	<	0.03	0.03	0.01	0.02	<	0.07	0.12	0.06	<	<	0.04	1.08
SW 11	<	0.01	0.04	0.03	0.02	<	0.11	<	0.4	<	<	0.03	<
SW 12	<	<	0.04	0.03	0.04	0.03	0.04	0.01	0.02	0.04	0.08	<	0.02
SW 13	<	0.05	0.03	0.04	0.05	<	0.02	0.06	0.06	<	0.03	0.04	0.01
SW 14	0.03	0.06	0.03	0.02	<	<	0.04	<	0.07	<	<	0.03	0.04
SW 15	0.01	0.06	0.04	0.03	0.04	<	0.04	0.03	0.10	0.01	0.01	0.04	0.06
Min.	0.01	0.01	0.02	0.01	0.02	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02
Max.	0.07	0.06	0.13	0.03	0.05	0.31	0.22	0.12	0.40	0.01	0.08	2.51	66.76
Mean	0.01	0.03	0.03	0.03	0.03	0.03	0.10	0.03	0.05	0.01	0.03	0.26	8.53
WHO limit.	2.00	0.01	3.00	0.70	0.03	0.05	0.02	0.01	0.01	0.003	-	0.50	3.00

Key
<: Below detection limit

Table 3: Principal component loadings

Variables	Comp.1	Comp. 2	Comp.3	Comp. 4	Comp. 5	Communalities
Cu	0.95					0.924
Zn	0.938					0.935
Cr	0.936					0.962
Ni	0.875	0.42				0.971
Fe	0.746	0.579				0.974
As		-0.862				0.842
Mn		0.762				0.865
Se		-0.543			0.478	0.589
Cd			0.952			0.914
Be			0.948			0.944
Mo				0.924		0.931
Co				0.756		0.831
Pb					-0.895	0.824
Variance (%)	31.584	18.176	16.366	12.27	10.127	
Cumulative (%)	31.584	49.76	66.126	78.396	88.524	
Total	4.106	2.363	2.128	1.595	1.317	

Cluster analysis resulted in dendrogram (Fig. 2), grouping all the fifteen locations into two statistically significant clusters as group. Locations 1 to 5 and 8 to 11, form group 1, which were enriched in cadmium, beryllium, molybdenum, cobalt, arsenic, copper, zinc, selenium and lead. Locations 6, 7 and 12 to 15 form group 2, these locations were enriched in chromium, nickel, manganese and iron.

Principal component 1 signifies that the elements emanated from the parent rocks in the localities. Mico *et al*. (2006) in their work on assessing heavy metals sources in European Agricultural soils found that the metals zinc, chromium and iron were having positive loadings with maximum variance of 29.56%. In this study, these elements have a total variance of 31.58% and strong positive loadings for copper, zinc, chromium and iron. Principal component 2 showed 49.76% of total variance, it has strong positive loadings on nickel, arsenic and manganese. These elements occurred as soluble oxyanions in oxidizing waters (Hem, 1989). Principal component 3 and PC 4 have strong loadings for cadmium, beryllium, molybdenum and cobalt which were correlated with parent rocks in the area. The results corroborate the findings of Chen *et al*., (2007). Principal component 5 explaining 88.52% of the total variance has strong negative loading on lead. Negative loading of lead has been associated with anthropogenic activities (Sallau *et al*., 2017).

Ramesh *et al*. (1995) identified three principal components in the application of principal component analysis to reflect the extent of pollution in Madras City, India. Principal component 1 was characterized by a strong positive load on cobalt, principal component 3 has high negative load for lead. In this study, five principal components were identified; cobalt showed a strong loading in component 4, while principal component 5 has a high negative loading for lead. Findings from this study are in agreement with Ramesh et al., (1995) and other similar research (Chen *et al*., 2007) where lead was mainly from anthropogenic sources.

Two distinct clusters (groups) emanated from cluster analysis and this suggests that two distinct sets of influences contribute trace elements to the groundwater in the study area. The influences could be natural sources from the parent materials through weathering and erosion, while the second influence could be from anthropogenic inputs such as mining, waste disposal and agricultural activities (Ezeh and Anike, 2009). The groundwaters in group 1 were severely enriched in molybdenum, cobalt, copper, zinc, beryllium and cadmium. The presence of molybdenum in the groundwater was due to its ability to form oxyanions (Sallau, 2015). Molybdenum is highly mobile in oxidizing waters and predominant as MoO4 in groundwater.

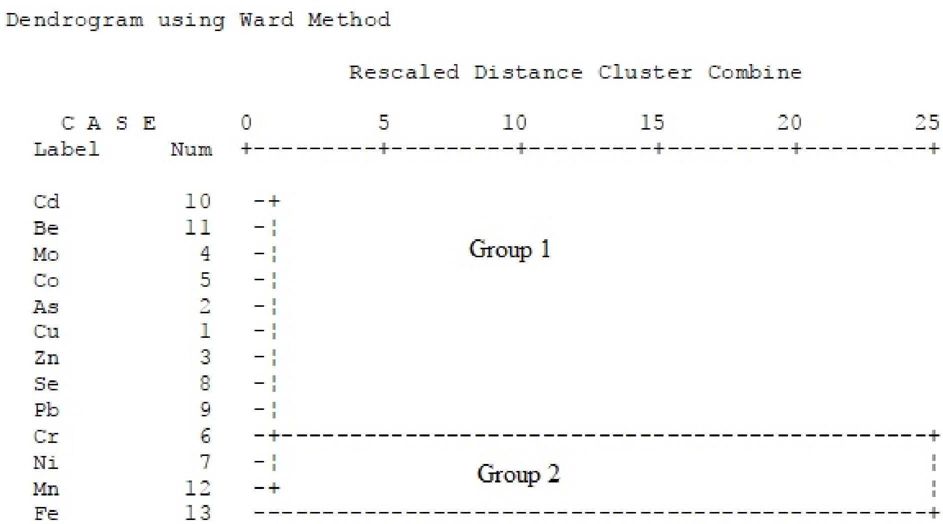

Figure 2: Dendrogram of the hierarchical cluster analysis using the Ward method

It readily co-precipitatesalongside with iron, copper, zinc and lead (Chen, 2007). In this study, cluster 1 reflected the oxidizing conditions within groundwater. The influences on cluster 1 are most likely to be anthropogenic sources such as agricultural practices and mining.

Zhang *et al*. (2014) have reported that the groundwater of Yinchuan plain in northwest China were influenced by anthropogenic sources such as the application of pesticides, insecticides and fertilizers in irrigation farming. In this study, we found that groundwater were enriched in arsenic and lead which are likely from anthropogenic sources. Cluster 2 was characterized by chromium, nickel, manganese and iron. These elements were mainly from the parent rock materials through natural processes such as weathering and erosion (Mico *et al*., 2005).

4.Conclusion

The groundwaters in the area were enriched in nickel, iron and arsenic. Results of the PCA produced five PCs explaining 88.52% of the total variance. The following trace elements chromium, arsenic, molybdenum, and beryllium with positive loadings occurred as soluble oxyanions in the groundwater, while lead with negative loadings was soluble in oxygen depleted groundwater. Cluster analysis grouped the entire groundwater in the area into two clusters, groundwater that were enriched in cadmium, beryllium, molybdenum, cobalt, arsenic, copper, zinc, selenium and lead. The second groups of groundwater were enriched in chromium, nickel, manganese and iron. These trace elements were mainly derived from anthropogenic sources and parent rock materials in the area of study. Arsenic concentrations in some of the groundwater were above WHO allowable limit for drinking water. This will threaten exploitation of this groundwater for drinking and domestic purposes.

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