WASOT
www.wasot2012.or

Aemere Ogunlaja et al Toxicology Digest Vol. 2 (1): 13-26 (2018)

Toxicology Digest

Risk Assessment and Profiling of Selected Heavy Metals in Water Sources Within a Petroleum Refinery Host Community

Aemere Ogunlaja*[1, 2], Olumuyiwa Ogunlaja[3], Dorcas M. Okewole[4]

1. Department of Biological Sciences, Redeemer's university, Osun state, Nigeria.
2. School of Life Sciences, University of KwaZulu-Natal, Durban, 4000, South Africa
3. Chemistry Department, Lead City University, Oyo State, Nigeria.
4. Mathematics Department, Redeemer's University, Osun state, Nigeria

E-mail: aigbomere@yahoo.com

Abstract

The contamination of water sources by industrial effluents may result into accumulation of heavy metals, leading to potential public health risk. Ubeji community is one of the host communities for Warri refinery and petrochemicals company (WRPC) located in Warri south local government area of Delta State. Effluents from the refinery are deposited into their stream and this may impact the available water resources. The daily human exposure assessment to Cd, Cu, Fe, Ni and Pb through the ingestion pathway was evaluated using the average daily dose, ADD and Principal component analysis (PCA). Cluster analysis (CA) was also used to study the interactions between metals, and identify the possible sources of contamination. Eighteen groundwater and two surface water samples were collected. The hazard quotients (HQ) for Cd and Pb exceeded 1 for all water sources while the hazard index (HI) ranged from 18.0 to 14052 for all studied heavy metals. HQ revealed that well 16 and 17 were the most impacted by the studied heavy metals. The borehole had highest HQ of 14000, 6.7 and 22.3 for Cd, Cu and Fe respectively. Residents of the Ubeji may be at risk of developing diseases from consumption of ground water. Data from this study suggests that local people living in refinery host community should take precautions before drinking water sources especially groundwater within such areas.

Keywords: *Heavy metals, Petroleum contamination, Principal component and cluster analyses, risk assessment, groundwater contamination.*

Introduction

Man's continuous existence depends largely on the availability and quality of drinking water (UNSCD, 2000). In developing countries, rapid industrial revolution is a constant threat to the availability of portable water, because industries generate wastes and disposal is not usually done properly. About 4 million children under the age of five die yearly in developing countries due to water related problems (USAID, 1990) and throughout the world about 2.3 billion people suffer from diseases that are linked to water related problems (WHO, 1997). In Niger-Delta, oil spills are usual occurrences that often leads to the introduction of contaminants into water sources within such industrial layout. Besides oil spills as source of water pollution, wastes discharged into freshwater swamps and into the sea are other sources (Akpofure, 2008).

The effluent from crude oil exploration and processing consists of oil and an assortment of chemicals that include acids, alkalis, phenols, sulphides, hydrocarbons, heavy metals and other toxic components (Boon *et al*, 1992). These are substances that have been proven from studies to be carcinogenic in nature (Chu *et. al,* 1992). The release of these contaminants have polluted water sources, contaminated agricultural raw materials and destroyed fishery resources (NDDC, 2004).

Heavy metals are defined as that group of elements that has specific weights higher than 5 g/cm^3 (Holleman and Wiberg, 1985). There are about 40 elements that fall into this category. As a result of the industrial revolution, there is enormous and increasing demand for heavy metals that lead to high anthropogenic emission of heavy metals into the biosphere (Ayres, 1992). Apart from the release of some emissions into the atmosphere in the form of dust particles or vapours, these heavy metals stay largely in the aquatic and soil phases of the planet. Heavy metals interact with several functional groups of proteins, primarily SH-groups. As a result, protein conformation is changed, and many enzymes with SH-groups in their active centres lose their activities (Ivanov *et al.,* 1998). This precludes, for instance, an inducible system. All heavy metals, both essential (copper (Cu), zinc (Zn)) and nonessential (Cd, Pb) can cause toxic effects on plants and humans, if found in high concentrations (Alloway, 1990).

The objective of this study was to assess the potential health risk inhabitants of Ubeji community are exposed to through the ingestion pathway to Cd, Cu, Fe, Ni and Pb in various water sources using hazard quotient (HQ) and hazard index analysis (HI). This study also investigated the possible sources of Cd, Cu, Fe, Ni and Pb and the interactions between these metals in various water sources using PCA and cluster analysis (CA), respectively.

Materials and Methods

2.1 Description of study Area

Ubeji community is one of the host communities for Warri refinery and petrochemicals company (WRPC) located between 5.5736° N, 5.701paint0° E in Warri south local government area of Delta State. Effluents from the refinery are deposited into their stream, which empties into the Crawford creek which eventually flows into Warri River. The map of the area, along with sampling points is as shown in figure 1.

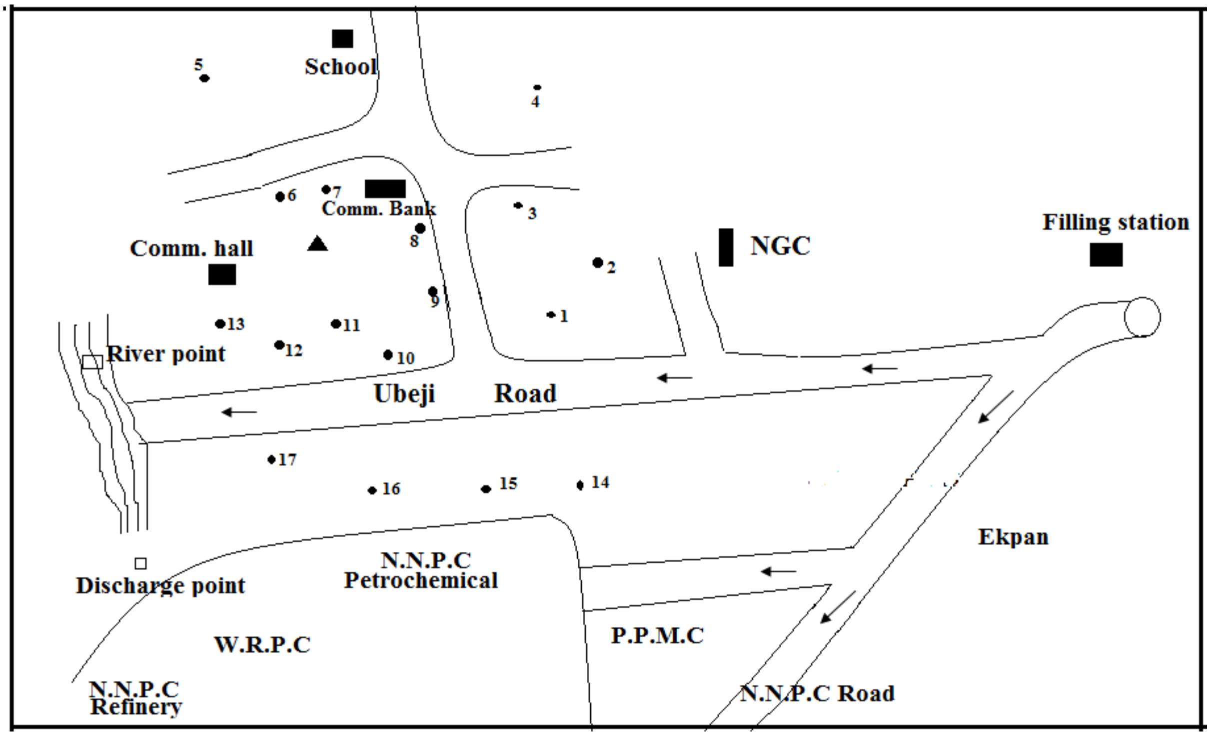

Fig. 1 Sketch map of Study area (Ubeji) showing sampling points

2.2 Reagents, Analytical quality assurance and standards

All chemicals for this study was supplied by Sigma Aldrich (St. Louis, USA) and Merck (Kenilworth, USA) chemical companies. Analytical reagent grade chemicals were used for samples and spectroscopic grade were used for standards. Elemental calibration standards were prepared from spectroscopic grade stock standard solutions of 1000 mg L^{-1}. For quality control, blanks were analysed after every 10 sample analyses. All plastic containers for sampling were washed with double distilled water and then soaked overnight in 1M HNO_3. Glassware and other equipment were also cleaned with 6M HNO_3 and rinsed off with double distilled water to prevent contamination before usage. Deionized water was used throughout the experiments.

2.3 Digestion and elemental analysis of samples

Water samples were digested according to the method described by Ogunlaja *et al.* (2017) with slight modification.

All digested samples were analysed for Cd, Cu, Fe, Pb and Ni by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) using Perkin Elmer® Optima™ 5300 Dual View ICP-OES (Billerica, Massachusetts, USA). The analytical wavelength for each element was selected by picking the one with minimum spectral interferences in order to achieve maximum analytical performance. The accuracy of analytical procedures was checked by analysing certified reference materials (CRMs), WatR™ Supply Metals for water samples obtained from ERA (A Waters Company, Golden, CO, USA).

2.4 Statistical analysis

The concentrations of the heavy metals were subjected to multivariate statistical analysis. Multivariate statistical analysis was done using Principal component analysis (PCA) and hierarchical cluster analysis (CA), the most commonly used multivariate statistical methods in environmental studies (Dı ́az et al., 2002; Han et al., 2006; Lu et al., 2010; Tahri et al., 2005). PCA was used to substantially reduce the dataset, detect structure in the relationships of different variables and to extract a small number of dormant factors (principal components, PCs) for analysing relationships among the observed variables (Rencher, 2002; Loska and Wiechuya, 2003). Additionally, hierarchical cluster analysis (CA) was performed on dataset in order to identify homogenous groups. A dendrogram was also constructed to assess the cohesiveness of the clusters formed, in which correlations among elements can readily be seen. Pearson's correlation matrix was used to investigate the possible sources of different metals in the water sources. All statistical analyses were performed using the Statistical Package for the Social Sciences, (PASW version 24, IBM Corporation, Cornell, NY, USA).

2.5 *Health risk assessments*

Previous study revealed elevated levels of some heavy metals such as Ni, Cd and Pb in different water sources within Ubeji Community (Ogunlaja and Ogunlaja, 2010) and suggested a potential health risk on humans. Hence, this study assessed the chronic health hazard associated with the consumption of groundwater in Ubeji Community.

The daily human exposure assessment to the studied heavy metals through the ingestion pathway was evaluated using the average daily dose, ADD as described by Adamu et al., (2015) for the different water sources (equation 1).

$$ADD = C \times IR \times ED \times EF/BW \times AT \quad \ldots\ldots (1)$$

where ADD is the exposure duration (mg/kg-day), C is the concentration of the heavy metal in water (mg L^{-1}), IR is the ingestion rate per unit time (L/day), ED is the exposure duration (years), EF is the exposure frequency (days/year), BW is body weight (kg), AT is the average time (years). The principal exposure factors that have been taken into account to carry out the risk assessment calculations are shown in Table 1.

Table 1: Input parameters to characterize the ADD value

Exposure parameters (symbol)	**Value**	**Source**
Concentration		This study
Exposure duration (ED)	30	US EPA (1977)
Exposure Frequency (EF)	350	US EPA (1977)
Average time (AT)	52	World Bank (2014)
Body weight (BW)	60	Wongsasuluk et al. (2014)
Ingestion rate (IR)	2	EPA (2004)

The non-carcinogenic hazard was evaluated by the hazard quotient (HQ) by equation 2 (USEPA, 1999).

$$HQ = ADD/ R\mathit{f}D \quad \ldots\ldots (2)$$

where R*f*D is the oral reference dose (mg/kg/day) for individual heavy metal that human can be exposed to, and for this study were obtained from USEPA (USEPA IRIS, 2011). HQ is calculated for each heavy metal and the sum of HQ of all metals is used to determine the non-carcinogenic risk, hazard index (HI)

(USEPA, 1999). If HQ < 1, it is considered safe for human health, 1< HQ ≤ 5 is low risk, 5 < HQ ≤ 10 is medium risk and HQ > 10 is considered high risk.

3.0 Result and Discussion

The accuracy of the digestion and elemental procedures was authenticated by concurrent analysis of CRM. The measured results were compared with certified results as shown in Table 2. The measured values compared well to the certified values (P < 0.05) with recovery percentages being within acceptable limits.

Table 2. Validation of the analytical method using water certified reference material.

	Measured	Certified	Acceptable limit
Cd	34.8 ± 0.97	33.6[a]	28.3 - 37.3
Pb	79.9 ± 0.18	81.9[a]	69.5 - 95.0
Zn	355 ± 0.45	351[a]	318 – 386

*Values are in µg g^{-1} dry mass (mean ± standard deviation, 95% confidence interval, n = 3).
[a] Indicative values (without uncertainty).

Although the elemental concentrations for Cd, Cu, Fe, Pb and Ni are not shown in this report because they were consistent with earlier study (Ogunlaja and Ogunlaja, 2010), but they were used to estimate the non-carcinogen health risk assessment of consuming the ground water within Ubeli community.

3.1 *Human health risk assessment*

3.1.1 *Hazard Quotient (HQ)*

Fundamentally, risk assessment comprises of hazard identification, exposure assessment, dose response (toxicity) and risk characterization (Lee et al., 2005). The health risk assessment of Cd, Cu, Fe, Pb and Ni in ground water was estimated based on the toxicity risk index, reference dose (RfD) for non-carcinogen characterization (Lim et al., 2008) as shown in Table 3.

Table 4 summarised the non-carcinogenic risk (HQ) estimates for Cd, Cu, Fe, Pb and Ni for water sources in Ubeji community. Although the HQ values for Cu, Fe and Ni for most wells were < 1, the HQ values for Cd, and Pb were all > 1 for all the wells, indicating an unacceptable non-carcinogenic risk to human health for these heavy metals.

Table 3: The toxicity responses to heavy metals as the oral reference dose (RfD)

Metals	**Oral RfD (mg/kg/day)***
Cd	5.0×10^{-4}
Cu	4.0×10^{-2}
Fe	7.0×10^{-1}
Pb	3.5×10^{-3}
Ni	2.0×10^{-2}

* US EPA IRIS (2011).

The HI values were > 1 across all water sources, suggesting an un-acceptable risk of non-carcinogenic effects on health of the local inhabitants (ECETOC, 2001). Increased levels of toxic metals in the environment as result of point and diffuse sources can have both lethal and sub-lethal effects on organisms. Sub-lethal concentrations of toxicants in the environment do not necessarily result in outright mortality of organisms but could have significant effects, which can result in several physiological dysfunctions in organisms, hence need for proper effluent management.

Table 4: Non-carcinogenic risk (hazard quotient, HQ) and overall toxic risk (hazard index, HI)

	Child HQ					**HI**
	Cu	Pd	Fe	Cd	Ni	
W_1	0.2	3.8	0.01	40.4	0.3	44.7
W_2	0.3	5.8	0.01	40.4	0.3	46.8
W_3	0.2	1.9	0.01	26.9	0.3	29.4
W_4	0.2	3.8	0.01	26.9	0.3	31.3
W_5	0.2	3.8	4.0	13.5	0.7	22.2
W_6	0.2	3.8	0.01	26.9	0.3	31.3
W_7	0.2	3.8	0.01	26.9	1.0	32.0
W_8	0.2	3.8	0.03	13.5	1.0	18.5
W_9	0.3	1.9	0.02	40.4	0.3	43.0
W_{10}	0.3	1.9	0.03	40.4	0.3	43.0
W_{11}	0.5	3.8	0.03	13.5	0.3	18.2
W_{12}	0.5	1.9	1.4	40.4	0.3	44.6
W_{13}	0.3	3.8	0.01	13.5	0.3	18.0
W_{14}	0.2	3.8	0.01	26.9	0.3	31.3
W_{15}	0.3	3.8	0.01	26.9	0.7	31.8
W_{16}	3.4	38.5	0.8	269	10.1	322
W_{17}	3.4	76.9	0.5	404	13.5	498

BH	6.7	19.2	22.3	14000	3.4	14052
PD down	1.7	231	8.6	7000	47.1	7288
Riv up	40.4	327	1.8	8212	57.2	8638

* BH- Borehole water, Riv Up- Up stream, Riv Down-Down stream

3.2 Multivariate statistics

3.2.1 Principal component analysis (PCA)

The PCA was applied to assist in the identification of contamination sources in the of various water sources in Ubeji community. Table 5 shows the results of the PCA for the heavy metal concentrations in water samples. Two principal components dominated the PCA analysis, accounting for 94.0 % of the total variance. The high loadings and close association between Cu, Pb and Ni in PC 1 could suggest their common anthropogenic sources (Refinery effluents). These heavy metals are normal constituents of fossil fuel (Carls et al., 1995; Kisic et al., 2009; Krzyzanowski, 2012).

The Cu loading of 0.89 is not as high as that of other elements of the component, suggesting a quasi-independent behaviour within the group, which was further corroborated by a relatively large distance in Figure 2 and confirming the influence of different source (parent material).

Table 5. Rotated component matrix for variables in water samples (n = 100)

	Component	
Element	1	2
Cu	**0.89**	0.15
Pb	**0.97**	0.17
Fe	0.02	**0.99**
Cd	0.44	**0.89**
Ni	**0.95**	0.18
Eigenvalues	3.35	1.35
% Total variance	67.0	27.0
Cumulative %	67.0	94.0

Extraction Method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization.

Iron was found to be strongly associated with Cd in PC 2, contributing 27.0 % to the total variance with high loadings of 0.99 and 0.89 respectively. This may be due to their natural geological origin. The relatively large distance in the 3-D PCA loading plot (Figure 2), may also suggests a poor correlation, and an influence of different source.

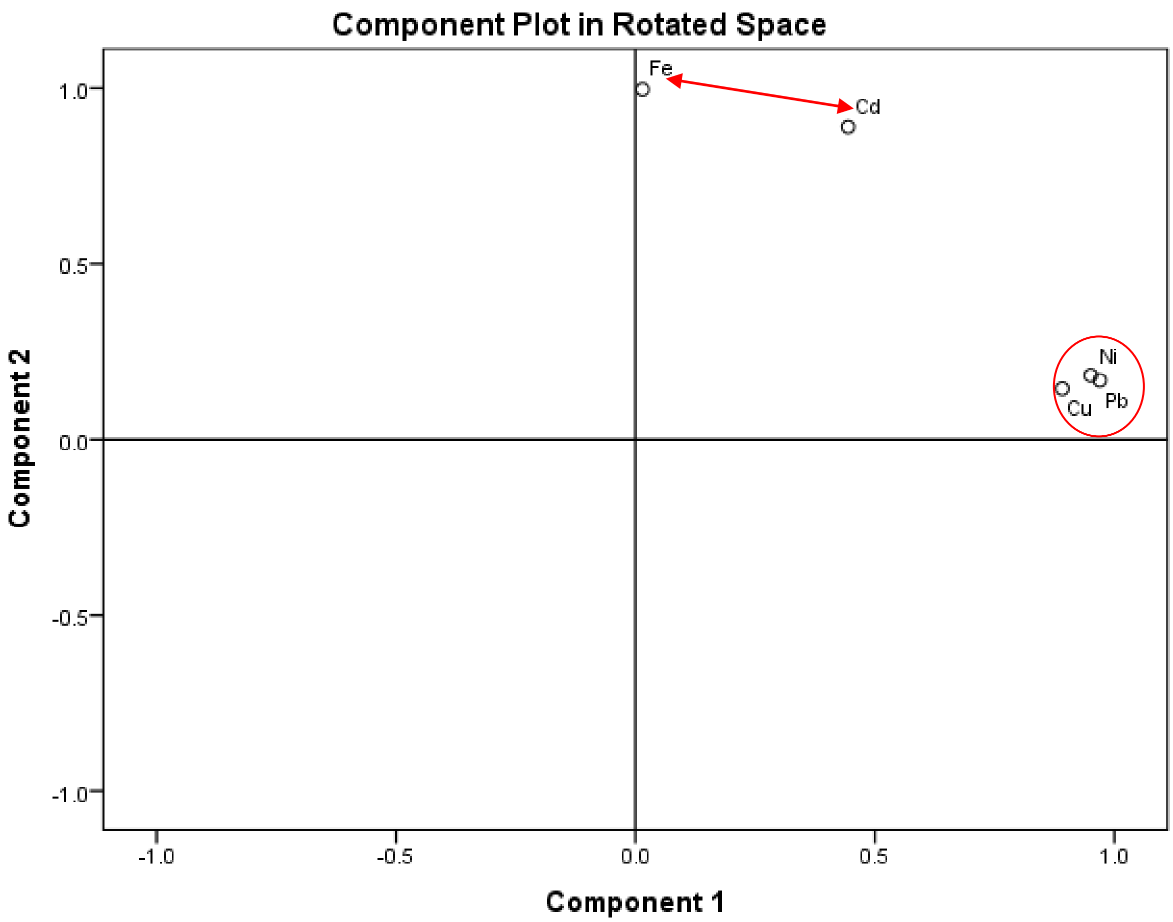

Figure 2. PCA analysis loading 3-D plot (PC1 vs PC2) for five heavy metals in water samples.

Similarly, Figure 3 shows the rotated component matrix dot plot for the five metals concentrations in water samples, there was a strong positive correlation between Ni and Pb, depicting an anthropogenic association of elements in water derived from the petroleum contamination. The relatively weak association between Fe and Cd was also corroborated by the relatively large distance although they both high loadings.

Furthermore, Pearson correlation analysis showed significant two way correlations ($P < 0.05$) of Cu with Pb and Ni (Table 6). These strong associations were attributed to similar origin. There was also a weak, and not significant ($P > 0.05$) correlation between Cu and Cd. This poor correlation was attributed to differences in sources of materials and geochemical distribution of studied heavy metals. These results were also corroborated by the results of PCA and CA analyses (Figure 2 and 4).

Table 6: Results of Correlation coefficients for heavy metals

	Cu	Pd	Fe	Cd	Ni
Cu	1				
Pd	0.8	1			
Fe	0.1	0.2	1		
Cd	0.5	0.6	0.9	1	
Ni	0.8	1.0	0.2	0.6	1

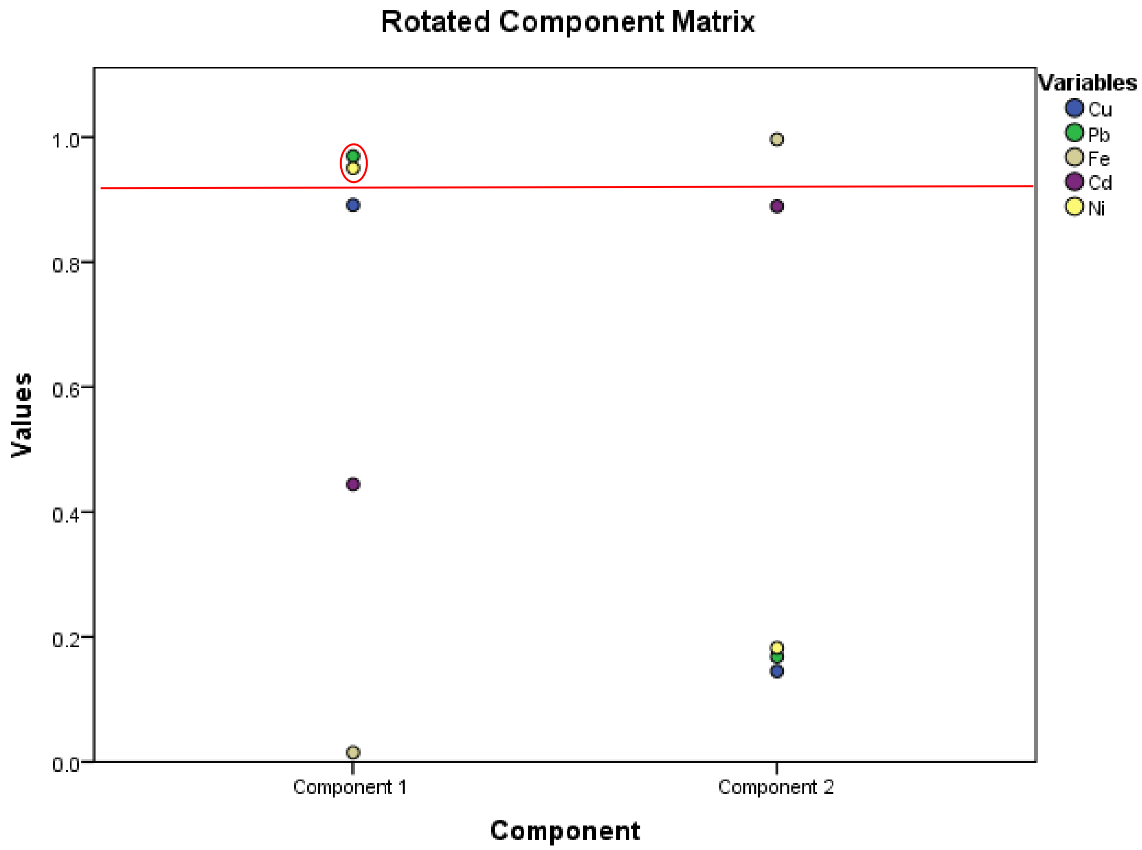

Figure 3. Rotated Component Matrix dot plot for metals concentration in water samples

3.2.2. Hierarchical Cluster Analysis (CA)

In addition, cluster analysis was performed on the elemental concentrations in water samples. The result is shown in the dendrogram (Figures 4). The degree of association between the metals is depicted by the distance between clusters. Figure 4 shows that the studied elements in the water samples were grouped into two main clusters (A and B). Cluster A contains two lower clusters, A1 (Pb, Ni and Cu) and A2 (Cd) while cluster B consisted of Fe. Cluster A1 and A2 are joined together at a relatively high level, implying perhaps a common source.

The proximity of Ni and Pb in cluster A1 further confirm their common origin. Figure 4 also showed that Cu joined together to Pb and Ni at a relatively high level, implying a different source. Figure 4 showed and confirmed that there is a quasi-independent behavior within cluster A, therefore corroborating the influence of different source for Cu. Cluster A2 and B are joined together at a much higher level, and this is consistence with PCA result.

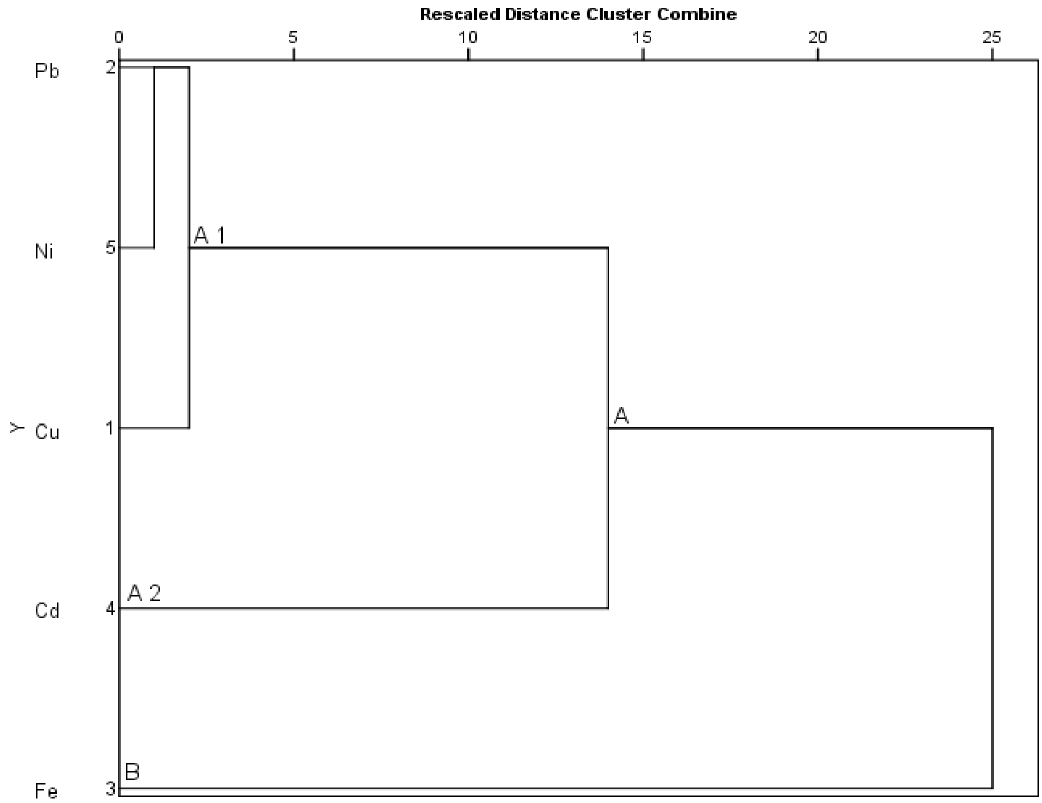

Figure 4. Hierarchical Cluster analysis dendrogram showing the relationship between five water samples (the distances reflect the degree of correlation between different elements)

4.0 Conclusion and Recommendation

Previous study of various water sources in Ubeji community showed an elevated levels of some of the studied heavy metals. This study however, showed that there is a significant relationship between elevated levels of heavy metals such as Pb and Ni in water sources and activities of the petroleum refinery. The PCA and CA analyses revealed that the discharge of effluent from the refinery caused significant enrichments of heavy metals, such as Ni and Pb in the water sources, altering the normal clustering pattern in these environmental media. Thus, a potential pollution risk may exist, which might contribute to heavy metal loading of Ubeji water sources.

Furthermore, data from this study indicated that there is a risk that local inhabitants who consume groundwater at Ubeji may develop sicknesses as a result of contamination of wells with Cd, Ni and, Pb. The results from this study may be used to educate host communities, on groundwater consumption safety, in order to prevent adverse human health risks from potentially contaminated groundwater.

Reference

Adamu, C.I., Nganje, T.N., and Edet, A. (2015). Heavy metal contamination and health risk assessment associated with abandoned barite mines in Cross River State, southeastern Nigeria. Environmental Nanotechnology, Monitoring and Management 3 10–21.

Akpofure, E. A. (2008). Oil Spillage in the Nigeria's Niger-Delta. Psycho-morphological and Empirical Overview, International Association of Impact Assessment, Opulence Environmental Service Ltd.

Alloway BJ (1990). Introduction. In: Allowey BJ (ed). Heavy metals in soils, Blackie and Son Ltd., pp. 3-6.

Ayres RU (1992). Toxic heavy metals: materials cycle optimization. Proc. Natl. Acad. Sci. USA, 89: 815-820.

Boon, J.P., E. Van Arnhem, S. Jansen, N. Kanman and G. Petrick, 1992. In: Marine
Ecosystems, (Eds) C.H. Walker and D.R. Livingstone, pp. 119- 160. Pergamon Press, Oxford.

Carls, E.G., Fenn, D.B., and Chaffey, S.A. (1995). Soil contamination by oil and gas drilling and production operations in Padre Island National Seashore, Texas, USA. Journal of Environmental Management, 45(3): 273-286.

Chu, I., C.A.M. Sazuki, D.C. Villeneuve and V.E. Vallli, 1992. Evaluation of Coal Processing Products in he Rats. *Fundum Appl. Toxicol*, 19: 246-257.

Dı ´az, RV., Aldape, J., and Flores, M. (2002). Identification of airborne particulate sources, of samples collected in Ticoma ´n, Mexico, using PIXE and multivariate analysis. Nucl Instrum Methods Phys Res, B Beam Interact Mater Atoms, 189:249–253.

ECETOC (European Centre for Ecotoxicology of Chemicals). (2001). Aquatic toxicity of mixtures. Technical report 80, Brussels, Belgium.

EPA, 2004. US EPA Office of Water. Office of Science and Technology (EPA-822- R-00-001). Environmental Protection Agency Region I, Washington, DC 20460
www.epe.gov/safewater

Han, Y.M., Du, P.X., Cao, J.J., and Posmentier, E.S. (2006). Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China. Sci. Total Environ. 355, 176–186.

Holleman AF, Wiberg E (1985). Lehrbuch der anorganischen chemie. Walter de Gruyter, Berlin, p. 868.

Ivanov VB, Bystrova EI, Dubrovsky JG, Ploshinskaya ME (1998). Duration of lateral root formation in maize seedlings as effected by diverse factors. In: Box JE (ed). Root demographics and their efficiencies in sustainable agriculture, grasslands and forest ecosystems, Dordrecht: Kluwer, pp. 777-787.

Kisic, I., Mesic, S., Basic, F., Brkic, V., Mesic, M., Durn, G., Zgorelec, Z., and Bertovic, L. (2009). The effect of drilling fluids and crude oil on some chemical characteristics of Soil and crops. Geoderma, 149(3): 209 –216.

Krzyzanowski, J. (2012). Environmental pathways of potential impacts to human health from Oil and gas development in northeast British Columbia, Canada. Environmental Reviews, 20(2): 122-134.

Niger Delta Development Commission, 2004. News Bulletin, 2(1): 5 - 6.

Lee, J.-S., Chon, H.-T., Kim, K.-W., 2005. Human risk assessment of As, Cd, Cu and Zn in the abandoned metal mine site. Environ. Geochem. Health 27, 185–191.

Lim, H.S., Lee, J.S., Chon, H.T., Sager, M., 2008. Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au–Ag mine in Korea. J. Geochem. Explor. 96, 223–230.

Loska, K., Wiechuya, D. (2003). Application of principle component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. Chemoshere; 51 723–33.

Lu, X., Wang, L., Li, L.Y., Lei, K., Huang, L., and Kang, D. (2010). Multivariate statistical analysis of heavy metals in street dust of Baoji, NW China. J. Hazard. Mater, 173: 744-749.

Ogunlaja, O.O., Moodley, R., Baijnath, H., and Jonnalagadda, S.B. (2017). Nutritional evaluation, bioaccumulation and toxicological assessment of heavy metals in edible fruits of *Ficus sur* (Moraceae). Journal of Environmental Science and Health, part B, 52(2): 84-91.

Ogunlaja, O.O., and Ogunlaja, A. 2010. Toxicological impact of water sources within a Nigerian Petroleum refinery Community on albino mice. Proceedings of Second IASTED International Conference Environmental Management and Engineering (EME2010) July 15-17, 2010. Banff, Alberta, Canada 761-768.

Rencher, A.C 2002. Methods of ultivariate analysis. 2nd Edition Brigham Young University John Wiley and Sons, Inc., New York.

Tahri, M., Benyaich, F., Bounakhla, M., Bilal, E., Gruffat, J.J., Moutte, J., Garcia, D., 2005. Multivariate analysis of heavy metal contents in soils. Sediments and water in the Region of Meknes (central Morocco), Environ. Monit. Assess. 102, 405–417.

USEPA (US Environmental Protection Agency). 1999. Guidance for Performing Aggregate Exposure and Risk Assessments, Office of Pesticide Programs, Washington, DC.

United States Agency for International Development (USAID) (1990). Strategies for linking water and sanitation programs to child survival. USAID, Washington, D.C

United Nation Commission on Sustainable Development. (UNCSD) (2000). Comprehensive assessment of the Freshwater Resources of the World. UN, New York.

USEPA IRIS (US Environmental Protection Agency's Integrated Risk Information System). (2011). http://www.epa. gov/iris/. Accessed 07/17/2017.

US EPA, 1977. Exposure Factor Handbook (EPA/600/p-95/002Fa) (Update to Exposure Factors Handbook EPA/600/8-89/043). Environmental Protection Agency Region I, Washington, DC.

Wongsasuluk, P., Chotpantarat, S., Siriwong, W., Robson, M., 2014. Heavy metal contamination and human health risk assessment in drinking water from shallow groundwater wells in an agricultural area in Ubon Ratchathani province, Thailand. Environ. Geochem. Health 36, 169–182.

World Bank, 2014. The World Bank Group: Average Life Expectancy in Nigeria: 2009–2013. www.goggle.com.ng/#9=life+expectancy+in+Nigeria

World Health Organization (1997). Health and Environment in Sustainable Development. Five years after the earth summit. (WHO) Geneva, (WHO/EHG/97.8). p. 245.