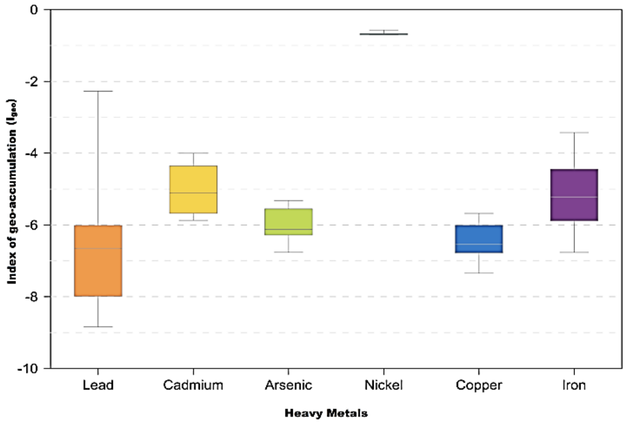

Figure 3: Index of geo-accumulation of stream sediments, in all sampled locations during the rainy season.

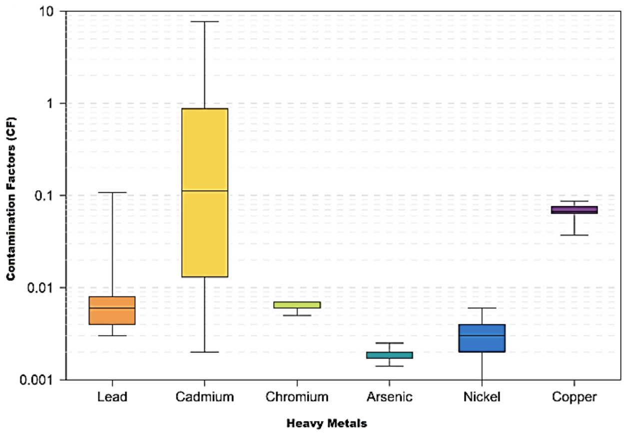

Figure 4: Contamination factors of heavy metals in stream sediments in the study locations in the dry season

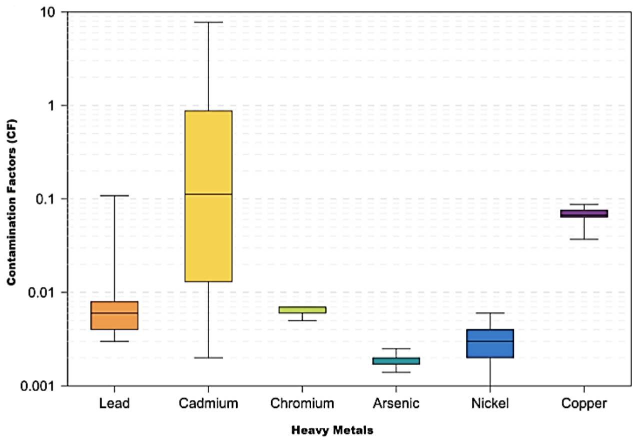

Figure 5: Contamination factors of heavy metals in stream sediments in the study locations in the rainy season

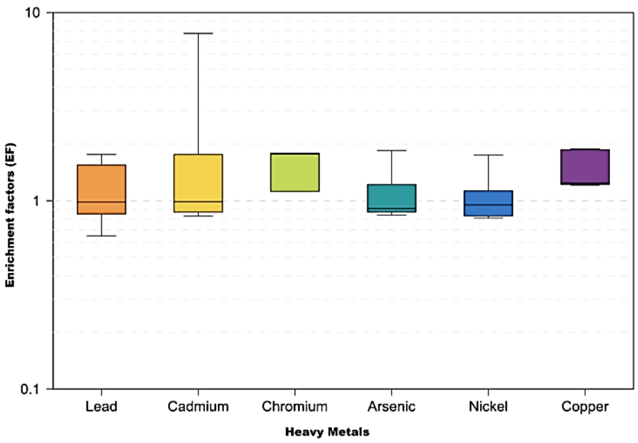

Figure 6: Enrichment factors of metals in stream sediments of the study area in the dry season

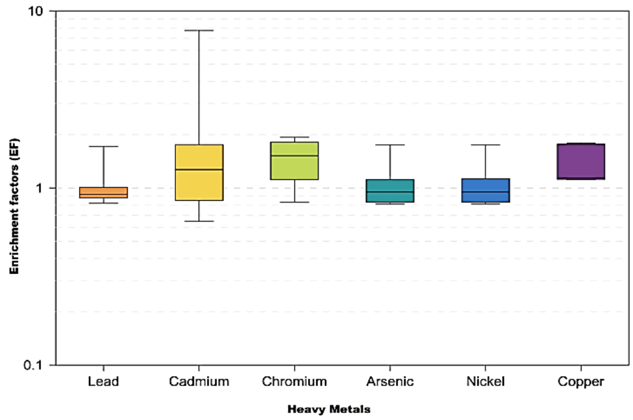

Figure 7: Enrichment factors of metals in stream sediments of the study area in the rainy season.

3.4 Correlation Analysis

The geochemical data was statistically examined using Pearson's Correlation to determine the important correlations between the heavy metals studied. The Pearson correlation results are presented in Tables 5 – 6. From the correlation matrix given in Table 5, there was a significant correlation among the heavy metal levels in the sediment samples during the rainy season. When the p-value is less than 0.05, the correlation is considered to be significant. Lead had a strong positive correlation with Arsenic with a correlation value of 0.971 and a *p*-value of 0.000. Cadmium had a strong positive correlation with both Zinc and Nickel. Their correlation values are 0.915 and 0.805 respectively while their *p*-values are 0.001 and 0.009.

Copper has a strong positive correlation with Zinc with a correlation value of 0.866 and a p-value of 0.003. Zinc had a strong positive correlation with Nickel, with a correlation value of 0.789 while *p*-value of 0.012. During the dry season, the Pearson correlation of heavy metal concentrations in the sediments of the studied area revealed significant correlations. Lead had a strong positive correlation with Arsenic with a correlation value of 0.789 and a *p*-value of 0.012. Cadmium had a strong positive correlation with both Zinc and Nickel. Their correlation values are 0.678 and 0.800 respectively while their *p*-values are 0.045 and 0.010. Copper has a moderate positive correlation with Zinc with a correlation value of 0.675 and a *p*-value of 0.046.

Table 6: Pearson Correlation Coefficient of Heavy Metal Concentrations in The Sediments of Warri River During The Rainy Season.

	Pb	Cd	Cr	As	Cu	Fe	Zn	Ni
Pb	1							
Cd	.046	1						
Cr	-.282	.244	1					
As	.971**	.130	-.215	1				
Cu	.532	.664	.217	.601	1			
Fe	.292	.146	-.288	.284	.105	1		
Zn	.222	.915**	.300	.270	.866**	.129	1	
Ni	-.073	.805**	.413	-.101	.432	.192	.789*	1

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 7: Pearson Correlation Coefficient of Heavy Metal Concentration in Sediments of Warri River During The Dry Season.

	Pb	Cd	Cr	As	Ni	Cu	Fe	Zn
Pb	1							
Cd	-.123	1						
Cr	-.208	.190	1					
As	.789*	-.093	-.135	1				
Ni	-.006	.678*	.311	-.379	1			
Cu	.539	.403	.378	.479	.444	1		
Fe	.203	.258	-.252	.223	.019	.178	1	
Zn	.041	.800**	.145	.166	.539	.675*	.129	1

3.5 Clustering Analysis

The heavy metal source apportionments in stream sediment samples are shown using cluster multivariate analysis. Cluster multivariate analysis of the metal content of sediment sample collected in the dry season followed a similar trend with the rainy season results. From the dendrograms two cluster groups were identified, there were two types of sources: crustal or geogenic (Iron) and anthropogenic (Fe, Cd, As, Ni, Pb, Cr, Cu and Zn).

4. Conclusion

Due to urbanization and increasing population, Warri River receives industrial and domestic waste from various sources in addition to discharge from drains and as a result of several activities which occur along its banks. Anthropogenic activities identified to contribute to heavy metal contamination in this present work were discharge of untreated effluent, sewage disposal, urban storm, water runoff, leaching of metals, and hazardous e-waste from garbage and open waste dump sites oil spillage, agrochemicals and wastewater used for irrigation. More so, considerable amounts of heavy metal may enter the study area through precipitation and atmospheric deposition. The weathering of parent rocks was identified as the primary source of heavy metals in the study area.

The stream sediments of the research area were found to be unpolluted when contamination indexes such as enrichment factor, geo-accumulation index, and contamination factor values were computed from heavy metal concentrations. It was therefore concluded that the metals had not accumulated significantly. Pearson's correlation analysis for the dry and rainy seasons showed significant correlations among the heavy metal concentration in the sediment samples. Hierarchical cluster analysis (HCA) revealed that the heavy metals in all the samples were associated with two cluster groups of anthropogenic and geogenic sources. When compared to the data obtained during the wet season, all of the heavy metals examined had higher concentrations during the dry season; however, the differences observed in the seasons were not significant.

However, the metal concentrations in the sediment were elevated at some sampled points. Based on the aforementioned, it is therefore recommended that annual monitoring of the stream sediments of the study area is undertaken. Monitoring the physiochemical characteristics and sediment quality of Warri River is important because it will aid in preserving and restoring its biological integrity, as well as protecting aquatic life and human health. Also, sustainable practices should be employed in order to conserve the resources of the Warri River. Mitigation measures such as establishing water protection areas and imposing penalties for illegal activities that degrade the river are required to reduce heavy metal influx into the river by anthropogenic activities.

References

Adamu, C.I., Nganje, T.N., Edet, A., 2014. Heavy Metal Contamination and Health Risk Assessment Associated with Abandoned Barite Mines in Cross River State, Southeastern Nigeria. Journal of Environmental Nanotechnology, Monitoring & Management, 3, Pp. 10-21.

Adelekan, B., Abegunde, K., 2011. Heavy metal contamination of soil and ground water at automobile mechanic village in Ibadan, Nigeria. International Journal of the Physical Sciences, 6 (5), Pp. 1045-1058.

Akoto, O., Ephraim, J.H., Darko, G., 2008. Heavy metal pollution in surface soils in the vicinity of abundant railway servicing workshop in Kumasi, Ghanaian. Journal of Environmental Resources, 2 (4), Pp. 359–364.

Akpoborie, I.A., 2011. Aspects of the Hydrology of the Western Niger Delta Wetlands: Groundwater conditions in the Neogene (Recent) deposits of the Ndokwa Area. Proceedings of the Environmental Management Conference: Managing Coastal and Wetland Areas of Nigeria, Sept. Pp. 12-14, Abeokuta.

Allen, S.E., Grimshaw, H.M., Rowland, A.P., 1986. Chemical analysis. P.D. Moore, S.B. Chapman (Eds.), Methods in Plant Ecology, Blackwell Scientific Publication, Oxford, London, Pp. 285-344.

Alloway, B.J., 1995. The Origins of heavy Metals in Soils. In B. J. Alloway (Ed.) Heavy Metals in Soils, Blackie Academic and professional, Pp. 38 – 57.

Andem, A.B., Okorafor, K.A., Oku, E.E., Ugwumba, A.A., 2015. Evaluation and Characterization of Trace Metals Contamination in the Surface Sediment Using Pollution Load Index (PLI) and Geo-Accumulation Index (Igeo) Of Ona River, Western Nigeria. International Journal of Scientific and Technological Research, 4 (1), Pp. 29-34.

Argese, E., Bettiol C., 2001. Heavy metal partitioning in sediments from the lagoon of Venice (Italy). Toxicological and Environmental Chemistry, 79 (3-4), Pp. 157-170.

Bonnail, E., Sarmiento, A.M., Del T.A., Valls, J.M., Riba, I., 2016. Assessment of metal contamination, bioavailability, toxicity and bioaccumulation in extreme metallic environments (Iberian Pyrite Belt) using Corbicula fluminea. Science of Total Environment, 544 (2), Pp. 1031-1044.

Calmano, W., Hong, J., Forstner, U., 1993. Binding and Mobilization of Heavy Metals in Contaminated Sediments Affected by pH and Redox Potential. Water Science & Technology 28 (8-9), 223-235.

Daskalakis, K.D, O'connor, T.P., 1995. Distribution of chemical concentrations in US coastal and estuarine sediment. Marine Environmental Research, 40 (4), Pp. 381-398.

Davies, O.A., Allison, M.E., Uyi, H.S., 2006. Bioaccumulation of heavy metals in water, sediment and periwinkle (Tympanotonus fuscatus var radula) from the Elechi Creek, Niger Delta. African Journal of Biotechnology, 5 (10), Pp. 968-973.

Fagbote, E.O., Olanipekun, E.O., 2010. Evaluation of the status of heavy metal pollution of sediment of Agbabu bitumen deposit area Nigeria. European Jour. f Scientific Research, 41 (3), Pp. 373–382.

Hanif, N., Equani, S.A.M.A.S., and Ali, S.M., 2016. Geo-accumulation and enrichment of trace metals in sediments and their associated risks in the Chenab River, Pakistan. Journal of Geochemical Exploration, 165, Pp. 62 – 70.

Iwuoha, G.N., Osuji, L.C., Horsfall, M. (Jnr). 2012. Index Model Analysis Approach to Heavy Metal Pollution Assessment in Sediments of Nworie and Otamiri Rivers in Imo State of Nigeria. Research Journal of Chemical Sciences, 2 (8), Pp. 1 - 8.

Izah, S.C., Anganye, T.C.N., 2016. Heavy metal concentration in fishes from surface water in Nigeria: Potential sources of pollutants and mitigation measures. Sky Journal of Biochemistry Research, 5 (4), Pp. 31 – 47.

Li, Q., Wu, Z., Chu, B., Zhang, N., Cai,S., Fang, J., 2007. Heavy metals in coastal sediments of the Pearl River Estuary, China. Environmental Pollution, 149, Pp. 158–164.

Lin, Q., Liu, E., Zhang, E., Li, K., Shen, J., 2016. Spatial distribution, contamination and ecological risk assessment of heavy metals in surface sediments of Erhai Lake, a large eutrophic plateau lake in southwest China. Catena, 145, Pp. 193-203.

Muller, G., 1969. Index of geoaccumulation in sediments of the Rhine River. Geojournal, 2, Pp. 108 – 18.

NEDECO (Netherlands Engineering Consultants). 1954. The waters of the Western Niger Delta. The Hague, (2nd) Revised edition.

Nigerian Meteorological Agency (NIMET). 2003. Asaba Meteorological Bulletin‖. In: National Meteorological Report.

Nwadinigwe, C.A., Nworgu, O.N., 1999. Metal contaminants in some Nigerian wellhead's crudes, a comparative analysis. Journal of Chemical Society of Nigeria, 24, Pp. 118-121.

Nwajide, C.S., 2013. Geology of Nigeria's Sedimentary Basins. CSS Bookshop Ltd., Lagos.

Nyamangara, J., and Mzezewa, J., 1999. The effects of long-term sewage sludge application on Zn, Cu, Ni and Pb levels in clay loam soil under pasture grass in Zimbabwe. Agri. Ecosys. Environ., 73, Pp. 199-204.

Olobaniyi, S., Ogala, B., Nfor, N.B., 2007. Hydrogeochemical and Bacteriological Investigation of Groundwater in Agbor Area, Southern Nigeria‖. Journal of Mining and Geology, 43 (1), Pp. 79-89.

Ong, M.C., Kamaruzzaman, Y., 2019. Sediment and Organisms as Marker for Metal Pollution. DOI: 10.5772/intechopen.85569

Rastmanesh, F., Moore, F., Kopaei, M.K., Keshavarzi, B., Behrouz, M., 2010. Heavy metal enrichment of soil in Sarcheshmeh Copper Complex, Kerman Iran. Environ. Earth Sci., 62, Pp. 329-336.

Remeikaite-Nikiene, N., Garnaga-Burde, G., Lujaniene, G., Joksas, K., Stankevicius, A., Bariseviciute, R., 2018. Distribution of metals and extent of contamination in sediments from the south-eastern Baltic Sea (Lithuanian zone). Oceanologia, 60 (2), Pp. 193-206.

Rubio, B., Nombela, M.A., Vilas, F., 2000. Geochemistry of major and trace elements in Ssediments of the Ria de Vigo (NW Spain): An assessment of metal pollution. Marine Pollution Bulletin, 40 (11), Pp. 968-980.

Sekabira, K., Oryem, H.O., Basamba, T. A., Mutumba, G., Kakudidi, E., 2010. Assessment of heavy metal pollution in the urban stream sediments and it, tributaries. Intern. Journal of Environment, Science and Technology, 7 (3), Pp. 435-446.

Siegel, F.R., 2002. Environmental Geochemistry of potentially toxic metals. New York: Springer.

Singh M.R., Gupta, A., Beeteswari, K.H., 2010. Physico-Chemical Properties of Water Samples from Manipur River System, India. Journal of Applied Science and Environment, 14 (4), Pp. 85 – 89.

Surthland, R.A., Tolosa, C.A., Tack, F.M.G., Verloo, M.G., 2000. Characterization of elected element concentrations and enrichment ratios in background and anthropogenically impacted roadside areas. Arch. Environ. Contamination Toxicology, 38 (4), Pp. 428-48.

Tavakoly, S.B., Sulaiman, A.H., Monazami, G.H., Salleh, A., 2011. Assessment of sediment quality according to heavy metal status in the West Port of Malaysia. World Academy of Science, Engineering and Technology International Journal of Geological and Environmental Engineering, 5 (2), Pp. 111-115.

Taylor, S.R., McLennan, S.M., 1985. The continental crust: its composition and evolution. Blackwell Publications, Oxford.

Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the elements in Some Major Units of the Earth's Crust. Geological Society of America. Bulletin, 72, Pp. 175-192.

Voet, E., Guinee, B., Udode, H., 2008. Heavy metals: A problem solved?. Dordrecht, Netherlands: Kluwer Academic.

Wang, Y.Q., Yang, L.Y., Kong, L.H., Liu, E.F., Zhu, J.R., 2015. Spatial distribution, ecological risk assessment and source identification for heavy metals in surface sediments from Dongping Lake, Shandong, East China. Catena, 125 (3), Pp. 200-205.

Wuana, R.A., Okieimen, F.E., 2011. Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry, Risks and Best Available Strategies for Remediation. International Scholarly Research Notices.

Zahra, A., Hashimi, M.Z., Malik, R.N., 2014. Enrichment and geo-accumulation of heavy metals and risk assessment of sediments of the Kurang Nallah feeding tributary of the Rawal Lake Pakistan. Science of Total environment, Pp. 925-933.

Zhang and Liu, 2002. Riverine Composition and Estuarine Geochemistry of Particulate Metals in China—Weathering Features, Anthropogenic Impact and Chemical Fluxes. Elsevier: Estuarine, Coastal and Shelf Science, 54 (6), Pp. 1051- 1070.

Zheng, N., Wang, Q., Liang, Z., Zheng, D., 2008. Characterisation of heavy metal concentrations in the sediments of three freshwater rivers in Huludao City, Northeast China. Journal of Environmental Pollution, 154 (1), Pp. 135-142.