

Assessment of Cobalt, Manganese and Lead Pollution in Sediments from the Bank of Komadugu River in Gashua, Yobe State, Nigeria

Dagari M.S.^{1*}, Saleh I. S.² and Kanada Y.B³

^{1,2}Department of Chemistry, Faculty of Science, Federal University, Gashua, P. M. B. 1005, Gashua, Yobe State, Nigeria

³Department of Science Laboratory Technology, Ramat Polytechnic, Maiduguri, Borno State, Nigeria

Abstract: This study aims at assessment of sediment contamination by cobalt (Co), manganese (Mn) and lead (Pb) in four sampling points at the bank of Komadugu River in Gashua, Yobe State. After microwave digestion of the sediments, the extracts were analyzed for Mn, Co and Pb. Concentrations of Mn, Co and Pb, were below the limits set by the World Health Organization (WHO), United States Environmental Protection Agency (USEPA), Average Shell Value (ASV), Toxicity Reference Value (TRV), Indian River System (IRS) and World River System (WRS). The contamination factors as well as the degree of contamination of Mn, Co and Pb indicated low contamination of the sampling sites by Hakanson (1980) classification. The geo-accumulation indices of the metals were all negative, indicating that the sample sites were practically uncontaminated with the elements by Muller (1979) classification.

Keywords: Assessment; Sediment; Geo-accumulation indices; Hakanson (1980) classification; Muller (1979) classification

1. Introduction

Heavy metal pollution has gradually become a major concern worldwide. Nowadays, anthropogenic activities are the major causes of contamination of water columns of rivers and lakes (Theofains *et al.*, 2001; Arribera *et al.*, 2002). In aquatic environments, heavy metal is usually distributed in the order: of water-soluble species, colloids, suspended forms and sedimentary phases. However, unlike organic pollutants, natural processes of decomposition do not remove heavy metals (Akçay *et al.*, 2003; Susana *et al.*, 2005). On the contrary, they are usually enriched in sediment by organisms or some other compounds. In some conditions, more than 99% of heavy metal entering into river can be stored in river sediments in various forms. However, heavy metals cannot be fixed in sediment forever. With the variation of the physical–chemical characteristics of water conditions, part of these fixed metals will re-enter the overlying water and become available to living organisms. Thus, sediment often acts as both carriers and potential sources of metals in aquatic environments (Theofains *et al.*, 2001).

2. Materials and Methods

2.1 The Study Area

The Yobe River, also known as the Komadugu Yobe River is a river in West Africa that flows into Lake Chad through Nigeria and Niger. In Yobe State, it is located on longitude 12°52'N and latitude 10°58'E in Gashua, Bade Local Government Area. Its tributaries include River Hadejia, River Jama'are, and the Komadugu Gana River. The river forms a small part of the international border between Niger and Nigeria with 150 km and flows a total of 320 km (KYBP, 2006). There are concerns about changes in the river flow, economy and ecology due to upstream dams, the largest at present being the Tiga Dam in Kano State, with plans for the Kafin Zaki dam in Bauchi State (NPC, 2006). The River Yobe provides a means of subsistence for hundreds of thousands of people who work in a variety of commercial and agricultural endeavours along its almost 200 km length in the state's northern region, which spans seven local government areas (LGAs) from Nguru to Yunusari. Notable towns near the river include Gashua, Geidam and Damasak in Nigeria, and Diffa in Niger (Wakawa *et al*, 2017).

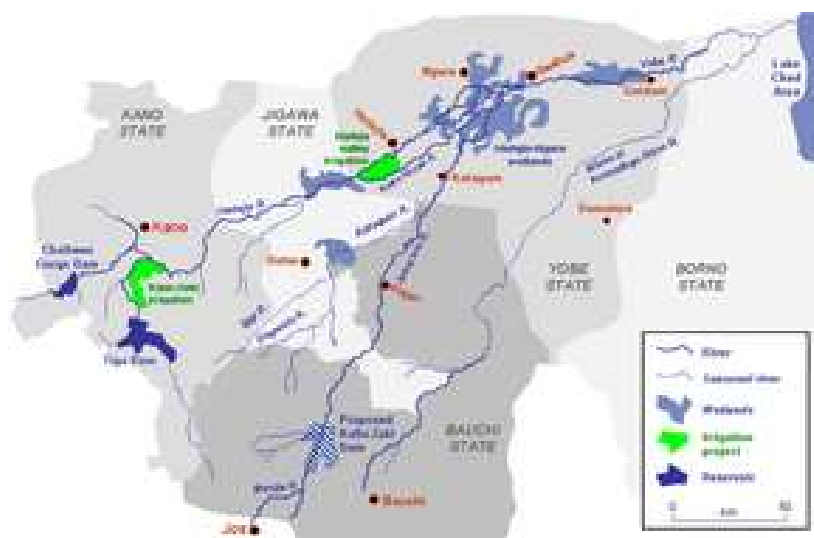


Figure 1: Catchment Area of the Komadugu River

2.2 Instruments, Apparatus and Reagents

All equipment and instruments used in this research were calibrated before conducting the experiments. All glassware used were thoroughly washed with detergents and tap water and then rinsed with deionized water. Suspected contaminants wares were cleaned with 10% concentrated nitric acid (HNO_3) and metal surfaces rinsed with deionized water. The digestion tubes were soaked with 1% (w/v) potassium dichromate in 98% (v/v) H_2SO_4 .

In preparation of reagents, chemicals of analytical grade purity and distilled water were used. All glassware and plastic containers were washed with detergents.

2.3 Digestion of Sediment Samples

The sediment samples were allowed to dry in a hot oven (Model 30GC). After removing the debris and grinding into fine powder by using a porcelain mortar and pestle, it was sieved through a 2mm mesh. A microwave digester (Master 40 serial No: 40G106M) was used in digesting the sediment samples in a digestion tube to which 0.1g of sample was added at a time, followed by 6mL of 65%

HNO₃ and 2mL of 30% H₂O₂ and allowed to stand for a while. The digestion was carried out at 180°C, 1800W in a time of 30mins. The digestion was followed by cooling at room temperature in the microwave and the sample was diluted with de-ionized water. Potential presences of selected heavy metals in chemicals used in digestion were determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality (SINEO, 2013).

2.4 Atomic Absorption Spectrometric Analysis

The sediment extracts were analyzed for cobalt (240.7nm), manganese (279.5nm) and lead (283.5nm) using flame atomic absorption spectrophotometry. Blank determinations were made prior to sample analysis. Heavy metal concentrations in sediment extracts were obtained in triplicates from calibration curves and expressed as mg/kg. Metals in chemicals used in digestion were determined. Blanks were used simultaneously in each batch of the analysis to authenticate the analytical quality (SINEO, 2013).

2.5 Statistical Analysis

The data were analyzed in triplets and expressed as mean and standard deviation. The mean of all treatments was subjected to a One-way analysis of variance (ANOVA) using IBM SPSS Statistics 23 software and mean differences were performed using the Tukey test. All graphs were plotted using Microsoft Excel 2013.

3. Results and Discussion

3.1 Heavy Metal Pollution in Aquatic Environment

Increasing pollution by heavy metals in aquatic environment brought about by urbanization and industrialization have significant adverse health effects on invertebrates, fish and humans (Yi *et al.*, 2011; Islam *et al.*, 2014; Mir *et al.*, 2016). In aquatic environment, sediments have been widely used as environmental indicators for assessment of metal pollution in natural water. Assessment of heavy metal contamination in sediments is an indispensable tool to assess the risk of an aquatic environment. It is therefore necessary to investigate the current status of heavy metals in sediments of River Yobe in Gashua for a healthier community.

3.2 Abundance of Heavy Metals in Surface Sediments

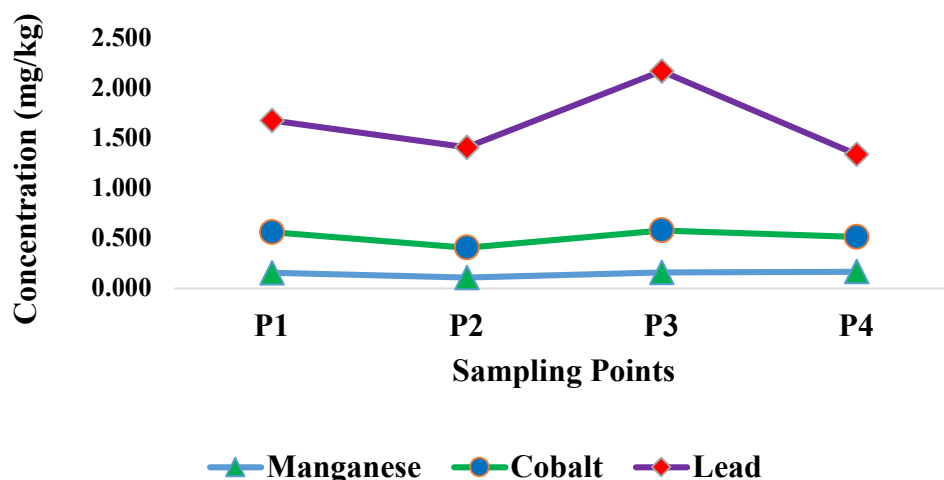
The maximum and minimum values of cobalt, manganese and lead in the sample points P1, P2, P3 and P4 are shown in the table below

Table 1: Concentrations of Cobalt, Manganese and Lead in Sediments

Sample Point	Co (mg/kg)		Mn (mg/kg)		Pb (mg/kg)	
	Min.	Max.	Min.	Max.	Min.	Max.
P1	0.265	0.623	0.145	0.165	1.050	1.210
P2	0.275	0.324	0.099	0.120	0.800	1.200
P3	0.376	0.464	0.149	0.168	1.360	1.820
P4	0.265	0.426	0.145	0.184	0.680	0.980

Cobalt, manganese and lead were detected in sediments collected from the four sample points. The concentrations of Co, Mn and Pb ranged from 0.265 - 0.623, 0.099 – 0.184 and 0.680 – 1.820 mg/kg respectively. Average concentrations of cobalt, manganese and lead in sediments are shown in **figure 2**.

Figure 2: Concentrations of Cobalt, Lead and Manganese in Sediments



3.2.1 Cobalt

Average concentrations of cobalt in sediment samples ranged from 0.298 ± 0.02 to 0.420 ± 0.04 mg/kg which are below the permissible limits of 50 mg/kg set by USEPA, 19 mg/kg by Average shale value (ASV) (Turekian and Wedepohl, 1961) and 20 mg/kg by World River System (WRS) (Martin and Meybeck 1979). They are also below the values reported by Huang *et al.*, (2020): 1.88 – 30.88 mg/kg; Hernández -Mendoza *et al.*, (2011): 3.2 ± 0.3 – 9.3 ± 0.2 mg/kg, Guilherme *et al.*, (2011): 6.5 ± 3.2 mg/kg. P3 had the highest value of 0.420 ± 0.04 mg/kg while P1, P2 and P4 had 0.403 ± 0.19 mg/kg, 0.298 ± 0.02 mg/kg and 0.346 ± 0.08 mg/kg respectively. The results followed the order of $P3 > P1 > P4 > P2$.

Cobalt is essential for human health because it is a part of vitamin B₁₂. It is used to treat anaemia in pregnant women because it stimulates the production of red blood cells. Very high concentration of Co may damage human health, causing lung effects like asthma and pneumonia (Frank and Cleon, 1992).

3.2.2 Manganese

The manganese concentrations in sediment samples were found to be in the range 0.106 ± 0.01 to 0.166 ± 0.02 mg/kg, which are below the permissible limit of 200 mg/kg set by WHO and values reported by Perumal *et al.*, (2021): 425 – 896 mg/kg and Hernández – Mendoza *et al.*, (2018): 269.1 ± 5.5 – 654.7 ± 33.3 mg/kg. P4 has the highest Mn concentration of 0.166 ± 0.02 mg/kg. Concentrations of Mn in other sample points are P1 with 0.155 ± 0.01 mg/kg, P2 with 0.106 ± 0.01 mg/kg and P3 with 0.156 ± 0.01 mg/kg. The concentrations are in the order $P4 > P3 > P1 > P2$.

For animals, manganese is an essential component of over 36 enzymes that are used for carbohydrate, protein and fat metabolism. With animals that eat too little, manganese interference of normal growth, bone formation and reproduction will occur. For some animals the lethal dose of manganese when these exceed the essential dose. Manganese substances can cause lung liver and vascular disturbances, declines in blood pressure, failure in development of animal fetuses and brain damage. In plants, manganese ions are transported to the leaves after uptake from soils. When too little manganese can be absorbed from the soil this causes disturbances in plant mechanisms such as disturbance of the division of water to hydrogen and oxygen, in which Mn plays an important part. Mn can cause both toxicity and deficiency symptoms in plants. Manganese deficiencies are more common in soils with low pH values. Highly toxic concentrations of Mn in soil can cause swellings of cell walls, withering of leaves and brown sports on leaves (Lenntech, 2004; Frank and Cleon, 1992).

3.2.3 Lead

Concentrations of lead in sediment samples was ranged from 1.113 ± 0.09 to 0.823 ± 0.15 mg/kg which are below the permissible limits 70, 35.5, 20m and 31mg/kg set by World Health Organization (WHO), United States Environmental Protection Agency (USEPA), Average shale value (ASV) and Toxicity Reference Value (TRV) respectively, and values reported by Huang *et al.* (2020): 23.3-359.4 mg/kg, Perumal *et al.* (2021): 10.2-19.5mg/kg and Hernández -mendoza *et al.* (2018): $147.2 \pm 61 - 444.3 \pm 13.3$ mg/kg. P3 had the highest Pb concentration of 1.587 ± 0.23 mg/kg. Concentrations of Pb in other sample points were; P1 with 1.113 ± 0.09 mg/kg, P2 with 1.000 ± 0.20 mg/kg while P4 had the lowest Pb concentration of 0.823 ± 0.15 mg/kg. Concentration of Pb in the samples was found to be in the order $P3 > P1 > P2 > P4$.

Lead (Pb) is one of the oldest heavy metals used in the past for hair dyes, insecticides, and pottery glazes (Ye and Wong, 2006). It is a naturally occurring bluish-gray metal, highly malleable and ductile and shiny when just cut. Lead is also found in the environment as a result of radioactive decompositions, because it is a natural product of the decay of uranium. Lead is a dense metal, with a specific gravity of 11.35 and an atomic weight of 207.2 gmol^{-1} . It is present in many inorganic forms (acetates, nitrates, carbonates, sulphates and chlorides) especially in the earth's crust and ores (Enghag, 2004).

3.3 Pollution Indices of Heavy Metals in Sediments

The two most commonly used criteria to evaluate the heavy metal pollution in sediments are the geo-accumulation index (I_{geo}) and contamination factor (C_f) (Saha and Hossain, 2011).

3.3.1 Contamination Factor

Contamination factor (C_f) is a ratio of the measured concentration of a metal in a sediment to its background concentration;

$$C_f = \frac{\text{Measured Concentration}}{\text{Background Concentration}} \dots\dots\dots (1)$$

The degree of contamination is the sum of all contamination factors

$$D C = \sum_{i=1}^n C_{f_i} = C_{f_1} + C_{f_2} + \dots + C_{f_n} \dots\dots\dots(2)$$

The background concentration is the world geochemical background value in average shale (Turekian and Wedepohl, 1961). The average shale values of the heavy metals under investigation are; Co = 19, Mn = 800, Pb = 20,

Table 2: Contamination Factor and Level of Contamination (Hakanson, 1980)

Contamination Factor (C_f)	Level of Contamination
$C_f < 1$	Low contamination
$1 \leq C_f < 3$	Moderate contamination
$3 \leq C_f < 6$	Considerable contamination
$C_f > 6$	Very high contamination

3.3.2 Geo-accumulation Factor (I_{geo})

Geo-accumulation factor (I_{geo}) which was originally defined by Muller (1979) to determine metals contamination in sediments, by comparing current concentrations with pre-industrial levels and can be calculated by the following equation;

$$I_{geo} = \log_2 \left(\frac{C_n}{1.5 B_n} \right) \dots\dots\dots(3)$$

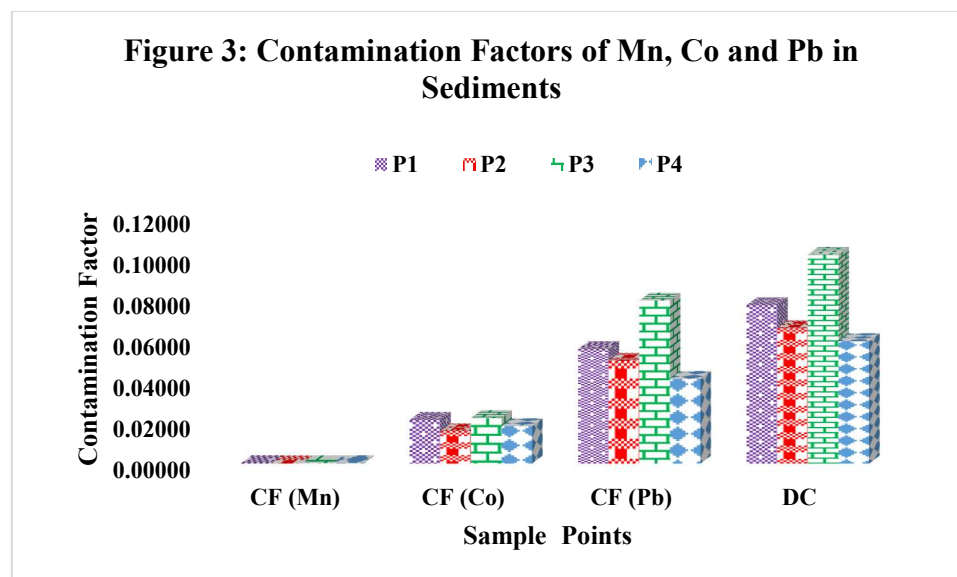
Where, C_n is the concentration of element 'n' and B_n is the geochemical background value. The geo-accumulation index (I_{geo}) scale consists of seven grades (0-6) ranging from unpolluted to extremely polluted as shown in **table 2**.

Table 3: Muller's Classification for Geo- accumulation Index

I_{geo} Value	Class	Sediment Quality
≤ 0	0	Unpolluted
0 -1	1	From unpolluted to moderately polluted
1 -2	2	Moderately polluted
2 -3	3	From moderately to strongly polluted
3 -4	4	Strongly polluted
4 - 5	5	From strongly to extremely polluted
> 6	6	Extremely polluted

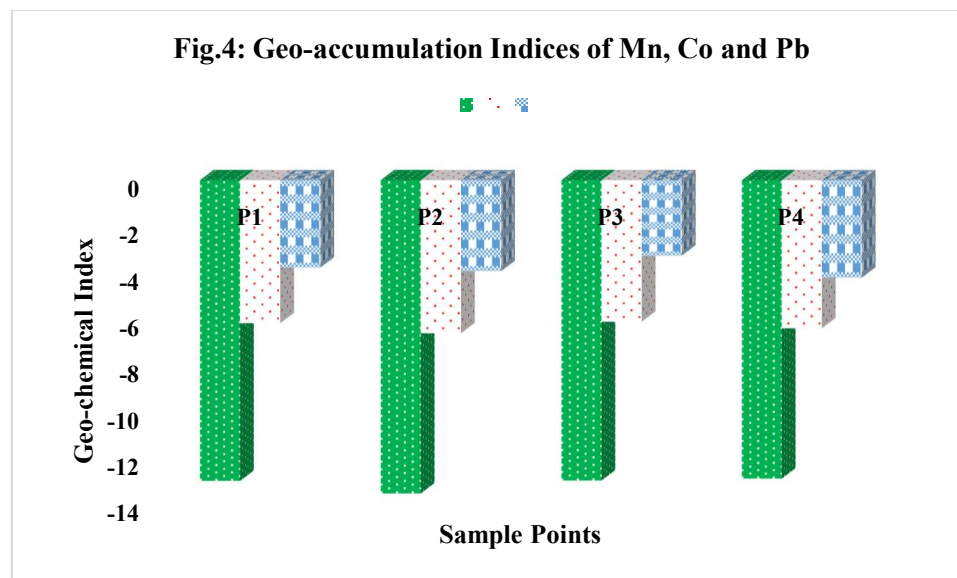
3.4 Assessment of Heavy Metal Pollution in Sediments

The contamination factors of Mn, Co and Pb in the sampling sites are shown on **figure 3**.



The contamination factors of Mn, Co and Pb were in the range 0.00013 to 0.00021, 0.01570 to 0.02212, 0.04117 to 0.07933 respectively. The degree of contamination varied from 0.05957 to 0.10165, which by Hakanson (1980) classification indicate low contamination by Mn, Co and Pb of the sampling sites. The level of contamination by the metals was in the order Pb > Co > Mn.

Figure 4 shows the geo-accumulation indices of Mn, Co and Pb in the sampling sites.



The geo-chemical indices of Mn, Co and Pb were in the range -13.4622 to -12.9216, -6.5779 to -6.0833 and -4.1873 to -3.2409 respectively. All geo-chemical indices of the elements were negative, indicating that the sample sites were practically uncontaminated with Mn, Co and Pb by Muller (1979) classification. For all sample sites the geo-chemical indices decreased in the order Mn > Co > Pb.

4. Conclusion

Assessment of pollution status of sediments collected at the bank of Komadugu River in Gashua, Yobe State revealed that the contamination factors as well as the degree of contamination of Mn, Co and Pb indicated low contamination of the sampling sites by Hakanson (1980) classification. The geo-accumulation indices of the metals were all negative, indicating that the sample sites were practically uncontaminated with the elements by Muller (1979) classification.

Acknowledgement

The authors are grateful to Mal. Idris Baba of Chemistry Research Laboratory, Yobe State University, Damaturu for his invaluable contribution in the sample analysis.

Authors' Contributions

Dagari M.S.: Conceptualization, design and supervision of the research work; Editing of the write-up

Saleh I. S.: Undertaking the research work, write-up and data analysis.

References

- Akcay, H., Oguz, A. and Karapire, C. (2003). Study of Heavy Metal Pollution and Speciation in BuyakMenderes and Gediz River Sediments, *Water Res.* 37:813–822.
- Arribere, M. A., Ribeiro, G. S., Sanchez, R. S., Gil. M. I., Roman, R. G., Daurade, L. E., Fajon, V., Horvat, M., Alcalde, R. and Kestelman, A. J. (2002). Heavy Metals in the Vicinity of Achlor-alkali Factory in the Upper Negro River Ecosystem, Northern Patagonia, Argentina, *Sci. Total Environ.* 301: 187–203.
- Enghag, P. (2004). *Encyclopedia of the Elements; Technical Data History Processing Applications.* Weinheim. WILEY-VCH Verlag GmbH & Co. KGaA.
- Frank, B. S. and Cleon, W. R. (1992). *Mineral Nutrition, Plant Physiology*, 4th edn., Wardsworth Publishing Company, Belmont, California USA, Pp 116–129.
- Guilherme, M. Guimarães, Robson, L., Franklin, Ana, M.G., Figueiredo1 Paulo., Silva1 S.C., Déborah I. and Fávaro, T. (2011). Enrichment Factor and Geoaccumulation Index Applied to Sediment Samples from the Guarapiranga Reservoir, Brazil, for Metal and trace element Assessment, *2011 International Nuclear Atlantic Conference - INAC 2011 Belo Horizonte, MG, Brazil, ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN* ISBN: 978-85-99141-04-5.
- Hakanson, L. (1980), “An Ecological Risk Index for Aquatic Pollution Control, A Sedimentological Approaches, “*Water Research*, 14, 975– 1001

- Hernández-Mendoza, H., Ríos-Lugo, M. J., Romero-Guzmán, E. T., Reyes Gutiérrez, L. R. and Ketterer, M. E. (2018). Heavy Metals Monitoring in Sediments from Lerma River in West-Central Mexico, *American Journal of Analytical Chemistry*, 9:77-87.
- Huang, Z., Liu C., Zhao, X., Dong, J. and Zheng, B. (2020). Risk Assessment of Heavy Metals in the Surface Sediment at the Drinking Water Source of the Xiangjiang River in South China, *Environmental Sciences Europe*, 32: 23, 2 -9.
- Islam, M. S., Ahmed, M. K., Habibullah-AlMamun, M., Islam, K. N., Ibrahim M. and Masunaga, S. (2014). Arsenic and Lead in Foods: A Potential Threat to Human Health in Bangladesh, *Food Addit. Contam. Part A*, 31(12):1982–1992.
- KYBP (2006). *Komadugu Yobe Basin Water Audit Report* by Afremedev Consultancy Services Limited for FMWR IUCN-NCF Komadugu Yobe Basin Project, Kano, Nigeria
- Lenntech, (2004). http://www.lenntech.com/periodic-chart-element/fe.mn.Zn_and_nien.htm. Retrieved on 14/3/2009.
- Martin, J. M. and Meybeck, M. (1979). Elemental Mass Balance of Materials Carried by Major World Rivers, *Mar Chem.*, 7:173-206.
- Mir, M. A., Mohammad, L. A., Saiful, I. and Zillur, R. (2016). Preliminary Assessment of Heavy Metals in Water and Sediment of Karnaphuli River, Bangladesh. *Environ. Nanotechnology, Mon. & Manag.* 5:27-35.
- Muller, G. (1979). Heavy Metals in the Sediment of the Rhine-Changes Seity. Umschau in *Wissenschaft and Technik*, 79:778-783
- NPC (2006). National Population Commission, <http://www.population.gov.ng>
- Perumal, K., Antony, J. and Muthuramalingam, S. (2021). Heavy Metal Pollutants and their Spatial Distribution in Surface Sediments from Thondi Coast, Palk Bay, South India, *Environ Sci Eur.*, 33:63, <https://doi.org/10.1186/s12302-021-00501-2>
- Saha, K. M. and Hossain, M. S. M. (2011). An Analysis of Present Production and Marketing Situation in Bangladesh, *Hortex Foundation Newsl*, 11:1-8.
- SINEO (2013). Operating Manual of Master 40 Microwave Digester.
- Susana, O.R., Daniel, D. L. R., Lazaro, L., David, W. G., Katia, D.,A., Jorge, B. and Francisco, M. (2005). Assessment of Heavy Metal Levels in Almendares River sediments—Havana City, Cuba, *Water Res.*, 39: 3945–3953.

- Theofanis, Z. U., Astrid, S., Lidia, G. and Calmano, W. G. (2001). Contaminants in sediments: Remobilisation and Demobilization, *Sci. Total Environ.*, 266(1):195-202.
- Turekian, K. K. and Wedepohl, K. H. (1961). Distribution of the Element in some Major Units of the Earth's Crust. *Geological Society of America Bulletin*, 72:175-192.
- Wakawa LD, Suleiman AA, Ibrahim Y, Adam LI (2017). Tree Species Biodiversity of a Sahelian Ecosystem in North-East Nigeria. *Bartın Orman Fakültesi Dergisi*, 19(2): 166-173.
- Ye, X. and Wong, O. (2006). Lead Exposure, Lead Poisoning, and Lead Regulatory Standards in China, 1990-2005. *Regul Toxicol Pharmacol.*, 46(2):157-62.
- Yi, Y., Yang, Z. and Zhang, S. (2011). Ecological Risk Assessment of Heavy Metals in Sediment and Human Health Risk Assessment of heavy Metals in Fishes in the Middle and Lower Reaches of the Yangtze River basin. *Environ. Pollut.*, 159:2575–2585.