Chemistry Research Journal, **2018, 3(2):66-77**

Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

Pollution Assessment of Heavy Metals in Water and Sediment from Mpape River in FCT, Abuja, Nigeria

Eze O.C.[*], Tukura B.W., Atolaiye B.O., Opaluwa, O.D.

Department of Chemistry Department, Nasarawa State University, Keffi, Nasarawa State Nigeria

Abstract Levels of heavy metals (Cr, Mn, Cu, Fe, Zn, Cd, Ni, Pb) in water and sediment from Mpape River in FCT, Abuja were assessed. The study was carried out between 2015 and 2017. Water and Sediment samples were collected from five sites during dry and rainy seasons. Metal levels were quantified using AAS. Metal levels in water were generally below detectable limits, except for concentrations of Fe (0.30±0.20 mg/L) and Pb(0.22±0.30 mg/L) that were higher in dry and rainy seasons respectively. Pb level was above while Fe level was within permissible limits set by FAO/WHO. Concentrations of Mn (8.27±0.42 mg/Kg), Cu (0.57±0.09 mg/Kg), Zn (1.84±0.13 mg/Kg), Ni (0.16±0.06 mg/kg), Pb (2.63±0.19 mg/Kg) in sediment were significantly higher ($P \leq 0.05$) during rainy season while Cr (1.77±0.22 mg/Kg), Cd (0.05±0.24 mg/Kg) and Fe (24.80±0.38 mg/Kg) were higher in dry season. Concentrations of Cu, Zn, Ni, Pb and Cd were lower than the permissible limits set by WHO and USEPA except for Cr, Mn and Fe that were above the limits. Metal Pollution Index assessment of heavy metals in sediment samples showed that rainy season recorded the highest value at site S_3 (50.24). Correlation analysis showed that the relationships for Zn/Mn (0.941), Fe/Cu (0.853) and Pb/Cr (0.803) were strong and positive while Pb/Cd (- 0.781) was negative in dry season. However, strong positive; Ni/Cu (0.884), Zn/Mn (0.938) and Fe/Mn (0.952) correlations were recorded in rainy season. The strong positive correlation indicates that they have common source of pollution.

Keywords Pollution, Assessment, Metals, Water, Sediments

1. Introduction

Environmental degradation is assuming an alarming rate worldwide. This problem is as a result of the rapid industrialization, population growth and technological advancement being experienced in most parts of the world today. A long list of potential hazardous substances is released on a daily basis which contributes to the global pollution burden [1-2]. Most of these pollutants are discharged into the environment on a daily basis include buy not limited to heavy metals which are regarded as the most serious pollutants of the aquatic environment because of their environmental persistence and tendency to accumulate in aquatic organisms, their toxicity on plants, animals and human beings [2].

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous even at low concentrations; examples include mercury, lead, chromium and arsenic [3]. Chronic exposure to these metals especially at higher doses can have serious health consequences such as reduction in growth and development of foetuses in infants and young children, cancer, organ damage, nervous system damage, placenta and foetal brain damage, and in extreme cases death [3]. Humans are exposed to heavy metals through inhalation of air pollutants, consumption of contaminated drinking water, exposure to contaminated soils or industrial waste or consumption of contaminated food grown on contaminated land [4]. Anthropogenic activities such as mining, smelting, applications of pesticides and fertilizer to crops, may cause elevated levels of heavy metals in the environment [3,5].

In natural waters, metals can occur in dissolved and particulate forms. Dissolved metals may form dissolve organic and inorganic complexes depending on physicochemical properties of the water [5-6]. The build -up of metals in sediments has significant environmental implications for local communities, as well as for river - water quality. For instance, many fresh water invertebrates live on sediment as a food source, thus, be susceptible to bio-accumulation of toxic metals. This bio- accumulation can potentially threaten the health of many species at the top of the food chain especially bird, fish and humans [5,7]. Sediments can be a sensitive indicator to the quality of aquatic systems for both spatial and temporal trend monitoring. Moreover, sediments may not only act as sinks but also as sources of contamination in aquatic systems [7-8]. The distribution of metals in sediments adjacent to settlement areas can provide researchers with evidences of the anthropogenic impact on ecosystems and therefore, aid in assessing the risks associated with discharged human wastes [9-10].

Abuja Rivers are under increasing pressure from industrial activities such as block moulding, mechanic workshops, and car wash shops. Indiscriminate discharge of domestic wastes from homes, agricultural wastes and sewage pipes into the river also increase the pollution load of the water system on a daily basis, however, affecting the water and sediment quality, which poses potential threat not only to aquatic organisms but also to the economy and human wellbeing. However, some authors have carried out research on the heavy metal pollution of water and sediment of some rivers in Abuja, Federal Capital Territory [11-12] but limited information has been given on the pollution assessment of water and sediments from Mpape River. The objective of this study, therefore, is to assess the heavy metal pollution of water and sediment samples during dry and rainy seasons from Mpape River. Information from the present study would be a useful tool for further assessment and monitoring of the river quality.

2. Materials and Methods

2.1. Study Area

Abuja Federal Capital Territory is located in the geographical centre of Nigeria and lies between the latitude 9^o 10' 32" N and Longitude 7^o 10$^'$ 50" E with land mass of 8000 Km^2 as shown below.

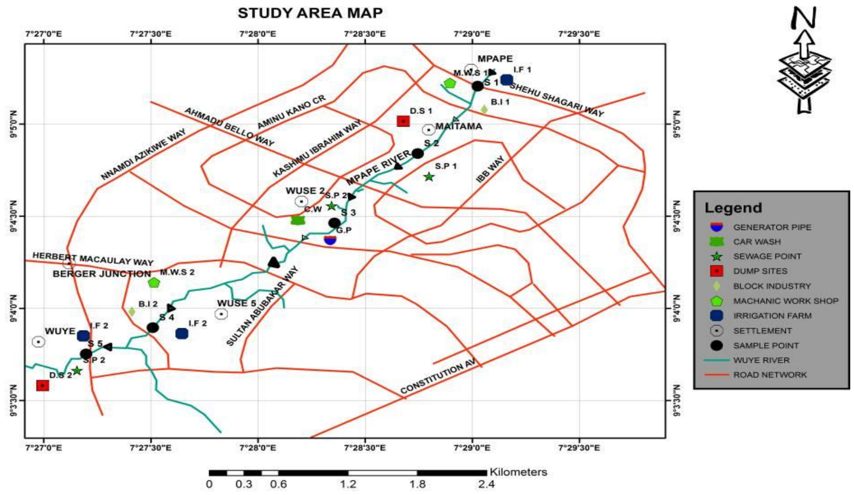

Figure 1: River Mpape showing sampling locations

The River experiences large influx of wastes from both points and non-point sources, especially during the rainy season. It is used majorly during dry seasons as source of water for irrigation purposes in the area. Inhabitants of this area, however, depend on the river for fishery activities and as well as source of water for domestic purposes. Some industrial activities such as block moulding industries, mechanic workshops, car wash shops take place along the bank of the river. Domestic sewage, agricultural runoffs and domestic wastes are often emptied into the river.

2.2. Sample collections and preparations

Water (100 cm^3) and sediment (5 kg) samples were collected simultaneously from each of the five sampling locations: Site 1- Mpape, Site 2- Maitama, Site 3- Wuse II, Site 4- Wuse Zone 5 and Site 5- Wuye village at distances of 6 km apart. Water and sediment samples were collected between 2015 and 2017, in January, March and May which constitute dry season and in June, August and October for the rainy season. Water samples were collected into 200cm^3 plastic bottles using a fetcher; by rinsing first with the sampled water before the samples were collected and then acidified with 2 drops of concentrated nitric acid (HNO_3) in order to retard biological action, hydrolysis of some chemical compounds and to reduce volatility of some chemical constituents. The water samples were filtered using 0.4 mm Whatman filter paper in a vacuum in order to remove particulate matters. Samples were digested with few drops of concentrated nitric acid (HNO_3) and re-transferred back to the plastic bottles. Sediment samples were collected into decontaminated polyethylene bags using soil auger. The samples were air-dried on a tray, ground and sieved with 2 mm mesh sieve. Sediment samples (5 g) were digested with 20 cm^3 aqua regia (3 HCl: 1 HNO_3). The filtrates were transferred into plastic bottles. They were stored at 4 ^{0}C before transportation to laboratory for metal analysis. The analyses were determined in triplicates according to standard methods [13], [14]. Elemental analysis was determined using Atomic Absorption Spectrophotometer (AAS) Perkin-Elmer (Model 403, Norwa, Uk, CT, USA) [13].

2.3. Statistical Analysis

One - way analysis of variance (ANOVA) and Tukey multiple Honestly Significant Difference (HSD) was used to evaluate the significant difference in the concentrations of the heavy metals in different samples at 95% confidence level. Correlations of heavy metal concentrations in the studied samples were also carried out at $P \leq 0.05$ level of significance.

2.4 Heavy Metal Pollution Index (MPI) of Sediment

This was calculated to estimate the total heavy metal load at individual sites by using the equation;

$$MPI = (C_{f1} \times C_{f2} \times C_{f3} \times \ldots\ldots.. C_{fn})^{1/n} \qquad (2.1)$$

Where, $C_f1 \ldots C_{fn}$ = Concentration of individual metals in the sample and N= Total number of metals under study [15, 16].

2.5Partition Coefficient (K_d) of Heavy Metals in Water and Sediment

This was calculated using the equation:

$$K_{\mathbf{d}} = \frac{Concentration \;\; of \; meta\,l \; in \; sediment \; \left(\frac{mg}{Kg}\right)}{Concnetration \;\; of \; metal \;\; in \; water \; \left(\frac{mg}{Kg}\right)} \qquad (2.2)$$

Where, $K_{\mathbf{d}}$= Partition coefficient [15]

3. Results and Discussion

3.1. Heavy Metal Concentrations in Water

Variations in the concentrations of heavy metals in water during the dry and rainy seasons are presented in Tables 1, 2 and 3 respectively. The concentrations of Cr, Cd, Cu, Zn and Ni in water samples in dry season were below detectable limits except for Fe levels that varied from 0.26±0.01 to 0.35±0.01 mg/L in dry season (Table 1) indicating the highest and lowest concentrations at sites S_1 and S_4 respectively. In rainy season, levels of Fe varied from 0.23±0.06 to 0.31±0.04 mg/L (Table 2), the highest and lowest concentrations were recorded at sites$S_5$and S_4 respectively. Pb concentrations varied from 0.06±0.06 to 0.27±0.18 mg/Lin dry season (Table 1). Highest concentration was recorded at site $S_3$and the lowest was recorded at $S_{2.}$ However, in rainy season, the levels of Pb varied from 0.06±0.06 to 0.27±0.18 mg/L (Table 2), indicating the lowest and highest concentrations at sites S_2 and S_4 respectively. Seasonal mean variation of heavy metals (Table 3) in water samples showed that higher concentration of Fe (0.30±0.03 mg/L) was recorded during the dry season while Pb recorded higher concentrations (0.22±0.09) during rainy season. The levels of Pb in this study were similar to the concentrations between (0.06 to

0.22 mg/L) reported for water samples in the North Delta Lakes, Egypt [17] and the 0.16±0.57 to 0.33±0.18 mg/L reported for Tanda Dam [18], however, exceeded the 0.01 mg/Lset by WHO/FAO, permissible limits [19] while Fe levels were within the 0.3 mg/L set by WHO/FAO, permissible limits for drinking water [19]. Higher concentrations of lead and iron at some sites could be due to anthropogenic activities along the sampling sites. Seasonal levels of Fe and Pb (Table 3) were significantly different (P≤0.05). Comparatively, higher metal concentrations recorded in rainy season (0.22±0.09) for Pb and dry seasons (0.30±0.03) for Fe were due to anthropogenic impact during the period [3-4].

Table 1: Concentrations (mg/L) of Heavy Metals in Water Samples in Dry season

Metals	**Sampling Points**					
Metals	**S_1**	**S_2**	**S_3**	**S_4**	**S_5**	**Mean±SD**
Cr	ND	ND	ND	ND	ND	ND
Mn	ND	ND	ND	ND	ND	ND
Cd	ND	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND	ND
Fe	0.35±0.01^{a}	0.29±0.03^{a}	0.28±0.0^{a}	0.26±0.01^{a}	0.30±0.01^{a}	0.30±0.03
Zn	ND	ND	ND	ND	ND	ND
Ni	ND	ND	ND	ND	ND	ND
Pb	0.09±0.00^{a}	0.06±0.06^{a}	0.27±0.18^{b}	0.21±0.14^{b}	0.22±0.01^{b}	0.17±0.09

Means levels with the same alphabets within the same row are not statistically different (P≤0.05), ND = Not Detected

Table 2: Concentrations of heavy metals in water samples during dry season

	Sampling Points					
Metals	**S_1**	**S_2**	**S_3**	**S_4**	**S_5**	**Mean**
Cr	ND	ND	ND	ND	ND	ND
Mn	ND	ND	ND	0.02±0.01^{a}	ND	ND
Cd	ND	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND	ND
Fe	0.28±0.10^{b}	0.27±0.30^{b}	0.29±0.25^{b}	0.23±0.06^{a}	0.31±0.04^{a}	0.28±0.03
Zn	ND	ND	ND	ND	ND	ND
Ni	ND	ND	ND	ND	ND	ND
Pb	0.32±0.20^{b}	0.10±0.01^{a}	0.28±0.21^{b}	0.23±0.06^{a}	0.17±0.05^{a}	0.22±0.09

Means levels with the same alphabets within the same row are not statistically different (P≤0.05), ND = Not Detected

Table 3: Seasonal Concentrations of heavy metals in water samples

Parameters	**Dry Season**	**Rainy Season**
Cr	ND	ND
Mn	ND	ND
Cd	ND	ND
Cu	ND	ND
Fe	0.30±0.03^{a}	0.28±0.03^{b}
Zn	ND	ND
Ni	ND	ND
Pb	0.17±0.09^{a}	0.22±0.09^{b}

Means levels with the same alphabets within the same row are not statistically different (P≤0.05), ND = Not Detected

3.2. Heavy Metal Concentrations in Sediment Samples

Heavy metal concentrations in sediment during dry and rainy seasons are presented in Figures 1 and 2 respectively. In aquatic environment, Cr is one of the bio-chemically active transition metals. Weathering of the earth's crust is the primary and natural source of chromium in the surface water [20, 21]. Concentration of Cr varied from 1.16 ± 0.24 to 2.84 ± 0.08 mg/Kg in dry season (Figure 1). The lowest and highest concentrations were detected at sites S_1 and S_2 respectively. In rainy season (Figure 2), levels of Cr ranged from 1.03 ± 0.09 to 1.97 ± 0.14 mg/Kg indicating the lowest and highest concentration at sites S_2 and S_3respectively.

Seasonal mean comparison of metal concentrations (Table 4) revealed higher concentration of Cr (1.77±0.66 mg/Kg) in dry season. The levels were lower than the concentrations (35.49±1.31 mg/Kg to 43.24±6.15 mg/Kg) of sediment samples from River Osogbo [22], and the concentrations of 25.57 to 59.0 mg/Kg reported for sediment samples from Karatas Lake [23], however, higher than the concentrations 0.15 to 0.21 mg/Kg reported for sediments along Abonnema Shoreline [24]. The levels of Cr were above 0.05 mg/kg permissible limits set by WHO [25-26]. Higher concentration observed in dry season was probably due to lithogenic (weathering of the earth's crust) and anthropogenic effects such as leachates from municipal waste, laundry chemicals, road run-offs from tire wear, corrosion of bushings, brake wires and radiators [17,23-24]. The concentrations of Cr were significantly not different in both seasons (P≤0.005).

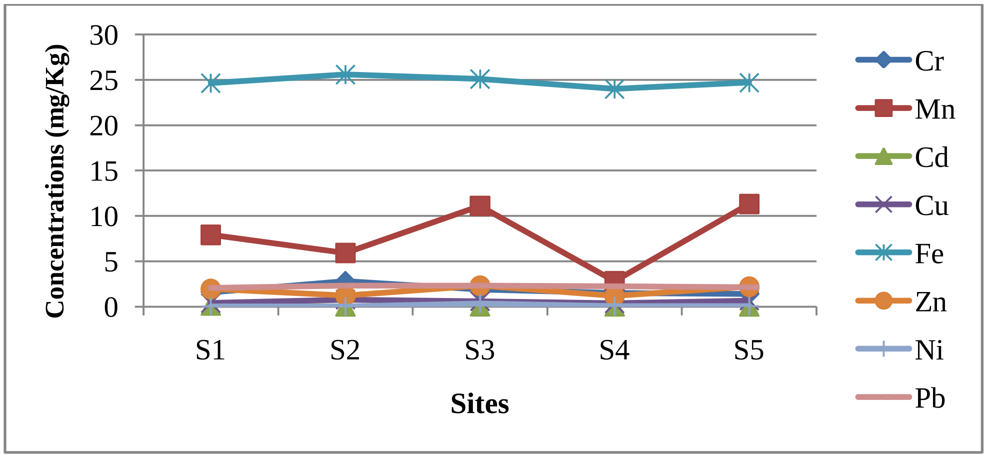

Figure 1: Mean Concentrations (mg/kg) of Heavy Metals in Sediment Samples in Dry season

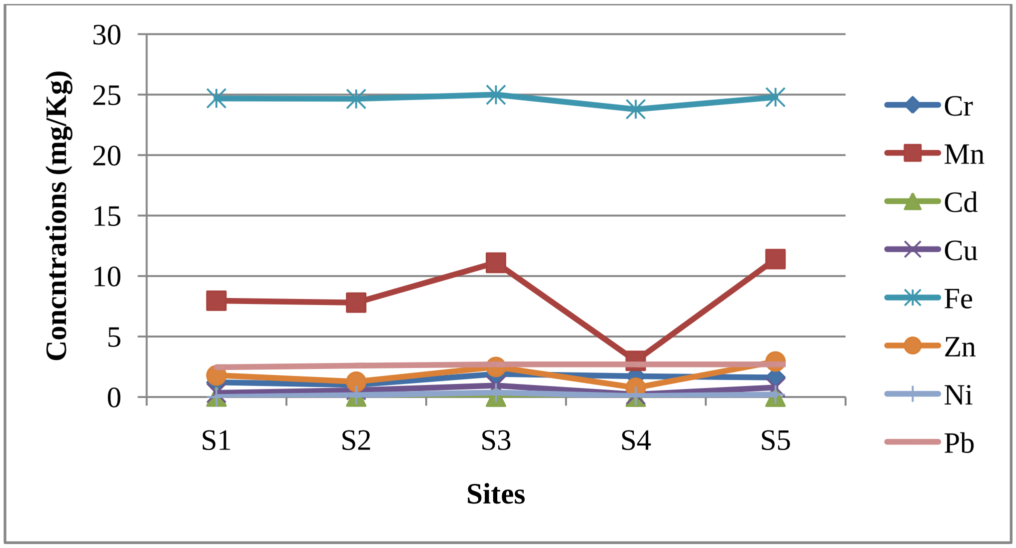

Figure 2: Mean Concentrations (mg/kg) of Heavy Metals in Sediment Samples in Rainy season

Table 4: Seasonal Mean Concentrations (mg/kg) of Heavy Metals in Sediment Samples

Metals	**Dry Season**	**Rainy Season**
pH	6.23 ± 0.15^{b}	6.40 ± 0.15^{b}
Cr	1.77 ± 0.68^{a}	1.51 ± 0.38^{a}
Mn	7.80 ± 3.60^{a}	8.27 ± 3.40^{a}
Cd	0.05 ± 0.04^{a}	0.03 ± 0.01^{a}
Cu	0.56 ± 0.18^{a}	0.57 ± 0.32^{a}
Fe	24.80 ± 0.59^{a}	24.61 ± 0.46^{a}
Zn	1.76 ± 0.54^{a}	1.84 ± 0.88^{a}
Ni	0.09 ± 0.10^{a}	0.16 ± 0.14^{b}
Pb	2.20 ± 0.15^{a}	2.63 ± 0.11^{a}

Means levels with the same alphabets within the same row are not statistically different ($P\leq0.05$), ND = Not Detected

Mn is an essential metal for both plants and animals but higher accumulation of it can have repercussions on the central nervous system of humans [8, 10]. Concentrations of Mn ranged from 2.76 ±0.31 to 11.25 ± 0.60 mg/Kg in dry season (Figure 1) indicating lowest and highest levels at sites S_4 and S_5 respectively and from 3.00 ± 0.38 to 11.44 ± 0.41 mg/Kg in rainy season (Figure 2), site S_5 recorded the highest concentration and site S_4 indicated the lowest concentration. Seasonal variations showed that higher concentration of Mn (8.27 ± 3.40 mg/Kg) was recorded in rainy season (Table 4). Levels of Mn were below the concentrations (10.97 mg/Kg) reported for sediment of Tekeze Dam in Ethiopia [27], and 52.07 mg/Kg reported for sediment in River Kubanni in Zaria [28]. However, the values were higher than 0.5 mg/Kg permissible limits set by WHO [25], [26] for sediments. This might be due to higher anthropogenic activities [17], [23]. Levels of Mn varied significantly according to season ($P\leq0.05$).

The levels of Cd in sediment samples were highest and lowest at sites S_1 and S_5 while the concentrations varied from 0.03 ± 0.03 to 0.13 ± 0.02 mg/Kg in dry season (Figure 1) respectively. Rainy season ranged from 0.03 ± 0.03 to 0.04 ± 0.02 mg/Kg(Figure 2) indicating the highest concentration at site $S_1$and lowest concentration at site S_4. Seasonal mean comparison (Table 4) showed that higher concentration of Cd (0.05±0.04 mg/Kg) was recorded in dry season in contrast to the low concentration (0.03±0.01 mg/Kg) recorded in rainy season. The levels of Cd recorded in the present study were below the concentrations (5.54±2.55 mg/Kg to 3.39±1.34 mg/Kg) reported for sediment in Osogbo River [22]and concentration 1.36 mg/kg reported for sediment from Jabi Lake [11]; but in the same range with the concentration (0.03 mg/Kg) reported for sediment of Kubukun Village, Abuja [12]. The values were within recommended limits of 0.03-0.05 mg/Kg for Cd set by WHO [25-26]. Cd levels did not vary significantly according to season ($P\leq0.05$). Higher concentration of Cadmium is extremely toxic to fish population and their effects on the growth rate have been observed even for concentrations between 0.005 and 0.01 mg/Kg [2].

Cu is widely used in electrical wiring, roofing and in various alloys, cooking utensil, pipelines and Chemical industry and also in fungicides and insecticides [12,23]. They are also added to fertilizers and animal feeds as nutrient to support plant and animal growth. Copper components are also used to control biological growths in reservoirs and distribution pipes, but in higher concentrations, it can cause anaemia, liver and kidney damage [4,6]. Concentrations of Cu varied from 0.36 ± 0.07 to 0.78 ± 0.03 mg/Kg in dry season (Figure 1) with highest and lowest concentrations at sites S_2andS_4respectively. For the rainy season, it ranged from 0.20 ± 0.09 to 0.96 ± 0.08 mg/Kg (Figure 2). The highest and lowest concentrations of Cu were recorded at sites S_3 and S_4 respectively. Seasonal comparison indicated that higher concentration of Cu (0.57±0.32 mg/Kg) was recorded in rainy season (Table 4) in contrast to the concentration (0.56±0.18 mg/kg) in dry season. The levels recorded for both seasons were below the concentrations (16.02±2.11 mg/kg and 19.47±3.68 mg/kg) reported for sediments during dry and rainy seasons in Osogbo River [22], however, were below 18.70 - 31.60 (mg/kg) recommended limits for Cu set by USEPA [29] and 2 mg/kg set by WHO [25,26]. The higher levels observed in rainy season could be due to high levels of contaminations due to increased anthropogenic activities [6, 8]. Cu levels did not vary significantly in both seasons ($P \leq 0.005$).

Iron is one of the essential elements in human nutrition; however their presence at elevated levels in human nutrition and aquatic eco system poses serious pollution and health problems. Iron is present in natural waters in varying amounts depending on the geological and chemical components of the water way and its deficiency may lead to failure of blood clothing [3, 10]. Levels of Fe ranged from 23.96 ± 0.55 to 25.57 ± 0.14 mg/Kg in dry season (Figure 1) indicating highest and lowest concentrations at sites S_2 and S_4 respectively; and from 23.82±0.22 to 25.01±0.29 mg/Kg in rainy season (Figure 2). The highest concentration was recorded at site S_3 and the lowest concentration at S_4respectively. Seasonal mean comparison (Table 4) revealed higher concentration of Fe (24.80 ± 0.59 mg/kg) in dry season which may be of anthropogenic and lithogenic origins [36]. These values were far below the concentration (75.15 to 150.30 mg/Kg) reported for similar work done in the sediments of Tekeze River Ethopia [27] and concentrations (72.81 mg/kg) reported for sediment of Kubokun village, Abuja [12]. Fe levels were higher than 0.3- 0.5 mg/kg permissible limits recommended by WHO [25]. ANOVA showed that the seasonal levels of Fe were not significantly different ($P \leq 0.05$).

Zinc plays biochemical role in the life processes of all aquatic plants and animals; therefore, they are essential in the aquatic environment. However, at an elevated level, it is toxic to some species of aquatic lives [31, 32]. The levels of Zn in the sediment samples ranged from 1.17± 0.10 to 2.30±0.24 mg/Kg in dry season (Figure 1) with highest and lowest concentrations recorded at sites S_3 and S_4 respectively. In rainy season, levels of Zn ranged from 0.76± 0.12 to 2.93 ±0.18 mg/Kg (Figure 2) indicating the lowest and highest levels at sites $S_4$and S_5respectively. Seasonal comparison (Table 4) revealed highest concentration of Zn (1.84 ± 0.88 mg/Kg) during rainy season due to high rainfall and eventually run-offs from irrigated farmlands into the river. The concentrations recorded in the present study were far lower than the concentrations (155.10 ± 5.86 to 250.20 ±30.6 mg/Kg) reported for similar work done on sediments of Seybo use River in Annaba [30], concentrations (12.92 mg/kg) reported for sediment of Karatas River [23], concentrations (2.40 to 2.68 mg/Kg) reported for sediment of River Delimi, Jos [33]. The levels of Zn recorded in the present study were far below 5.0 mg/kg recommended limits set by WHO [25] and 121-124 mg/kg recommended limits set by USEPA [29]. It could be inferred that both geochemical and anthropogenic factors would have contributed to high level of Zn in Mpape River sediment. Zn levels did not vary significantly in both seasons ($P \leq 0.05$).

Nickel is useful in blending phosphate fertilizer. This is the main source of nickel in the soil. When above certain threshold level, Ni can cause allergic skin reactions in humans following either dermal or oral exposure [4, 6, 34]. Levels of Ni varied from 0.01 ± 0.01 to 0.33 ± 0.06 mg/Kg in dry season(Figure 1) showing the highest and lowest concentrations at sites S_1, S_2 and S_3 in dry season respectively. Rainy season ranged from 0.09±0.03 to 0.37 ± 0.08 mg/Kg (Figure 2) with the highest and lowest concentrations recorded at sites S_3 and S_4respectively. However, Ni was below detectable limit at site $S_{1.}$ Higher concentrations of Ni at some sites could come from debris from mechanic and car wash shops through surface runoffs [35]. Seasonal comparison (Table 4) showed that rainy season recorded the highest concentration of Ni (0.16 ± 0.14 mg/Kg). These values were above the concentrations (0.07 mg/kg) reported for sediment of Kubokun village in Abuja metropolis [12] and concentrations (0.064 to 0.07 mg/Kg) reported for sediment of River Ekulu in Enugu [36], however, they were lower than (3.75 ± 1.67 mg/Kg and 4.56 ± 1.21 mg/Kg) reported for sediments of Osogbo River during rainy and dry season [22]. The levels reported in the present study were within 0.07 mg/kg recommended limits for Ni set by WHO [25], [26]. Ni levels varied significantly in both seasons ($P \leq 0.05$).

Lead is naturally highly toxic even in a small concentration and can lead to the damage of the brain, kidney, nervous system and red blood cells [34]. The Pb concentrations from Mpape River sediments ranged from 2.06 ± 0.03 to 2.29 ± 0.05 mg/Kg in dry season (Figure 1), showing the lowest and highest concentrations at sites S_1 and S_3 respectively. During the rainy season, the concentration of Pb ranged and from 2.45 ± 0.17 to 2.72 ±0.18mg/kg indicating lowest concentrations at sites S_1 and S_3 respectively (Figure 2). High concentrations of Pb at site S_2 in dry season may be due to fewer fluxes of lead-bearing suspended particles which had settled as part of the sediments during the dry season [36, 37]. Seasonal mean comparison (Table 4) recorded highest concentration of Pb (2.63 ± 0.11 mg/Kg) in rainy season. The levels recorded were lower than the concentrations (145.16 to 162.55 mg/kg) reported for sediment of River Annaba, Algeria [30, 37] and concentrations (119 to 128 mg/kg) reported for sediment of Saline Lake in Iran [38]. The levels of Pb recorded in the present studies were above 0.01 to 0.3 mg/kg recommended limits set by WHO [25-26]. Higher concentration of Pb recorded in rainy season was due to high anthropogenic impact. Pb level in rainy season was significantly higher than in dry season ($P \leq 0.05$) level of significant.

Table 5: Seasonal Partition Coefficient (K_d) of Heavy Metals in Water and Sediment

Metals	Dry Season	Rainy Season
Cr	1.77	1.51
Mn	7.8	8.27
Cd	0.05	0.03
Cu	0.56	0.57
Fe	82.67	87.89
Zn	1.76	1.84
Ni	0.09	0.16
Pb	12.94	11.95

3.3. Seasonal Partition Coefficients (K_d) of Heavy Metals in Water and Sediment

Seasonal Partition Coefficients (K_d) of heavy metals are presented in (Table 5). If K_d value ≥1, then more metals will be distributed in the sediment and when ≤ 1, metals will be distributed in water [15]. The seasonal partition coefficient of heavy metals decreased in the order of Fe >Pb>Mn> Cr > Zn > Cu > Ni > Cd and Fe >Pb>Mn> Zn > Cr > Cu > Ni > Cd in dry for rainy seasons respectively. The partition coefficients showed that rainy season recorded higher values in all the metals except for Cr and Pb that were higher in dry season. The highest and lowest concentrations of all the metals were recorded for Fe (87.89) and Cd (0.03) in rainy season. The higher values recorded for all the metals in both seasons except in Cd and Cu exceeded the partition coefficient guide which implies more adsorption onto sediment surfaces, however, will cause low solubility of metals which may be attributed to high influx of solid wastes into the river during the period; that eventually settled down as sediment [21]. Variation in physicochemical properties of the aquatic environment might have also influenced the observed trend. The results also showed that complexion of Fe, Pb and Mn with sediment surfaces were relatively high for both seasons.

Table 6: Pollution Index (MPI) of Metals in Sediment for Dry and Rainy seasons

Sampling Point	Dry Season	Rainy Season
S_1	5.42	30.09
S_2	4.23	12.09
S_3	37.45	50.24
S_4	3.11	2.93
S_5	10.87	33.66
Total	851.86	212.28

3.4 Heavy Metal Pollution Index (MPI) of Sediments

Pollution index of metals in sediments are presented in (Table) Metal pollution Index (MPI) during dry and rainy seasons were in the order; $S_4 < S_2 < S_1 < S_3 < S_5$ and $S_4 < S_2 < S_1 < S_5 < S_3$ respectively. During the rainy season, the highest and lowest MPI levels were recorded at sites S_3 (50.24) and S_4 (2.93) respectively. Comparing the two seasons, site S_3 was the most polluted by heavy metals. This might be attributed to higher discharge of wastes from agricultural, industrial and domestic run offs in Mpape River [15-16]. When MPI is <1, it reflects no need for remediation measures and classified as unpolluted and MPI > 1, reflects high pollution load. The greater the metal concentration on individual sediments, the greater the MPI values urging strong needs for rectification measures

[15-16]. The degree of sediment contamination varied from moderate at S_4 to ultra-high at S_3. Generally, the overall (MPI) was higher in dry season (851.86) which reflects ultra-high degree of pollution load. From the results, the values recorded in all the sampling sites were greater than 1 which implies that there is imposition of more risk to humans due to higher accumulation of heavy metals in the sediment samples [15,16,21]. Sediments were contaminated with varying degrees of heavy metals, thus risk was associated with them.

The degree of sediment contamination is classified as follows:
HPI < 1 = Excellent Quality
HPI≤ 1.5 =Nil to very low degree of contamination level
1.5≤ HPI<2 =Low degree of pollution level
2≤ HPI< 4 = Moderate degree of pollution level
4≤HPI =High degree of pollution level
8≤HPI<16 = very high degree of pollution level
16≤HPI<HPI<32 =Extremely High degree of pollution level
HPI≥32 = Ultra high degree of pollution level [15].

Table 7: Correlation Coefficient (r) values for Heavy Metal Concentrations in Sediment Samples from five sampling sites in Dry Season

	Cr	**Mn**	**Cd**	**Cu**	**Fe**	**Zn**	**Ni**	**Pb**
Cr	1***							
Mn	-0.168568	1***						
Cd	-0.549917*	-0.0053623	1***					
Cu	0.7462043**	0.41748728	-0.6006504*	1***				
Fe	0.767945**	0.40478528	-0.2065726	0.85349102**	1***			
Zn	-0.444977	0.94155571**	0.18734997	0.09057481	0.1292608	1***		
Ni	0.065994	0.53284532**	-0.2509702	0.11338681	0.2032152	0.58366453**	1***	
Pb	0.8031157**	-0.2889698	-0.7808502*	0.45422035	0.3533192	-0.4457749	0.36028679	1***

Correlation is significant at (P≤0.05) level
Correlation is significant at (P≤0.01) level
Correlation is significant at (P≤0.001) level

Table 8: Correlation Coefficient (r) values for Heavy Metal Concentrations in Sediment Samples from five sampling sites in Rainy Season

	Cr	Mn	Cd	Cu	Fe	Zn	Ni	Pb
Cr	1***							
Mn	0.1779	1***						
Cd	-0.9269*	-0.10243	1***					
Cu	0.4257	0.907024**	-0.35817	1***				
Fe	-0.0055	0.951895**	0.158145	0.8145294**	1***			
Zn	0.37027	0.937963**	-0.33615	0.8339929**	0.815264**	1***		
Ni	0.64044**	0.610237**	-0.55586*	0.8837722**	0.507428**	0.540445**	1***	
Pb	0.82138**	0.157421	-0.92413*	0.4955321	-0.09118	0.285025	0.7335319**	1***

*Correlation is significant at (P≤0.05) level, **Correlation is significant at (P≤0.01) level, ***Correlation is significant at (P≤0.001) level

The correlation analysis in dry season (Table 7) showed that the metals have varying correlations. The pairs of metals; Zn/Mn (0.941), Fe/Cu (0.853) and Pb/Cr (0.803) were positive and strongly correlated while Cd/Cr (- 0.

549), Cu/Cd (- 0.600) and Pb/Cd (- 0.781) varied from moderate to strong and where negative. During the rainy season (Table 8), relationships for Ni/Cu (0.884), Zn/Mn (0.938) and Fe/Mn (0.952) were positively strong while Cd/Cr (-0.9269), Ni/Cd (-0.555) were negatively strong. The strong and positive correlations in sediment samples is an indication that they have common source of pollution while the strong negative correlations observed is an attribute of different origin and sources of pollution load such as municipal and agricultural dumps, chemicals from irrigated farm lands and other small scale activities from the five sampling sites [15].

Correlation rating: > 0.91= very strong, 0.90-0.81= strong, 0.81-0.5= moderate, <0.5= weak [15].

Table 9: Permissible limits for Heavy Metals (mg/L) in Water

	Cr	**Mn**	**Cd**	**Cu**	**Fe**	**Zn**	**Ni**	**Pb**
WHO/FAO, 2011	0.05	0.4	0.003	2	0.3	3	0.07	0.01
WHO, 2008	0.05	0.05	0.01-0.05	0.2-0.5	0.3	5	0.07	0.01-0.03

Table 10: Permissible Limits for Heavy Metals (mg/kg) in Sediment

	Cr	**Mn**	**Cd**	**Cu**	**Fe**	**Zn**	**Ni**	**Pb**
WHO, 2008	0.05	0.5	0.03	2.00	0.3-0.5	5	0.07	0.01-0.3
USEPA, 2010	43.4	-	0.68-0.99	18.7-31.6	-	121-124	22.7	35.8

4. Conclusion

The levels of metals in surface water and sediment varied according to sites and seasons which have no specific trends. Concentrations of Fe increased in dry season which was within WHO/FAO permissible limits and Pb in rainy season which was above WHO/FAO permissible limits while concentrations of Cr, Mn, Cd, Cu, Zn and Ni were below detectable limits. Levels of metals in sediment samples increased significantly (P≤0.05) in dry season with the highest concentrations for Cr, Cd, Fe while in rainy season, Mn, Cu, Zn, Ni and Pb levels were higher. However, the concentrations of all the metals in the sediment samples exceeded the WHO recommended values except for Cu that was lower and Cd that was within the limits, indicating that the sediment samples from the study sites were contaminated by heavy metals. The variations showed that areas with high activities had highest concentrations for most metals. Rainy season recorded the highest and lowest partition coefficient values in Fe (87.89) and Cd (0.03) respectively. The lower K_d values recorded for Cu, Cd and Ni in both seasons suggests metals greater mobility and lower affinity tothe organic sediments while higher values recorded for Cr, Mn, Fe, Zn and Pb imply low solubility and greater retention of these metals onthe sediment. The highest (50.24) and lowest (2.93) metal pollution index were recorded at $S_3$and S_4in rainy season. The MPI values obtained in both seasons in all the sampling sites were greater than 1 suggesting strong needs for remediation measures. The correlation analysis showed varying strong positive correlations with Cu/Cr, Fe/Cr, Fe/Cu, Zn/Mn, Ni/Mn, Ni/Zn and Pb/Cr and negative correlations with Cd/Cr, Cu,Cd, Pb/Cd in both seasons. Higher metal levels observed at different sites showed that the probable source of the pollutants was of anthropogenic origin, therefore, water and sediment qualities of Mpape River, however, requires continuous monitoring because of discharge of waste from points and non-points sources into the river which may over time lead to disease outbreak. Changes in water and sediment chemistry might be responsible for the variations in the chemical properties.

Acknowledgement

We are grateful to Department of Chemistry, Nasarawa State University, Keffi and Sheda Science and Technology Complex for the use of their facilities for the research work.

References

1. Muchuweti, M., Birkett, J.W., Chinyanga, E., Zvauya, R., Scrimshaw, M.D., & Lester, J.N. (2006). Heavy metal content of vegetables irrigated with mixture of waste water and severe sludge in Zimbabwe. Implications for human health, *Journal of Agriculture, Ecosystem and Environment*. 112: 41-48.

2. Chipo, M. (2011). Assessment of Heavy Metal Accumulation in Wastewater Irrigated Soil and Uptake by maize plants (Zea Mays) at firle Farm in Harare. *Journal of Sustainable Development*, 4 (6): 132-137. Published by Canadian Centre of Science and Education.
3. Sharma, R., Sigh, A., K, Agrawal, M., & Marshal, F. A. (2008a). Risk assessment of heavy metal toxicity through contaminated vegetables from waste water irrigated area of Varanasi, India. *Journal of Tropical Ecology*, 51 (25): 375 – 387.
4. Ubani, N., Lamali, M. K., Kazi, T. G., Arain, M. B., Afridi, H. l., Memon, A.R., & Shah, A. (2007). Heavy metals from soil and domestic sewage sludge and their transfer to sorghum plants. *Journal of Environmental Chemistry*, 5: 29-218.
5. Arora, M., Kiran, B., Rani, S., Rain, A., Kaur, B., & Mittal, N. (2008). Heavy metal accumulation in vegetables irrigated with water from different sources. *Journal of Food Chemistry*, 111, 811-815.
6. Addo, M.A., Affum, H.A., Bottwe, B.O., Gbadago, J.K., & Acquah, S.A. (2012). Assessment of water quality and heavy metal levels in water and bottom sediment samples from Mokwe Lagoon, Accra, Ghana. *Research Journal of Environmental & Earth Science*, 4(2): 119-130.
7. State Environmental Protection Administration –SEPA (2005). *The limits of Pollutants in Food in China. GB2762.*
8. Wang, Y., Chen, P., Cui, R., Si, W., Zhang, Y., & Ji, W. (2010). Heavy Metal Concentration in Water, Sediments and tissues of two fish species (*Tripohysapappenheimi, Gobiohwanghensis)* from the Lanzhou section of the yellow River, China. *Journal of Environmental Monitoring Assessment.*165: 97-102.
9. Mehjbeen, J., &Nazura, U. (2014): Assessment of heavy metals (Cu, Ni, Fe, Co, Mn, Cr, Zn) in rivulet water, their accumulations and alterations in hematology of fish channapunctatus. *African Journal of Biotechnology*. 13 (3): 492 – 501.
10. Omojole, M. O., Ayejuyo, O.O., &Ojoniyi, O. J. (2010). Sediment load and bio-concentration of heavy metal by shrimp (*Peaneus notalis*) from Epe Lagoon, Nigeria. *Environmental Monitoring Assessment*, 163, 295-301.
11. Umar, M. A., & Ebong, M. C. (2013). Determination of heavy metals in soil, water, sediment, fish and crafish of Jabi Lake in the federal capital territory, FCT, Abuja – Nigeria. *International Journal of Research in Pure and Applied Chemistry*. 2 (1): 5 – 9.
12. Isaac, A. o., Bello, O. M., & Patricia E. O. (2013). Heavy metals evaluation of Madna Stream Sediment in Kubokun village of Abuja metropolis. *Journal of Advance in Applied Science Research*. 4 (6): 237 – 241.
13. AOAC, (2000). *Association of Oficial Analytical Chemist 16th edition*, Washington DC. 42: 13-26.
14. WHO. (2006). *Guidelines for drinking water quality*. 1st addendum to the 3rd edition., 1: 491 – 493.
15. Lacatusu, R. 2000. Appraising levels of soil contamination and pollution with heavy metals. *European Soil Bureau Research Report*, Number 4. of Upper Warri River, Niger Delta, Nigeria. *Journal of Science and Environment*. 2: 75 – 86.
16. Liu, D.W., Jiang, C., Liu, C., Xin, R., & Hon, W., (2005). Uptake and accumulation of lead by roots, hypocotyls and shoots of Indian Mustard [*Brassica Juncea (l)] Bioresource* Technology, 71(3), 273-277.
17. Samir, M. & Ibrahim, M.S. (2008): Assessment of heavy metal pollution in water and sediments and their effects on *oreochromis Niloticus* in the Northern Delta Lakes, Egypt: *Central Laboratory for Aquaculture Research, Agricultural Research, Limnology Department.* 2 (1): 221- 234.
18. Ruqia, N., Muslim, K., Muhammadu, M., Hameed, R., Naveed, R., Surrya, S., Nosheen, A., & Muhammadu, S. (2015). Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam Kohat. *Journal of Pharmaceutical Science and Research.*7 (3): 89 – 97.
19. FAO/WHO, (2011).*Joint FAO/WHO food standards programme codex committee on contaminants in food*, 5th Session, 64-89.

20. Xianfei, H., Jiwei, H., Cun -xiong, L., Jianjun, D., & Jian, L. (2009). Heavy Metal Pollution and Potential Ecological Risk Assessment of sediments from Baihua Lake, China. *International Journal of Environmental Health Research.19: 405- 419.*
21. Dixit, S., & Twari, S. (2008). Impact assessment of heavy metal pollution of Shahpura Lake, Bhopal. India. *International Journal of Environmental Research*.2 (1): 37 -42.
22. Oyekunle, J. A., Ogunfowokan. A. O. Akinni, M. S., & Torto, N. (2011). Seasonal mean levels of heavy metals in water and associated sediments from Ajawere in Oke – Osun Farm settlement, Osogbo, Nigeria.
23. Burcu, B. & Tekin–Ozan, S. (2012). Concentration of some heavy metals in water, sediment and tissues of Pikeperch (Sander Lucioperca) from Karatas, Lake related to physico-chemical parameters, fish size and seasons. *Pollution Journal of Environmental Studies*. 22 (3): 633 – 644.
24. Ideriah , I. J., David – Omiema, S., & Ogbonna, D. N. (2012). Distribution of Heavy Metals in water and sediment along Abonnema Shoreline, Nigeria: *Journal of Resources and Environmental*. 2 (1): 33 – 40.
25. WHO, (2008). *Guidelines for drinking water,* Geneva.
26. World Health Organization -WHO (2003). *Malathon in drinking water*. Background document for preparation of WHO guidelines for drinking water quality.
27. Mulu, B. D, Abraha, G. A., & Yirgalem, W. G. (2012). Health risk assessment of heavy metals bioaccumulation in water sediment and fish species (Labeobarbus Spp, Clarias Gariepinus of Tekeze River Dam in North Ethiopia). *Journal of Atmospheric and Earth Environment.*1 (1): 19 -29.
28. Butu, A. W. & Iguisi, E. O. (2013): Concentration of heavy metals in sediments of river Kubanni, Zaria, Nigeria. *Comprehensive Journal of Environmental and Earth Sciences*. 2 (1): 10 – 17.
29. USEPA. (2010). *Guidelines on evaluating sediment contamination results*. Division of surface water, standards and technical support section.
30. Anchour, L., Atika, H., & Mabrouka, A (2012): Determination of some heavy metal pollutants in sediments of the Seybouse River in Annaba, Algeria. *Journal of Air, soil and water research.*5: 91 – 101.
31. Green, W. J, Canfield, D. E., Lee. G. F., & Jones. R. A. (1986): Mn, Fe, cu, and Cu. Distribution and residence times in closed basin Lake Vanada (Wright valley, Antatica). *Journal of Hydrobiologia*. 134 (3): 237- 248.
32. Gomez, A. J, Giraldez, I. Sanchez – rodas, D., & Morales, E. (2000). Comparison of the feasibility of three extraction procedures for trace metal partitioning in sediments from south west Spain. *Journal of Science of the Total Environment.* 246 (2-3): 271 – 283.
33. Sabo, A., Gani, A. M., & Ibrahim, A. O. (2013). Pollution status of heavy metals in water and bottom sediment of river Delmi in Jos, Nigeria. *American Journal of Environmental Protection*. 1 (3): 47 – 53.
34. Mac-Grath, S., Chaudri, A. M., & Griller, K. E., (1995). Long term effects of metals in sewage sludge soils. Microorganisms and plants: journal of industrial microbial. 14: 94 – 104.
35. Environmental Agency, (2009). *Contaminants in soil uptake collation of toxicological data and intake values for humans*. Nickel. Science report SC050021/SR TOX8. Bistol: Environmental Agency.
36. Adaikpoh, E. O., Nwajei, G. E., and Ogala, J. E. (2005): Heavy metals concentration in coal and sediments from river Ekulu in Enugu, Coal City of Nigeria. *Journal of applied science and environmental management.*9 (3): 5 – 8.
37. Awofolu, O. R., Mbolekwa, Z., Mtshemla, V., & Fatoki, O.S. (2005). Levels of trace metals in water and sediment from Tyume River and its effects on an irrigated farmland. *Journal of Water Assessment.* 31(1): 27-34.
38. Moore, F., & Forghari, G. (2008). Impact of untreated wastewater irrigation on soils and crops in Shiraz sub urban area, SW Iran. *Environmental Monitoring & Assessment,* 141, 257-273.