

Heavy Metals Concentrations in Jare River Sediment, Katsina State, Nigeria

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Abstract

This study is essentially to investigate concentration of heavy metals (Fe, Mn, Zn, Mg, Ni, Co, Cd, Cr, and Pb) in Jare river sediment of Southern, part of Katsina State, Nigeria. Four different locations were selected, the Samples were collected from the selected areas and were analyzed for, Fe, Mn, Zn, Mg, Co Cr, Cd, Pb, Hg and Ni by Atomic Absorption Spectroscopy (AAS). The results revealed the presence of concentration of lead 3.986ppm, manganese 82.29ppm, magnesium 146.7ppm, cadmium 0.615ppm, chromium 25.64ppm, nickel 3.49ppm, iron 5415.54ppm and zinc 8.135ppm while cobalt, mercury and silver were found to be below the detection limit in the sample collected. The result shows that the element determined are above the WHO (1981) and FEPA (1991) standard limit.

Keys words: Jare, Katsina, Nigeria, Heavy Metals, Atomic Absorption Spectroscopy

1.0 Introduction

Certain chemical elements occur naturally in soils as components of minerals, yet they may be toxic at some concentrations. Other potentially harmful substances may end up in soils through human activities. This could happen if old industrial or agricultural lands are used for residential purposes, and contaminants remain in the soil. When it rains some of this element may be washed into the river. Spills, runoff, or aerial deposition of chemicals used for agriculture or industry can also cause soil contamination in residential areas. At times, the amount of some soil elements and other substances may exceed levels recommended for the health of humans, animals, or plants (Shyler *et al.*, 2009). Studies have found many soils around the world are contaminated with Pb, Cd, Hg, and others (Alloway, 1990). High concentrations of heavy metals in soils are caused by atmospheric deposition and applications of agrochemicals, fertilizers, and residues to soils. Such applications onto soils are becoming widespread not only in developed but also in developing countries (Sobrinho, *et al.*, 1992).

Presence of heavy metals in the environment may causes pollution. Environmental pollution by heavy metals is due to many activities whereas in the soil system, pollution by heavy metals is mainly due to both natural processes such as weathering of minerals and anthropogenic activities related to industry, agriculture, burning of fossil fuels, vehicular emission, mining and metallurgical processes and their waste disposal (Huu *et al.*, 2010). Soil serves as a sink and recycling factory for both liquid and solid wastes. Most of the sources of this sediment have

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been found to contain appreciable quantity of heavy metals such as Cd, Zn, Pb, Fe, and Cu etc (Idris, 2011). Potentially toxic elements in the environment could be naturally derived from anthropogenic activities. Naturally these elements could be introduced into the soil via breakdown of the metal-rich parent materials by weathering and pathogenic process, desert encroachment and other processes (Dampare *et al.*, 2006).

Sediments may have large concentration of metals from water, making crayfish and fish which are bottom dwelling to pick up these metals from the sediment which might be toxic for human consumption (Papagiannis, *et al.*, 2004). Nwaedozie, Agbaji and Nwaedozie (2011) evaluated some trace metals concentration in bank sediments of River Kaduna. The evaluation of six toxic metals of lead, Manganese, Nickel, Zinc, Cadmium and Cobalt was done using the Atomic Absorption Spectroscopy and it revealed that they are present in appreciable quantities as one move from less polluted area to areas with high pollution index. A similar research by (Aderinola *et al.*, 2009) reported varying concentration of heavy metals in surface water, sediments, fish and periwinkles of Lagos Lagoon. Their report showed that the mean levels of heavy metals in the sediments of Lagos lagoon were generally low and fell within the acceptable limits described by WHO and FEPA. It is therefore very possible that the study area may also have some concentration of these heavy elements considering the activities carried out around the catchment area of the river which ranges from farming, irrigation, quarrying to sewage draining are possible sources of these heavy metals.

In general, river sediment contains a wide range of heavy metals with varying concentrations depending on the surrounding geological environment and anthropogenic and natural activities occurring or that once occurred. These metals can be Fe, Cr, Mn, Cu, Pb, Hg, Cd, Co, etc. (Dube *et al.*, 2000). The present work is therefore aimed at the determination of the presence of heavy metals that are toxic to the environment and river sediment of the study area. The result will be essential for development of data base on the use and management of the environment in the study area and create awareness of the effect of those elements for the people living within the study area. An atomic Absorption Spectroscopy technique was chosen due to its sensitivity, simplicity and accuracy especially with regard to the analysis of the environmental samples.

2.0 Materials and Method

2.1 Atomic Absorption Spectroscopy (AAS)

AAS is an important tool in analytical laboratories. It offers sensitivity, selectivity and simplicity in the analysis of the concentrations of metals in solution. Metals commonly analysed include sodium, potassium, magnesium, zinc, chromium, mercury, cobalt, copper, cadmium, iron and arsenic. Up to sixty-eight (68) elements can be determined from part per billion (ppb) to percentage levels with good precision. In AAS, light of a specific wavelength is impinged on previously generated ground state atoms. The atoms absorb this light and a transition to a higher energy level occurs. This is called an excitation. To get the atomic absorption process to occur, the sample is aspirated into the burner chamber. Here the sample mixes as a fine aerosol with the fuel and oxidant gases of the metals still in solution in the fine aerosol droplets. These tiny droplets pass into the heat of the flame. In the flame, the process of evaporation or desolvation removes the solvent and leaves tiny solid particles of sample material. The simplest concept of atomic structure is that of positively charged nucleus containing protons and neutrons surrounded by electrons orbiting in space in the electric field created by the proton.

According to quantum mechanics such a system can exist in a stable state only if its energy is quantized even at the lowest energy level or ground state. All other levels are excited levels which can be induced by mechanical or electromagnetic means. Emission of light occurs when an atom reverts to a state of lower energy. Bohr equations express the conservation of energy by the relation

$$f = \frac{E_1 - E_2}{h} \quad 2.1$$

Or
$$\lambda = \frac{c}{f} = \frac{hc}{E_1 - E_2} \quad 2.2$$

Where c is the velocity of light (2.99793×10^8 m/s), h is the Planck's constant (6.62×10^{-34} Js), f is the frequency, λ is the wavelength and E_1 and E_2 are the energy levels of excited and ground state. (Welz and Sperling, 1999). When photons of frequency f interact with some atom of energy E_2 , the atom may be able to absorb the photon thus raising its energy to $E_2 + hf$, provided the energy level is equal to one of the excited energy levels of that atom. The general principle of atomic absorption spectrometric method is fundamentally based on Beer-Lambert Law (Welz and Sperling, 1999). According to the law absorbance is directly proportional to the path-length in flame and the concentration of gaseous atoms. However, both of these variables are difficult to determine, but the path-length can be made constant and the concentration of gaseous atoms is proportional to the analyte in the solution being aspirated.

Table 2.0 The corresponding wavelength values used in obtaining the concentrations of elements of interest.

Element	Pb	Mn	Mg	Cd	Cr	Ni	Fe	Co	Hg	Zn
wavelength(nm)	405.8	403.1	285.2	326.1	425.4	341.5	372	345.4	253.7	213.9

2.2 The Study Area

River Jare is located in Kafur local government area of Katsina state Nigeria within Latitude $11^{\circ}38'49.83''N$ and Longitude $7^{\circ}54'6.55''$ at an altitude 608m above sea level and it has a total area of 674km². The area falls in the southern part of the state and is bordered by Malumfashi LGA, Danja LGA, Bakori LGA of Katsina state and Rogo LGA of Kano State. Kafur LGA falls within a climate that is largely controlled by the Tropical Maritime Air Mass and Tropical Continental Air Mass. The interaction between these air masses determines the intensity and duration of the wet and dry seasons. The two seasons reflect the influence of the interaction of the warm moist tropical maritime air mass and the hot and dry tropical continental air mass during the respective seasons. The wet season starts in May and ends in early October and dry seasons last longer from November to April with total rainfall varying from 600-900mm annually, mean annual temperature of about 25°C. The area is characterized by high temperature of about 43°C, constant low relative humidity 50% and shorter raining season (Olofin, 1993).

The geology of the study area is underlain by crystalline basement complex which comprises mainly igneous and metamorphic rocks which were overlain by a thin mantle of decomposed weathered rocks which in turn were capped by a superficial laterite crust, top soil and alluvium.

2.3 Sample preparation

Sediment samples were collected randomly in four different locations in the river to a depth of approximately 0 to 20 cm. Sediment samples were crushed, air dried and sieved manually to powder. 80 ml of concentrated perchloric acid, 650 ml of concentrated Nitric acid (HNO₃) and 20 ml of concentrated sulphuric acid (H₂SO₄) were mixed together. Then 30 ml of the acid mixture was added to digest 1.0 g of the air dried samples. The resulting solution was covered and heated for 20 minutes. The digested solution was allowed to cool, filtered with Whatman number 42 filter paper into a 100 ml volumetric flask and made up to the 100 ml mark with distilled water. The digestion was carried out in triplicate for each of the sediment samples, and thereafter analyzed with AAS for the determination of heavy metals (Pb, Cr, Co, Mg, Fe, Ni, Mn, Hg, Ag, Zn and Cd). A blank solution was prepared and used for the background checks (Van Loon, 1980).

2.4. Determination of Heavy Metal Concentrations

Variante AAA-240F model equipped with a digital display was used for the analysis. Air acetylene was used as lean fuel. Appropriate hollow cathode lamp for each element determined was employed. Blank and standard solutions were aspirated and the absorbance readings in nanometers recorded. Three separate absorbance readings were taken for each sample aspirated and their average values computed. Similar procedure was followed for different samples and corresponding lamps. Average absorption reading of both standards and samples were corrected using blank readings. A calibration curve was constructed for the heavy metal standards with the absorbance (nm) versus concentration in (ppm). The concentrations of the elements (in ppm) were determined from the calibration graph by dividing the absorbance of the element by its gradient (obtained from the calibration curves).

3.0. Result and Discussion

AAS has been successfully used in determining the concentration of the elements present in Jare river sediment samples. The details of the elemental concentrations of the samples collected in the area were studied. The concentrations of eleven elements namely, Pb, Cd, Cr, Mn, Mg, Ni, Zn, Hg, Ag, Fe and Co, determined in the sediment are presented as mean values. The reliability of analytical result was checked using IAEA Soil-7 reference materials. It was found that the elemental concentrations are in good agreement with the certified values. Elements (Pb, Cd, Cr, Mn, Mg, Ni, Zn, Hg, Ag, Fe and Co), in the sediment sample are presented in the table 2.0 and 3.0 respectively.

Table 2.0 Concentration of the element determined in the study area using AAS in ppm

S/No	Sample Id	Pb	Mn	Mg	Cd	Cr
1	A	13.7	522.47	750.21	0.29	110.50
2	B	0.00	29.43	102.50	0.58	22.21
3	C	1.58	27.37	77.03	0.51	16.59
4	C	1.21	37.92	99.10	0.91	10.15
5	D	3.55	38.09	79.41	0.65	15.84
6	E	3.97	17.63	89.68	0.63	23.48
7	F	4.72	22.23	65.48	0.70	13.82
8	G	1.25	23.23	109.84	0.61	26.58
9	H	4.71	37.76	40.53	0.74	14.23
10	J	5.17	66.72	56.16	0.53	3.01
11	Average	3.986	82.285	146.702	0.615	25.641

Table 3.0 Concentration of the element determined in the study area using AAS in ppm

S/No	Sample Id	Ni	Fe	Co	Hg	Zn
1	A	30.29	38561.83	BDL	BDL	27.05
2	B	1.33	2348.90	BDL	BDL	7.00
3	C	ND	1366.54	BDL	BDL	6.46
4	C	ND	2345.60	BDL	BDL	3.20
5	D	ND	2910.80	BDL	BDL	6.58
6	E	ND	1017.12	BDL	BDL	5.99
7	F	ND	1292.16	BDL	BDL	6.58
8	G	2.38	3006.84	BDL	BDL	7.52
9	H	ND	1786.46	BDL	BDL	5.97
10	J	0.900	1828.38	BDL	BDL	5.01
11	Average	3.490	5415.535	BDL	BDL	8.135

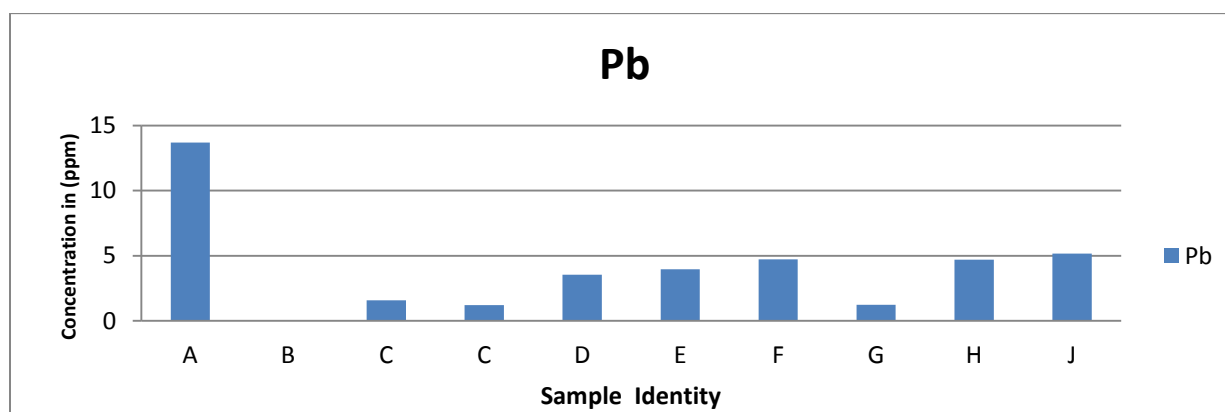


Fig 1: Concentration of lead in the sediment sample

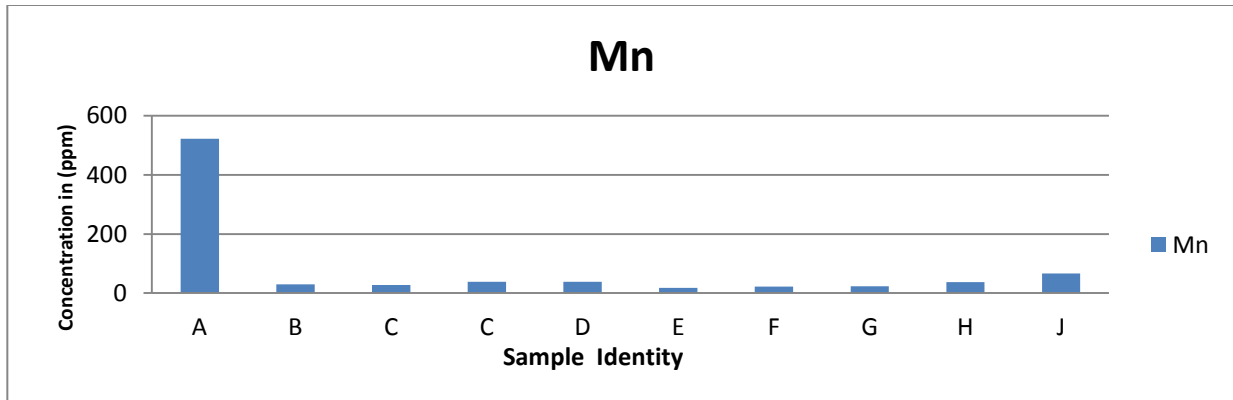


Fig 2: Concentration of manganese in the sediment sample

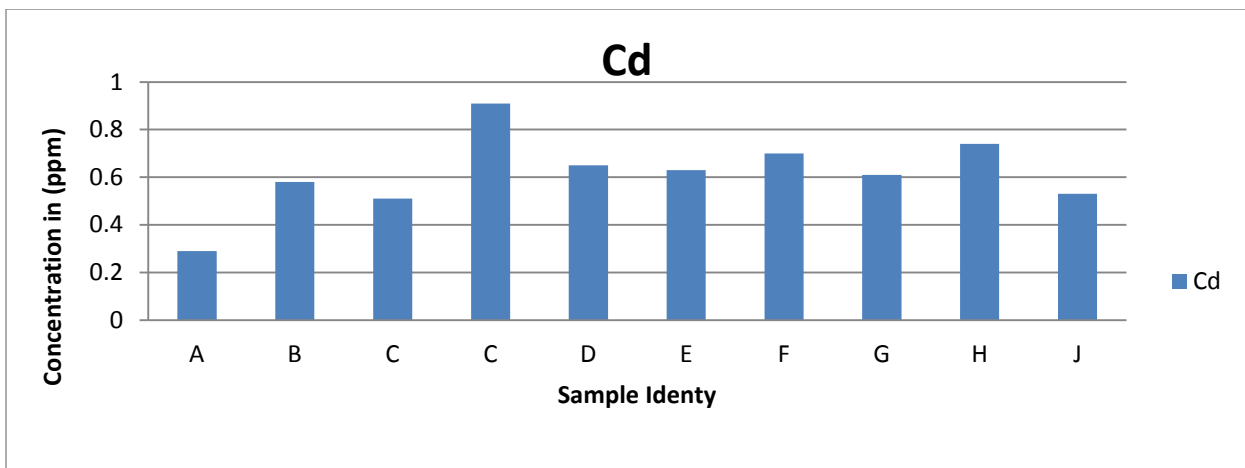


Fig 3: Concentration of cadmium in the sediment sample

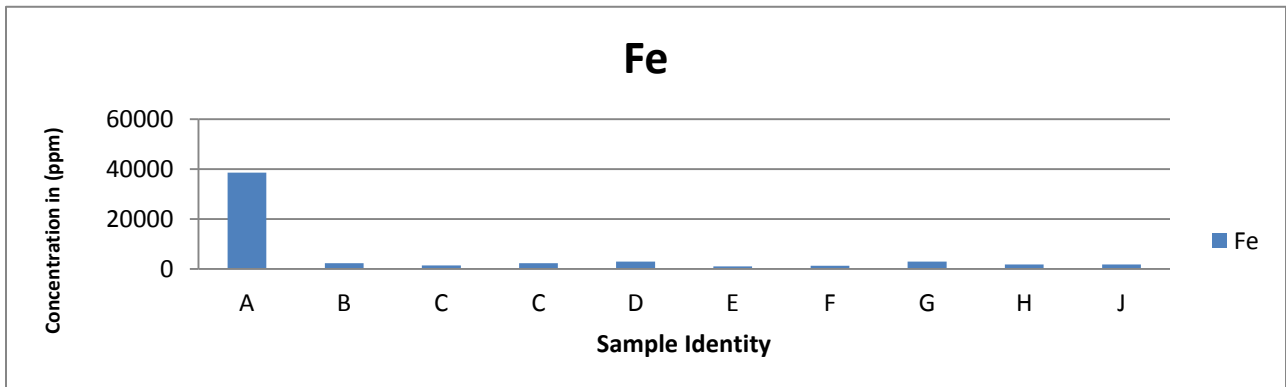


Fig 4: Concentration in ppm of iron in the sediment sample

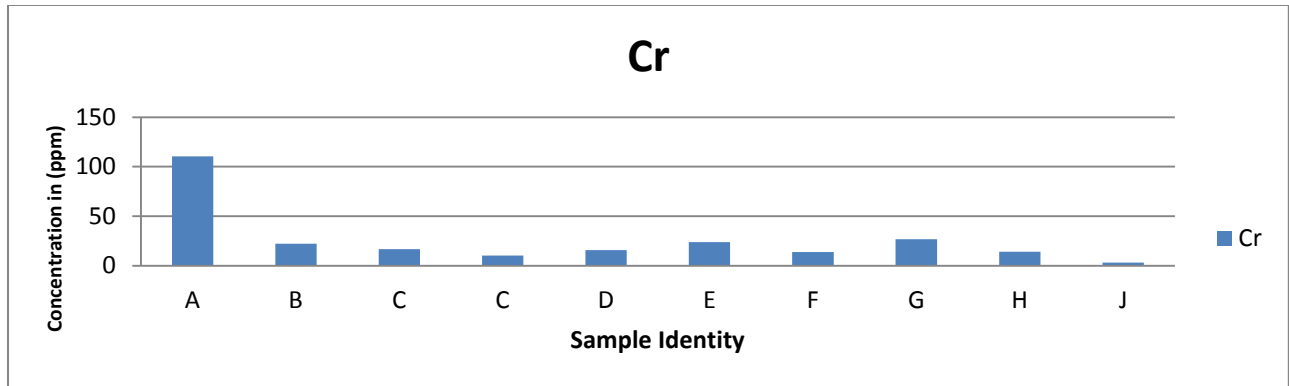


Fig 5: Concentrations of chromium the sediment sample

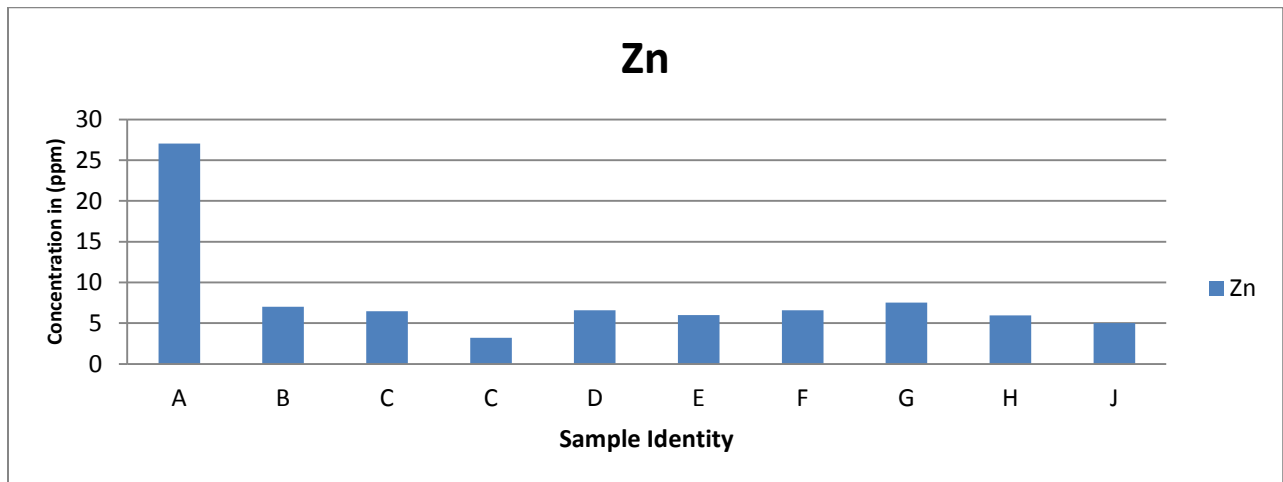


Fig 6: Concentration of zinc in the sediment sample

The variation of the elemental concentrations in the samples has clearly shown the influences of different factors as parent material, wind dust and other natural sources or anthropogenic activities. The concentration of Ni was found to be from 0.9 to 30.29ppm, the concentration of Fe ranges from 1292.16 to 38561.83ppm and the highest concentration of Fe was observed in sample A. The concentration of Co, Hg and was found to be below the detection limit in all the samples. The concentration of Zn ranges from 3.20 to 27.05ppm and the highest concentration was observed in sample A, the concentrations. The concentrations of Pb ranges from 1.21 to 13.7ppm and the highest concentrations of Zn were observed in sample A. The concentration of Mn in the sample ranges from 17.63 to 522.47ppm. The concentrations of Mg were found to be 400.53 to 750.21ppm. The concentrations of Cd range from 0.29 to 0.91ppm. The concentrations of Cr were found to be 3.01 to 110.5ppm, sample A was found to be slightly higher. The high concentration value of Fe in the entire sample may be due to the natural occurrence of iron in soil.

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Table 3.0 Comparison between the Average Concentration of the Element Determine in the Sediment Sample and that of WHO (1984)/Federal Environmental Protection Agency of Nigeria FEPA (1991)

Metals	Concentration (ppm)	WHO(1984)/FEPA(1991) ppm
Pb	3.986	0.01
Mn	82.285	0.05
Mg	146.72	NA
Cd	0.615	0.003
Cr	25.641	2.00
Ni	3.49	0.02
Fe	5415.535	0.30
Co	BDL	NA
Ag	BDL	NA
Zn	8.135	3.00

Na = Not available BDL = below the Detections Limit

From table 3.0 the comparison between the average concentrations of the elements determined in sediment it can be shown that the element determined are above the WHO (1981) and FEPA (1991) standard limit. The highest concentrations of Fe, Mn, Mg, Cr and Zn due to the contribution from anthropogenic sources, the farming and irrigation. There are however, considerable variations of this metals concentration by geographic region, the spatial temporal changes of geochemical back ground and possible effect of deep geological structures. From Table 4.0 it is clearly shown that the average concentrations of the elements determined are in good agreement and the entire element are within the soil global averages values.

Table 4.0: Comparison between the Average Concentration of the Element Determine in the Sediment Sample and That of Soil Global Average Values

S/No	Element	Obtained average ppm	Global average ppm
1	Pb	3.986	43
2	Mn	82.285	600
3	Mg	146.72	900
4	Cd	0.615	0.62
5	Cr	25.641	71
6	Hg	BDL	0.04
7	Ni	3.49	28
8	Fe	5415.535	36000
9	Zn	8.135	70
10	Co	BDL	8.15
11	Ag	BDL	0.22

The global average values for the elements in soil samples were obtained from Kabata-Pendias *et al.*,(1992).

4.0 Conclusion

This study has presented metal concentration (Pb, Cr, Co, Mg, Fe, Ni, Mn, Hg, Ag, Zn and Cd) in sediment sample of river Jare. The study revealed that the mean concentrations Fe, Mn, Cr and Zn, were found to be above standards prescribed by Nigerian Federal Environmental Protection Agency (FEPA, 1991) and World Health Organization (WHO, 1984). This result indicated that there is need to collect larger number of sample of the river sediment and soil sample in the study area in order to obtained reliable data for future work. Also there is need to investigate the contamination level in the study area by finding the pollution load index, enrichment index, geochemical accumulation and contamination factor in order to make the general recommendation. This work will therefore serve as baseline information for future work.

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