Assessing the Effects of Heavy Metal Concentration in Stream Sediments Within Onne and Environs Southeastern Nigeria

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Abstract

This study assessed the seasonal variations in heavy metal concentration of stream sediments in parts of Onne, Rivers state Southeastern Nigeria. River Ogu was mapped for the collection of stream sediments because of its prominence as a receptor of a lot of effluents discharge from the NNPC oil refinery, erosion and weathering of heavy metals from nearby towns. Stream sediment samples were obtained from eleven (11) strategic locations at 3km interval and; a control sample was obtained from Akpajo river to cover both the dry and wet seasons. Samples were analyzed with Atomic Absorption spectrometric method (AAS) and X-ray fluorescence spectroscopy (XRF) for Ni, Cu, Hg, Pb, Zn,Cd, As and Cr. The record of the relative abundance of the heavy metals in the stream sediments in decreasing order for both seasons is as follows; Zinc (Zn) > Nickel (Ni) > Cadmium (Cd) > Copper (Cu) > Chromium (Cr) > Mercury (Hg) > Lead (Pb) > Arsenic (As). Higher mean concentration values were generally recorded in the wet season than in dry season. Four elements (Zn, Cd, Ni and Cu) were found to be far higher than tolerable standard of the Federal Ministry of Environment (FME, 2006). The sources of the heavy metals are attributed to Onne refinery, Onne waste dump, runoff from roadside soil, acidic precipitation and effluents from petrochemical industries. Excessive concentrations of heavy metals in the stream sediments affects the aquatic life of the faunas and floras and have adverse effect on humans and this calls for regular monitoring of the chemistry of stream sediments in the area.

Keywords: Heavy metal, stream sediments, Atomic Absorption Spectrometry (AAS), x-ray fluorescence spectroscopy (XRF), River Ogu, Onne .

1. Introduction

There is paucity of information as regards heavy metal concentration on stream sediments in the area of study. However, a lot of work has been carried out on the physicochemical analysis of the study area. The present study is aimed at investigating the physicochemical characteristics of the stream sediments in the study area. It is a fact that excessive concentration of heavy metals that can cause adverse effects, except its effect on humans and aquatic life, can affect the quality of groundwater where there is a leak to the groundwater resources of the area.

Stream sediments are river bed materials commonly found as deposits under the water level. Stream sediments serve as reservoirs for heavy metals and minerals.

River sediments are a major potential sink for hydrophobic pollutants in the aquatic environment (Kreina et al., 2003; Schorer, 1997). The sediments are mainly sedimentary materials that must have undergone series of terrestrial and marine transportation through some weathering and erosion processes. Heavy metals from roadside runoffs and other anthropogenic sources (industrial, waste dump, sewage effluents from nearby residential areas) are washed into streams and tributaries contaminating both the surface water and the sediments that have settled under the water. These underwater sediments exhibit the capacity to store the various pollutants transported through the river course and also provide geologic information as may be required. Heavy metals enter the surroundings by natural means and through human activities. Various sources of heavy metals include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Morais *et al.*, 2012).

Heavy metals may enter into aquatic ecosystems from anthropogenic sources, such as industrial wastewater discharges, sewage wastewater, fossil fuel combustion and atmospheric deposition (Linnik and Zubenko, 2000; Campbell, 2001; Lwanga *et al.*, 2003; El Diwani and El Rafie, 2008; Idrees, 2009).

A polluted air has negative effects on the precipitation that falls into water bodies, stream sediments and soils. The precipitation can alter the chemistry of the soil, which, in turn, affects plant growth and water quality in a number of ways. This change is attributed principally to increased emissions of oxides of nitrogen and sulfur and their conversion to nitric and sulfuric acids (Galloway *et al.,* 1976).

Acid precipitation has a number of potential effects on terrestrial ecosystems including acidification of soils, altered nutrient supply, increased mobilization of aluminum and other shifts from acid sensitive to acid tolerant species of soil flora and fauna population, altered rates of decomposition of organics and nitrogen fixation (Jacobson *et al.,* 1988).

The dumping of solid waste in uncontrolled landfills can cause significant impacts on the environment and

human health (Dong et al. 2008). Of these wastes, the household (and similar commercial) wastes are expected to generate the highest amounts of landfill gas, strongly dominated by the main components, methane and carbon dioxide. Many municipal and industrial wastes are rich in trace toxic metals (Yusuf et al., 2003).

Soil contamination by heavy metals is of most important apprehension throughout the industrialized world (Hinojosa et. al., 2004). However, various studies have reported elevated concentrations of metals in stream sediments originating from landfill contamination sources. Studies of increased Cu, Pb, Zn, Cd, Ag, and Ba concentrations in stream sediments from landfills and water treatment facilities have been reported (Mantei and Coonrod, 1989; Mantei and Foster, 1991; Goncalves et al., 2004).

The extent of heavy metals from industrial effluents, acid rain deposition falling directly on the stream or through roadside runoffs and other man-made activities can pollute the aquatic ecosystems to a very high degree thereby negatively affecting the ecological balance of faunas in that environment.

The main objective of this work is to evaluate the impact of heavy metal concentration in stream sedimenst in the study area and thereby provide proper management strategy for sustainable development in the area. Some of the specific objectives are (1) determine the concentration of major pollutants with a view to assessing their level of pollution in the stream sediments of Ogu river. (2) establish the physico-chemical parameters in stream sediments to ascertain its pollution status and (3) develop some geochemical models and access the geochemical facies of the study area.

Heavy metals are significant environmental pollutants and their toxicity is a problem

of increasing significance for ecological, evolutionary, nutritional and environmental reasons (Jaishankar *et al.*, 2014; Nagajyoti *et al.*, 2010). The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment (Lambert *et*

al., 2000). This study was conducted during April 2018 to February 2019, along river Ogu in Onne, Eleme Local Government Area of River State Southern Nigeria.

2. Materials and Methods
2.1 Sample collection
Eleven (11) strategic locations of 3km interval was mapped out along the course of Ogu River for the collection of stream sediments while samples were collected from a control location along Akpajo river which is about 6km away amounting to 12 samples (fig 1). The top 20 cm of the stream sediment samples was collected from each sampling station using the Eckman bottom sampler. The stream sediment samples were pre-treated before final analysis.

2.2 Sample Treatment and Analysis
All the samples of sediments collected were allowed to thaw and air-dried at ambient temperature, sieved through 0.5 mm sieve and 2 g samples were digested using 25 ml 1:3:1 mixture of $HClO_4$, HNO_3 and H_2SO_4 acids in water bath. A 10 ml deionized water was added and decanted into 50 ml standard flask and after rinsing, the solution was made up to the mark with deionized water. Buck Scientific atomic absorption spectrophotometer model 200A and air-acetylene flame were used for trace metal analyses. Accuracy of the method was checked using a standard sediment sample PACS- 2. For organic carbon, 1 g dried, sieved sediment was weighed into 250 ml conical flask and digested with 10 ml 0.5 M $K_2Cr_2O_7$ and 20 ml conc H_2SO_4, for 30 min (Walkey and Black, 1934). 100 ml deionized water and 3 drops of Ferroin indicator were added and titrated with 0.25 M $FeSO_4$ solution. Organic matter was obtained by multiplying organic carbon values by 1.724.

3. Results /Discussion
The presence of anthropogenic sources of pollution in Onne area and its environs in Southeastern part of Nigeria has contributed to the contamination of the various aspects that constitute man's environment and most importantly as it pertains to this work, the stream sediments in river Ogu, in onne and its environs. The results acquired from an Atomic Absorption Spectrophotometry analysis of the stream sediments samples collected from river Ogu at 3km interval from April to August 2018 and from October 2018 to February 2019, covering both seasons of 2018 through 2019 are presented in Tables 1 and 2. The tables illustrate a higher mean concentration of heavy metals during the wet season compared to the data recorded during the dry season.

The mean values of heavy metal concentration for Zn (11.6mg/kg), Ni (2.37mg/kg), Cd (1.42mg/kg), Cu (1.13mg/kg), Cr (0.80mg/kg), Hg (0.66mg/kg), Pb (0.40mg/kg) and As (0.36mg/kg) recorded during the dry season are higher than the FME 2006 standards (fig 2 and Table 1) while the values recorded during the wet season are Zn (12.28mg/kg), Ni (2.51mg/kg), Cd (1.70mg/kg), Cu (1.23mg/kg), Cr (0.90mg/kg), Hg (0.76mg/kg), Pb (0.50mg/kg) and As (0.46mg/kg) which also record higher reading than the standard of the FME 2006) (figure 3 and Table 2). The general heavy metal data collected during the wet season is higher than the data obtained during the dry season. Although the heavy metal concentration of some elements are not very high above the tolerable

limit but the concentration of Zn, Cd, Ni and Cu recorded during the dry and wet season are far above the Federal Ministry of Environment (FME, 2006)) standard. The most abundant element measured from the sediment was Zn with 11.16mg/kg during the dry season and 12.16mg/kg in the wet season and are far above the FME 2006 limit. Generally, the metals in the stream sediment followed the same order of increasing concentration in both dry and wet seasons: Zinc (Zn) > Nickel (Ni) > Cadmium (Cd) > Copper (Cu) > Chromium (Cr) > Mercury (Hg) > Lead (Pb) > Arsenic (As). Several other metals analyzed were in the order Potassium (K) > Calcium (Ca) > Iron (Fe) > Vanadium (V) > Selenium (Se). The sample analyzed from the control point have lower mean concentration value except copper (Cu) and Cadmium (Cd) that shows the same mean concentration as recorded from the sampling locations.
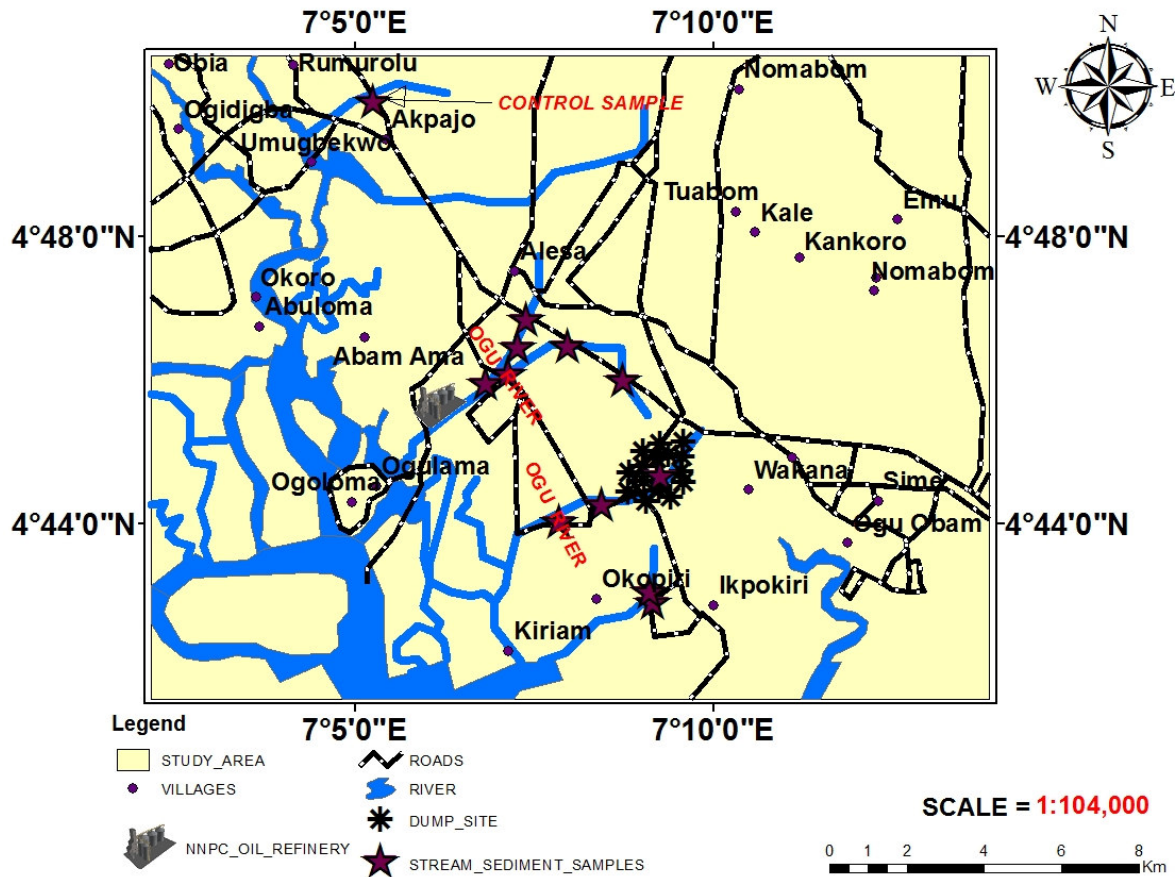

Fig.1: Location map showing stream sediment sampling location along Ogu river

Table 1. Onne Stream Sediments (Dry Season)

Parameters	1	2	3	4	5	6	7	8	9	10	11	Mean	Control Point (3km away)	FME 2006 Standards
Coordinates	N4⁰42.9' E 7⁰ 9.14'	N4⁰43.03' E 7⁰ 9.12'	N4⁰44.67' E 7⁰ 9.24'	N 4⁰44.11' E 7⁰ 8.45'	N4⁰44.03' E 7⁰ 7.85'	N4⁰46.01' E 7⁰ 8.74'	N4⁰46.49' E 7⁰ 7.97'	N4⁰45.96' E 7⁰ 6.82'	N4⁰46.09' E 7⁰ 7.14'	N4⁰46.48' E 7⁰ 7.29'	N4⁰46.85' E 7⁰ 7.39'		N4⁰49.9' E7⁰5.27'	
Elevation, m	7.92	9.14	24.30	19.20	19.50	21.33	21.64	16 .76	18.28	19.50	18.89		21.0	
pH@ 25⁰C	6.22	6.24	6.26	6.28	6.24	6.22	6.26	6.28	6.20	6.20	6.24	6.24	6.40	6.5 - 8.5
Electrical conductivity, μmhos/cm	694.90	70.00	74.00	695.50	69.60	72.00	75.70	76.20	68.30	74.00	69.05	185.38	190.30	1000
Ca, mg/kg	10.00	12.60	8.80	9.60	10.00	10.50	11.82	8.80	10.60	12.00	11.80	10.59	60	200
Na, mg/kg	12.68	12.00	10.80	12.83	11.80	12.00	12.40	11.00	12.00	11.60	12.60	11.97	80	NS
Mg, mg/kg	5.50	5.80	5.60	5.40	5.20	5.0	5.02	5.04	5.80	5.82	5.84	5.45	5.00	100
K, mg/kg	8.10	7.20	8.40	12.00	10.40	13.60	14.000	30	40	36	20	18.15	15	100
Cl, mg/kg	80.50	82.00	70.00	75.00	76.50	70.00	73.30	84.60	82.00	71.00	65.00	75.44	100	250
HCO₃, mg/kg	105.50	106.00	70.50	110.20	115.30	107.00	104.30	116.50	110.00	100.25	100.00	104.14	99.50	NS
SO₄, mg/kg	38.50	37.00	34.30	35.00	40.00	30.25	32.00	45.50	42.20	28.30	25.80	35.35	27.50	200
NO₃, mg/kg	76.00	76.50	60.20	80.50	82.20	76.00	75.80	85.80	76.80	70.00	68.80	75.32	65.90	50
Total Iron, mg/kg	0.80	0.70	0.50	0.40	0.405	0.30	0.20	0.90	0.77	0.40	0.30	0.51	0.30	
Ni, mg/kg	2.363	2.370	2.372	2.374	2.378	2.380	2.382	2.370	2.374	2.376	2.374	2.37	2.200	0.05
Cu, mg/l	1.130	1.133	1.134	1.130	1.128	1.132	1.130	1.136	1.134	1.132	1.130	1.13	1.118	0.10
Hg, mg/kg	0.668	0.670	0.672	0.666	0.664	0.662	0.660	0.658	0.656	0.654	0.652	0.66	0.0008	0.001
Pb, mg/kg	0.425	0.426	0.428	0.426	0.424	0.422	0.420	0.386	0.384	0.382	0.380	0.40	0.330	0.05
Zn, mg/kg	11.201	11.188	11.186	11.184	11.182	11.180	11.160	11.140	11.140	11.138	11.136	11.6	11.160	3.00
Cd, mg/kg	1.433	1.435	1.431	1.430	1.428	1.426	1.424	1.420	1.421	1.420	1.422	1.42	1.380	0.05
As, mg/kg	0.366	0.368	0.364	0.362	0.363	0.360	0.364	0.369	0.368	0.365	0.363	0.36	0.288	0.20
Cn, mg/kg	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	NS
Cr, mg/kg	0.808	0.806	0.805	0.810	0.811	0.803	0.802	0.800	0.802	0.802	0.788	0.80	0.700	0.05
V, mg/kg	0.06	0.07	0.06	0.08	0.05	0.04	0.03	0.04	0.04	0.03	0.02	0.04	0.01	0.05
Se, mg/kg	0.04	0.05	0.06	0.04	0.04	0.03	0.02	0.04	0.05	0.06	0.04	0.04	0.01	0.05
Oil and grease, mg/kg	0.02	0.02	0.03	0.03	0.04	0.03	0.02	0.02	0.03	0.03	0.02	0.025	0.006	5.00
TPH, mg/kg	0.02	0.03	0.04	0.02	0.03	0.04	0.03	0.02	0.02	0.03	0.02	0.026	0.007	NS
BETEX,mg/kg	0.059	0.058	0.062	0.064	0.066	0.064	0.062	0.060	0.062	0.060	0.060	0.061	0.050	NS

Table 2. Onne Stream Sediments (Wet Season)

| Parameters	1	2	3	4	5	6	7	8	9	10	11	Mean	Control Point (3km away)	FME 2006 Standards
Coordinates	N4⁰42.9' E 7⁰ 9.14'	N4⁰43.03' E 7⁰ 9.12'	N4⁰44.67' E 7⁰ 9.24'	N 4⁰44.11' E 7⁰ 8.45'	N4⁰44.03' E 7⁰ 7.85'	N4⁰46.01' E 7⁰ 8.74'	N4⁰46.49' E 7⁰ 7.97'	N4⁰45.96' E 7⁰ 6.82'	N4⁰46.09' E 7⁰ 7.14'	N4⁰46.48' E 7⁰ 7.29'	N4⁰46.85' E 7⁰ 7.39'		N4⁰49.9' E7⁰5.27'	
Elevation, m	7.92	9.14	24.30	19.20	19.50	21.33	21.64	16 .76	18.28	19.50	18.89		21.0	
pH@ 25⁰C	6.45	6.54	6.35	6.40	6.33	6.53	6.35	6.44	6.40	6.40	6.34	6.41	6.30	6.5-8.5
Electrical conductivity, μmhos/cm	696.90	85.00	84.00	699.50	89.60	82.00	85.70	86.20	78.30	84.00	75.05	195.11	200	1000
Ca, mg/kg	11.00	12.60	10.80	10.60	11.00	10.50	11.82	13.80	12.60	13.00	14.80	12.04	60	00
Na, mg/kg	14.68	13.00	13.80	13.83	12.80	15.00	14.40	13.00	12.00	12.60	14.60	13.61	80	NS
Mg, mg/kg	5.80	5.95	5.65	5.60	5.95	5.30	5.10	5.09	6.10	5.98	6.04	5.68	5.20	100
K, mg/kg	9.10	7.40	8.80	12.70	11.40	14.60	14.50	30.90	41.00	36.50	21.30	18.92	17	100
Cl, mg/kg	85.50	87.00	74.00	77.00	79.50	73.00	75.30	87.60	85.00	74.00	68.00	78.71	100	250
HCO₃, mg/kg	110.50	116.00	74.50	112.20	119.30	112.00	110.30	119.50	118.00	106.25	102.00	109.14	100.50	NS
SO₄, mg/kg	40.50	39.00	37.30	38.00	44.00	35.25	38.00	46.50	47.20	33.30	29.80	38.98	30.50	200
NO₃, mg/kg	79.20	78.50	65.00	84.50	86.20	78.00	80.80	88.80	80.80	73.00	72.80	78.87	69.90	50
Total Iron, mg/kg	0.90	0.80	0.60	0.50	0.45	0.35	0.30	0.95	0.80	0.45	0.38	0.58	0.40	
Ni, mg/kg	2.515	2.522	2.553	2.501	2.560	2.545	2.533	2.500	2.502	2.498	2.489	2.51	2.400	0.05
Cu, mg/l	1.230	1.233	1.234	1.230	1.228	1.232	1.230	1.236	1.234	1.232	1.230	1.23	1.201	0.10
Hg, mg/kg	0.768	0.770	0.772	0.766	0.764	0.762	0.760	0.758	0.756	0.754	0.752	0.76	0.001	0.001
Pb, mg/kg	0.525	0.526	0.528	0.526	0.524	0.522	0.520	0.486	0.484	0.482	0.480	0.50	0.430	0.05
Zn, mg/kg	13.201	12.188	12.186	12.184	12.182	12.180	12.160	12.140	12.340	12.238	12.136	12.28	12.160	3.00
Cd, mg/kg	1.733	1.735	1.731	1.730	1.728	1.726	1.724	1.720	1.721	1.620	1.622	1.70	1.580	0.05
As, mg/kg	0.466	0.468	0.464	0.462	0.463	0.460	0.464	0.469	0.468	0.465	0.463	0.46	0.388	0.20
Cn, mg/kg	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.00	ND	NS
Cr,mg/kg/kg	0.908	0.906	0.905	0.910	0.911	0.903	0.902	0.900	0.902	0.902	0.888	0.90	0.800	0.05
V, mg/kg	0.08	0.09	0.09	0.09	0.07	0.06	0.06	0.06	0.07	0.06	0.05	0.07	0.03	0.05
Se, mg/kg	0.06	0.07	0.08	0.07	0.06	0.05	0.05	0.06	0.07	0.08	0.07	0.06	0.03	0.05
Oil and grease, mg/kg	0.04	0.04	0.05	0.06	0.06	0.05	0.05	0.04	0.05	0.05	0.04	0.048	0.009	5.00
TPH, mg/kg	0.03	0.04	0.05	0.03	0.04	0.05	0.04	0.03	0.03	0.04	0.03	0.037	0.008	NS
BETEX,mg/kg	0.069	0.068	0.072	0.074	0.076	0.074	0.072	0.070	0.072	0.070	0.070	0.071	0.060	NS
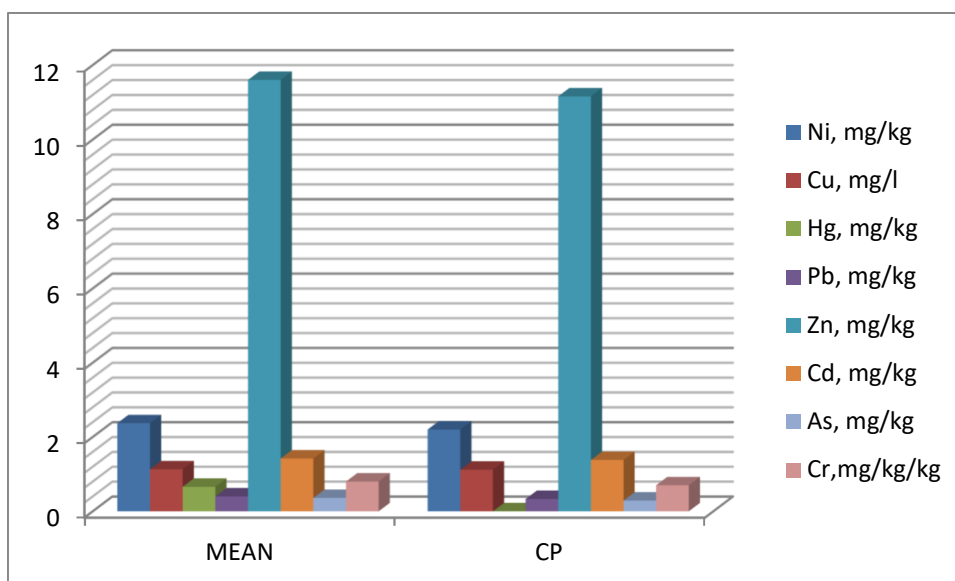
Fig. 2: Comparison of mean concentration of some heavy metals in stream sediments with the control point (Dry)
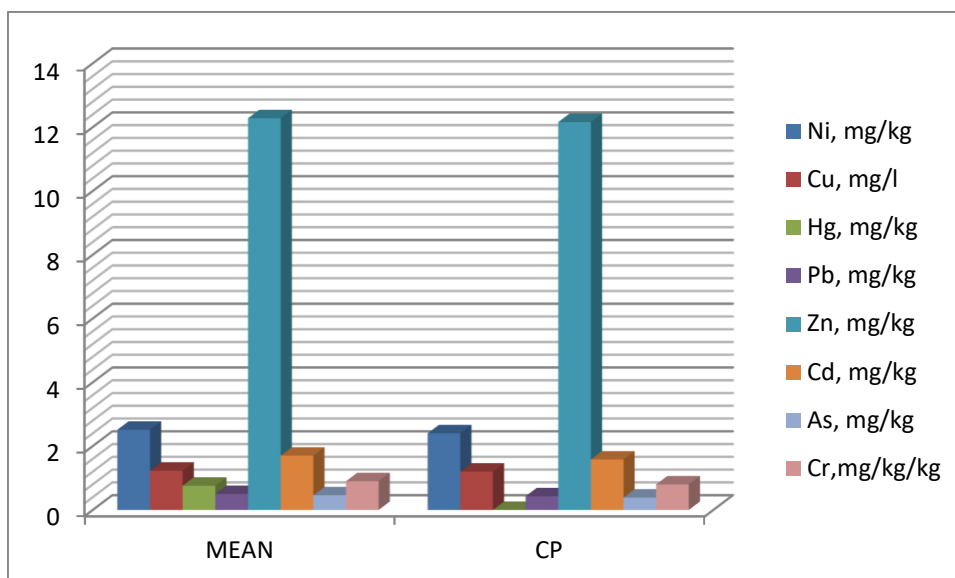

Fig 3: Comparison of mean concentration of some heavy metals in stream sediments with the control point (Wet)

4. Conclusion
The concentrations of heavy metals in stream sediment samples collected were analyzed and studied. The analysis carried out indicates that the concentration of Zn, Cd, Ni and Cu recorded during the dry and wet season are far above the Federal Ministry of Environment (FME, 2006) standard. The most abundant element measured from the sediment was Zn with 11.16mg/kg during the dry season and 12.16mg/kg in the wet season and are far above the FME (2006) limit. Heavy metal concentration in stream sediments is a serious issue most especially in the Niger Delta and Onne in particular hence to overcome this problem, substantial amount of research and development activities are needed as a key mitigation approach.

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