Original Research Article

Occurrence and fate of Polychlorinatedbiphenyl in water and sediments: A case study of Bodo River in Ogoni, River State Nigeria.

ABSTRACT

Contamination of water bodies due to the presence of persistent organic pollutant (POPs) has been a major concern in the environment. This study aims at determining the concentration of Polychlorobiphenyl Known as PCB and Heavy Metal in sediments and water samples in Bodo River. Standard Analytical techniques were employed during the sampling process in order to achieve high level of accuracy and precision. The samples were digested and the extracts were collected for GCMS determination of Polychorobiphenyl in the samples collected.The results of the analysis shows that the concentration of Polychlorobiphenyl were found to exceed the maximum residue limit of persistent organic pollutant. Therefore it is advised that farmland and borehole connected to the sampling location be evaluated so as to minimize the health risk associated with exposure to Polychlorobiphenyl.

Keywords: Heavy Metals, Polychlorobiphenyl, Persistent organic pollutants

1.0 INTRODUCTION

Water is one of the most critical natural resources worldwide and is essential for all known forms of life. The US Environmental Protection Agency (2001) lists rivers, lakes, estuaries, and wetlands to be among a nation's most precious resources. They significantly shape our ecosystem and are linked to the overall health of the environment. Waterways provide many benefits such as tourism, recreation, transport, ecosystem services, property uplift and regeneration as well as possess cultural and spiritual values. However, they can be easily impacted by anthropogenic and natural processes (US-EPA, 2001). Among the anthropogenic influences, population growth and urbanization pose significant threat to water quality and affect river health. High population growth and the consequent need for expanded food production, energy generation, and the protection of public health tend to produce high volumes of pollutants (Igbo *et al.*, 2018). In order to increase crop and livestock yields, farmers rely on the usage of pesticides, and fertilizers. Similarly, to protect public health, pesticides such as dichlorodiphenyltrichloroethane (DDT) and dieldrin have been utilised for mosquito and termite control. Most of these pesticides are non-biodegradable and adhere strongly to soil that can be eroded and washed into surface water. Likewise, worldwide usage fossil fuels such as refined crude oil (gasoline, diesel, and fuel oils), natural gas and coal have increased drastically. These fuels are essential to the global economy for energy production, transportation, petrochemical industries, and many other purposes. However, the extraction and processing of fossil fuels, in addition to their usage pose significant environmental challenges. Polychlorinated biphenyls also known as PCBs, are a group of 209 structurally related chemical compounds (congeners),consisting of two connected benzene rings and 1–10 chlorine atoms (Gilbert, 2014).

PCBs in the water environment originate solely from human activity. The aim of the study is to determine the concentration of Polychlorinated biphenyl (PCBs) and selected heavy metals in surface water and soil sediment in Bodo River in Ogoni Land, Rivers State Nigeria.

2.0 MATERIALS AND METHODS

2.1 Description of Sample Area

Bodo River is found in Gokana Local Government Area of Ogoni Land in Rivers State. It is bounded on the north and east by the Imo River, on the south by the coastal sand plains, and on the west by the Aba-Port Harcourt highway. The Delta region contains a range of environmental zones including coastal sand plains, deltaic and floodplains, mangrove forests, and barrier island habitats. The climate for the southern coastal region of Nigeria is hot and humid. The average temperatures in the area range between 77.0°F in August to 81.0°F in March and April. This area receives 93 inches of rainfall during per year; heaviest rains arrive during the months of July and August. The major occupation of the resident is fishing and various Agriculture activities. The map below shows the area of sample collection.

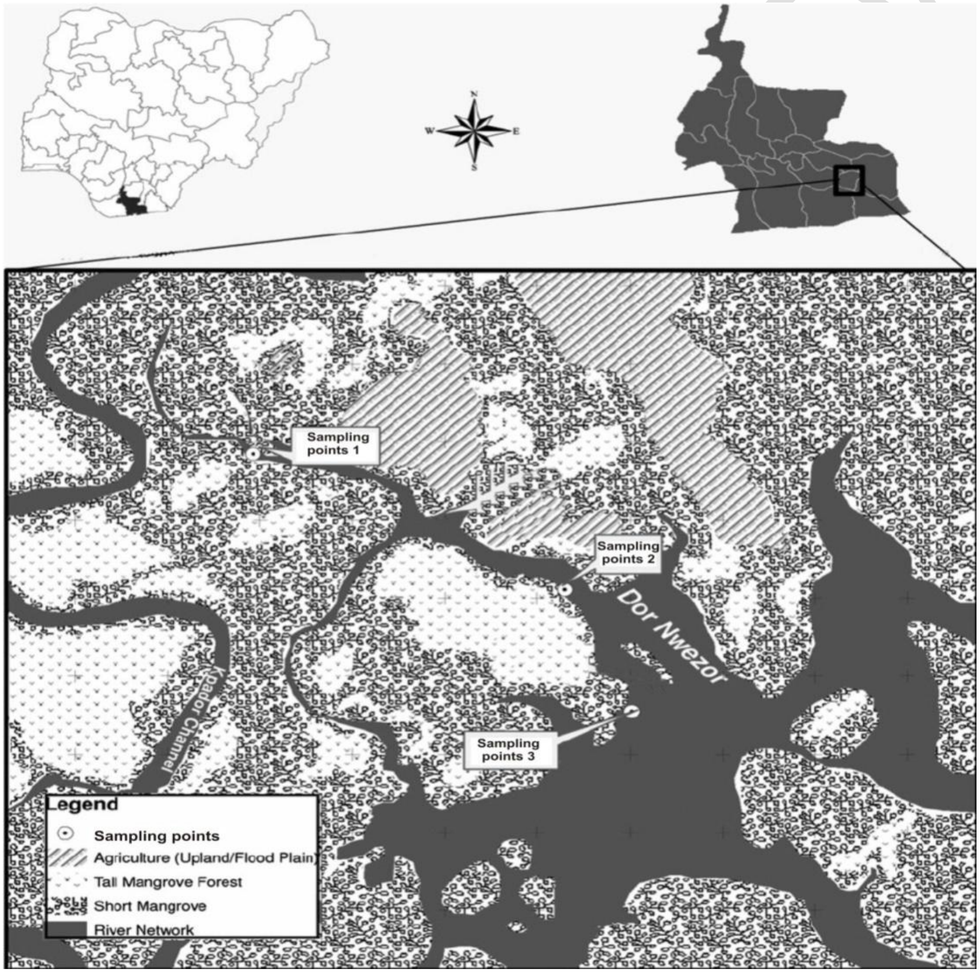

Fig 1: Map showing the study area

2.2 Sample Collection and Preparation

Three (3) water samples and three (3) soil sediments were collect from Bodo-River in Rivers State. The water samples were collected with the use of amber color bottle while the sediment samples were collected in sterile black polythene using a grab sampler. The samples were then taken to Maeve Research Laboratories, Awka and stored in a refrigerator for further analysis.

2.2.1 Sample Preparation for Water Samples and Soil Sediment

One hundred grams (100g) of the sediment sample was grinded into powder form with the help of a grinder (mortar and pestle). The samples were then transferred into three different sterilized 500ml conical flask ready for further analysis. The water samples were collected in 4L amber bottles and stored under refrigeration until filtration at the laboratory. The glass bottles were immersed and opened at 0.5 m in depth, avoiding contamination by the surface film. Samples were then filtered through already washed and decontaminated (45 °C for 6 h) 142-mm diameter and 0.7-μm pore size fibre glass membranes. The filters were frozen and later lyophilized for the analyses, whereas the filtrated waters were kept at 8–10 °C.

2.3 Apparatus and Materials

2.3.1 Equipment Used

The equipment used electric blender, grinder digital sensitive scale, 250ml and 500ml beaker,test tubes, injector, GC-MS(gas chromatography/ mass spectrometer), 0-1000ml micro pipette, digital weighing balance, magnetic starrier and shaker, sterilized sample bottles, injector, Absorption Spectrophotometer (Varian SpectrAA 600 model USA), fume cupboard, Heating mantle, Centrifuge tube, Glass wool.

2.3.2 Chemical Reagents Used

Trifluoroacetic anhydride (TFAA) and Trifluoroethanol (TFE) in excess, sodium hydroxide solution,methanol, sodium hydroxide, distilled water, acetonitrile,Calibration Solutions. Individual AMPA and PMG stock calibration solutions of 1000 pglmL were prepared by dissolving, Aliquots of each stock solution, working calibration solutions of 10, 1, and 0.1 pglmL, Concentrated H_2SO_4, concentrated perchloric acid ($HClO_4$).

2.4 Determination of PCBs in Soil Sediments and Water Samples

2.4.1 Environmental Protection Agency (EPA) 547.0 Method of PCBs Determination (2005):

Two grams (2g) of soil sediment samples was weighed into a 250ml conical flask. To each portion of the samples, 2ml methanol,4ml 0.5 of sodium hydroxide and 2ml distil water was added. The mixture was rinsed with 4ml 0.5M sodium hydroxide solution. 25ml of the solution was measured using measuring cylinder and 2ml hydrogen per oxide solution was added and stirred on a magnetic stirrer for 10mins to homogenize. 4ml of 0.5M HCL and acetonitrile was added and heated to evaporate in a water bath for 40-50mins then reconstituted with 20ml of distil water ready to be injected in GC-MS (Gas Chromatography/Mass Spectrometer). 1ml of each of the prepared sample and the replicate in a concentration of 1.0ml and 2.0ml were injected into GC-MS machine one after the other and their readings taken and recorded respectively for each of the four samples. For the water samples 1ml of the prepared water samples were injected into GC-MS directly.

2.5 Heavy Metal Analysis for Water and Sediment Samples (APHA, 2017)

2.5.1 Digestion of Soil Sediment Samples

2.0 g of each of the dried-sieved soil sediment samples were weighed with a digital weighing balance into 125 ml beakers. The samples were digested with (3ml 65% HNO_3: 1ml 35% HCl) for 3 hours on a hot plate (45℃). This was done to reduce the interference of organic matter. The digested samples were allowed to cool at room temperature and filtered using Whatman filter paper into 100ml volumetric flask. The sides of the beakers were washed with de-ionized water and diluted to a volume of 25 ml and transferred into the appropriate test tube.

2.5.2 Determination of heavy metal in soil sediment samples

A series of calibration solutions (standards) containing known amounts of analyte elements was prepared and used to calibrate the VARIAN Atomic Absorption Spectrometer AA240FS. Blanks were then atomized followed by the standards and calibration graphs plotted showing the response from the AAS. The concentrations were calculated based on the absorbance obtained using the Beer Lambert law. Responses of standard were then used to establish accurate performance of machine and accurate concentration values of element. The machine was calibrated after every triplicate analysis. Using the AAS, light was generated from a hollow cathode lamp at a wavelength characteristic to each analyte. Each analyte was then atomized using an atomizer to create free atoms from the samples. Air-acetylene gas was used as the source of energy for the production of free atoms for the elements. The samples were then introduced as an aerosol into the flame and the burner aligned in the optical path to allow the light beam pass through the flame where the light was absorbed. The light was then directed into a monochromator which then isolated the specific analytical wavelength of the light emitted by the hollow cathode lamp from the non-analytical. The sensitive light detector then measured the light and translated the response into analytical measurements. Calculation of concentration of heavy metals was done using the equation of the calibration curve.

$$\text{Conc. of metal}\left(\frac{\text{mg}}{\text{kg}}\right) = \frac{(\text{A} - \text{B})\ \text{X DF}}{\text{Wt of sample(g)}}$$

Where: A = concentration of metal in sample (mg/l), B = concentration of metal in blank (mg/l) DF= dilution factor

2.5.3 Determination of Heavy metals in water samples (APHA, 2017)

The water samples were filtered using a Whatman No 42 filter paper. 100 ml of the filtrate was then measured into a beaker. In addition, 15 ml concentrated nitric acid solution and 10 ml of 50% concentrated hydrochloric acid solution were added. The content was evaporated to almost dryness on a hot plate and 7 ml of 50% concentrated hydrochloric acid added and heated for 10 minutes. The solutions were allowed to cool, and then distilled water added to each and filtered into a 100 ml Pyrex volumetric flask using a Whatman No 42 filter paper. This was then made up to the mark with distilled water. The 100 ml each of the water samples was used for the heavy metal determination using VARIAN AA240FS-Flame Atomic Absorption Spectrometer model.

2.6 Analytical quality assurance and quality control

Proper quality assurance procedures and precautions were taken to ensure the reliability of the results. The samples were carefully handled to avoid any external influences that could interfere with the integrity of the sample and hence contaminate it. Glass wares were properly cleaned, and reagents were of analytical grades. Deionized water was used throughout the study. For validation of the analytical procedure, repeated analysis of the samples against internationally certified/standard reference material (SRM-1570) of National Institute of Standard and Technology were used.

2.7Statistical Analysis

The data collected were subjected to Two Way ANOVA at significant level of 0.05% to ascertain the level of significance of PCB's and heavy metals in each of the samples.

3.1 RESULTS

Table 1: Concentration of PCBs in soil in mg/kg

PCBs	**Retention Time(secs)**	**SOIL SAMPLES CONCENTRATION (mg/kg)**		
		Sample code		
Detected PCBs		**S_A**	**S_B**	**S_C**
Naphthalene	3.37	88.1 ± 0.001	21.2± 0.002	7.4 ± 0.016
1-Methyl-naphtalene	3.38	42.1 ± 0.012	34.5 ± 0.023	3.9 ± 0.012
2-Methyl-naphtalene	4.06	34.1 ± 0.011	ND	23.1 ± 0.13
Biphenyl	4.38	54.1 ± 0.002	9.2 ± 0.11	3.8 ± 0.013
Acenanaphthylene	4.74	52.1 ± 0.001	33.7 ± 0.023	9.4 ± 0.012
Acynanaphthylyne	4.89	53.1 ± 0.013	45.8 ± 0.001	2.32 ± 0.022
Fluorene	5.36	ND	ND	ND
Phenanthrene	6.18	78.1 ± 0.002	45.9 ± 0.002	12.3 ± 0.011
Anthracene	6.23	ND	20.6 ± 0.003	17.3 ± 0.045
PCB 31 (TriCB)	6.45	58.0± 0.001	54.6 ± 0.0023	16.9 ± 0.001
PCB 28 (TriCB)	6.47	56.0 ± 0.002	ND	17.8 ± 0.001
PCB 52 (TetraCB)	6.47	ND	7.3 ± 0.034	ND
Fluoranthene	7.21	20.1 ± 0.33	8.4 ± 0.015	5.2 ± 0.001
PCB 101 (PentaCB)	7.26	ND	25.9 ± 0.021	2.6 ± 0.001
Pyrene	7.39	22.1 ± 0.024	7.45 ± 0.025	6.67 ± 0.003
PCB 153 (HexaCB)	7.82	ND	23.1± 0.032	ND
MEAN		34.89	21.10	8.04

Results presented as mean ± standard deviation of three replicates. No significant difference at p<0.05.

Table 2: Concentration of PCBs residues in water in mg/l

PCBs	**Retention Time(secs)**	**WATER SAMPLES CONCENTRATION (mg/l)**		
Detected PCBs		**W_A**	**W_B**	**W_C**
Naphthalene	3.37	28.1 ± 0.001	12.2 ± 0.002	1.4 ± 0.016
1-Methyl-naphtalene	3.38	23.1 ± 0.012	8.9 ± 0.023	0.9 ± 0.002
2-Methyl-naphtalene	4.06	14.1 ± 0.011	21.8 ± 0.011	3.1 ± 0.113
Biphenyl	4.38	ND	3.2 ± 0.11	ND
Acenanaphthylene	4.74	36.1 ± 0.001	6.67 ± 0.023	ND
Acynanaphthylene	4.89	25.1 ± 0.013	8.87 ± 0.001	0.32 ± 0.002
Fluorene	5.36	ND	ND	ND
Phenanthrene	6.18	ND	13.45 ± 0.002	2.13 ± 0.011
Anthracene	6.23	37.1 ± 0.016	6.68 ± 0.003	7.2 ± 0.045
PCB 31 (TriCB)	6.45	21.0 ± 0.001	19.26 ± 0.0023	6.9 ± 0.0011
PCB 28 (TriCB)	6.47	ND	17.2 ± 0.001	1.8 ± 0.001
PCB 52 (TetraCB)	6.47	18.1 ± 0.002	0.23 ± 0.004	3.92 ± 0.032
Fluoranthene	7.21	7.1 ± 0.33	2.34 ± 0.015	2.02 ± 0.001
PCB 101 (PentaCB)	7.26	ND	ND	ND
Pyrene	7.39	5.6 ± 0.024	2.15 ± 0.025	0.67 ± 0.003
PCB 153 (HexaCB)	7.82	4.6 ± 0.011	0.91± 0.003	0.2 ± 0.002

Results presented as mean ± standard deviation of three replicates. No significant difference at $p<0.05$.

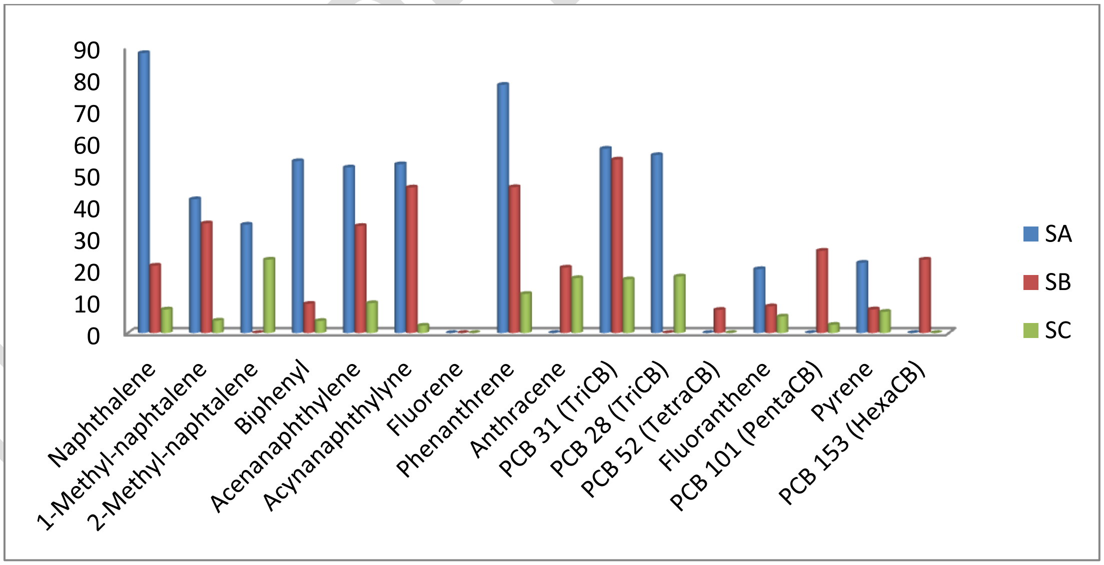

Fig2: Chart of PCBs Concentration in soil in mg/kg

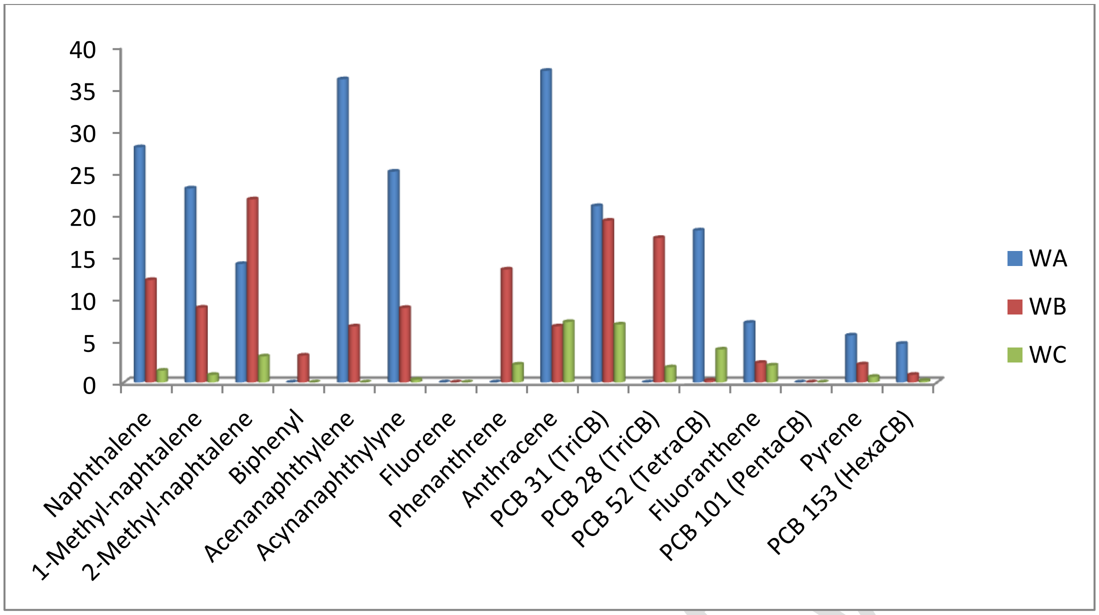

Fig 3: Chart of PCBs Concentration in water in mg/l

Table 3: Heavy metal concentrations (mg/kg) in soils of the study area

SAMPLE CODE	Hg	Pb	Mn	Cd	Cu
S_A	ND	25.4±0.001	24.2 ±0.12	4.2 ±0.011	14.44±0.02
S_B	ND	15.23±0.003	32.0 ±0.001	3.51 ±0.033	27.41 ±0.21
S_C	ND	7.47±0.01	13.33 ±0.001	2.24 ±0.002	12.19 ±0.12
MEAN	-	16.03	23.18	3.32	18.01

Results presented as mean ± standard deviation of three replicates. No significant difference at $p<0.05$.

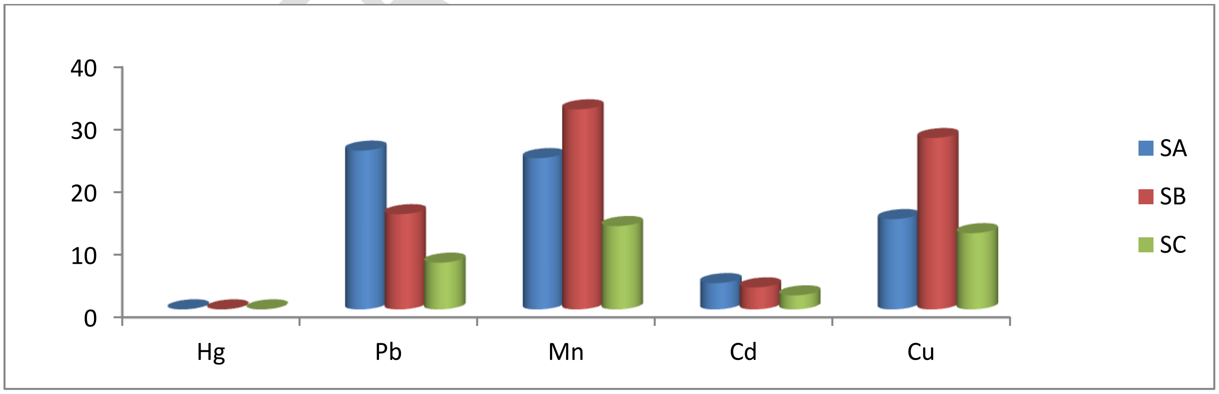

Fig 4: Chart of Heavy Metal Concentration in soil in mg/kg.

Table 4: Heavy metal concentrations (mg/l) in water of the study area

SAMPLE CODE	Hg	Pb	Mn	Cd	Cu
W_A	ND	16.0±0.001	12.0 ±0.02	1.2±0.002	11.0±0.002

W_B	ND	12.0±0.013	14.23±0.011	2.5±0.012	23.2±0.002
W_C	ND	2.0 ±0.015	5.0 ±0.021	1.6±0.022	7.7 ±0.01
MEAN	-	10.00	10.41	1.77	13.90

Results presented as mean ± standard deviation of three replicates. No significant difference at $p<0.05$.

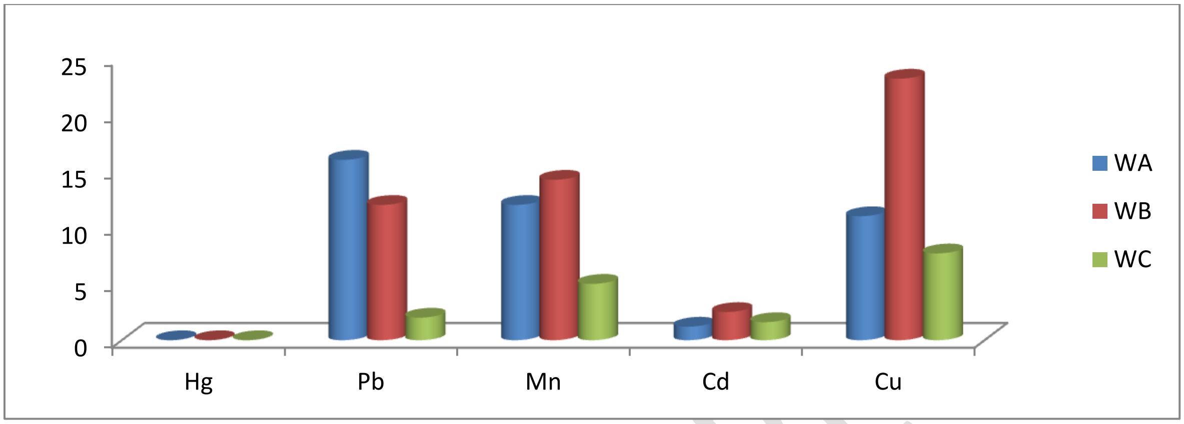

Fig 5: Chart of Heavy Metal Concentration in water in mg/l.

3.2 DISCUSSIONS

3.2.1 Concentrations of PCBs in soil and water samples

After sample extraction and clean-up, each extract was injected thrice into the GC/MS column. Comparing the results of the samples for the PCBs compounds (Table 3.1 and 3.2), the highest concentration of detected PCB both in soil and water samples decrease in the order $S_C<S_B<S_A$ and $W_C<W_B<W_A$ due to different spot of sample collection. Furthermore, this results shows that the concentration of PCBs tend to be too high and can be hazardous to population whose feeding activities comes from such source or discharge of the water bodies into farmlands. Also, in soil samples, Fluorene is not detected by the GC-MS probably due to its absence in the sample or low detection limit. Other PCB compounds were not detected in some samples as shown in Table 4.1. In Table 4.2, Fluorene and PCB 101 (PentaCB) were not detected in the water samples been analyzed due to low detection limit of the instruments. Hence, others categories of PCBs detected is a proof that the water is not considered safe for consumption and for farming activities around the area in dry seasons. Also the present results are high compared with the results obtained on samples from the industrialized area in Jordan, where nothing of the studied PCBs were found (Tarawneh *et al.*, 2012).

4.2 Concentrations of Heavy metals in soil and water samples

The distribution of mean concentration ±standard deviation of Hg, Pb, Mn, Cd and Cu present in the soils and water samples is shown in Table 4.3 and 4.4 respectively. The result shows that the heavy metal detected in the soils were found to be slightly higher than the heavy metals detected in water. Figure 4.3 and 4.4 shows the chart of different heavy metal analyzed. Mercury is not detected both in the soil and water samples analyzed. Lead was detected in all the sampling sites. The mean concentration of lead recorded from the various soils samples is 16.03 mg/kg in soil and 10.0mg/kg in water. The mean concentration of copper recorded across the sample sites were above WHO/FAO (1993) permissible limit of 3.5mg/kg for agricultural soils. Awokunmi *et al* (2010) reported higher levels of copper from 95 to 6726mg/kg from soils collected from several farmlands in Nigeria when compared with the levels of copper in the present study. Cadmium was found in small concentrations in all the samples. This indicates that waste carrying cadmium was present at low concentrations in the river. The low concentration could be attributed to the absence of cadmium based industries, low use of materials containing cadmium and smelting activities at the studied dumpsites. Manganese was detected in all the sampling sites. The mean concentration of Mn in the soils is 23.18mg/kg while in water it is10.41mg/kg. Manganese concentrations in the soils were generally above standard limits (0.05 mg/kg) set by WHO (1993). Sources of Mn in the soil could be due to waste consisting of manganese-chromium batteries, coloured polythene bags, empty diesel engines utilizing anti-corrosive agents and discarded plastic materials. Manganese is associated with allergic dermatitis in humans (Scragg, 2006). The concentration range reported in this study for Mn was lower to the range of values reported by Adelekan and Abegunde (2011) being (13.15 – 75.55 mg/kg), Awokunmi *et al*. (2010) (212.00 – 2020.00 mg/kg) but within the range of value recorded by Ukpong *et al* (2013) being (1.00 – 4.50 mg/kg).

4.0 CONCLUSION

In this thesis, the results obtained after PCBs and metal analysis using GC/MS and AAS respectively indicated that total PCBs concentrations in the soil across the study sites were observed to be above the World Health Organization (WHO) limit of 1.0 mg/kg (WHO, 2008). Heavy metal concentrations in soil samples were observed in order of Mn>Cu>Pb>Cd>Hg as compared to Cu>Mn>Pb>Cd>Hg in water. The results showed that the concentrations of some heavy metals detected were above WHO acceptable limits. The values of PCBs observed in the different river sites were higher than the acceptable limit of 10 mg/l stipulated by Federal ministry of environment for drinking water**.** These results implies that Bodo River is polluted judging by the level of PCBs and heavy metals detected. It is therefore important to create awareness on a possible health hazard around the area and people residing around the environment. Farmers planting on soil should be conscious of the PCBs, heavy metal status and the possibility of pollutant uptake in the edible parts of crops. it is also recommended that Government should sensitize and discourage people/farmers living close to the river from using the water and cultivating close to River pending when containment measures are carried out due to bioaccumulation of PCBs and toxic heavy metals that may find their way into the food chain with the associated health risks.

COMPETING INTERESTS DISCLAIMER:

Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

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