

Determination of some Heavy Metals Concentrations in Water and Irrigation Farms along Wulmi River in Pankshin Local Government, Plateau State, Nigeria.

Abstract

Levels of four heavy metals (Co, Cu, Pb and Cd) and three physico-chemical parameters (pH, temperature, total dissolved solids) were determined from Wulmi River at five sampling points (S₁-S₅) at an interval of 200m between points using atomic absorption spectrophotometer (AAS) and approved standard procedures respectively, and the control site located about 1000 meters away from the study area. The sampling was done monthly in wet season from May-December 2017. The weighted means of physico-chemical parameters determined at each sampling point in the river were in the range 6.53±0.21 - 6.85±0.17 for pH which is within the permissible limit of 6.5-8.5 (WHO,2004), 25.35±0.79 °C - 25.92±2.31°C for temperature which is within the permissible limit of 30°C (USEPA,2002), 9.43±3.90 mg/l - 26.71±2.75 mg/l for TDS which is also within the permissible limit of 1000 mg/l (USEPA,2002). The weighted mean of heavy metal concentrations in water at sampling points in the river ranged between 0.11±0.07 mg/l - 0.29 ± 0.19 mg/l for copper, 1.17±0.39 mg/l - 1.76± 0.31 mg/l for cadmium, 0.08 ± 0.05 mg/l - 0.91±0.03 mg/l for lead, 1.53± 0.39 mg/l - 6.48± 3.36 mg/l for cobalt. The soil samples from five irrigation farmlands (F1-F5) around the Wulmi River were also analysed for the heavy metals concentrations. The heavy metals concentrations in the soil ranged between 12.27 ± 3.46 µg/g - 28.05 ± 1.99 µg/g for copper, 5.49 ± 3.09 µg/g - 17.92 ± 2.18 µg/g for cadmium, 2.24 ± 0.02µg/g - 9.85 ± 1.43 µg/g for Lead, 13.48 ± 3.72 µg/g - 27.82 ± 2.65 µg/g for cobalt. Lead and cobalt concentrations in the soils are within the permissible limit set by USEPA (2002) and WHO (2004) of 10µg/g and 50µg/g respectively. All the metals under investigation have geo-accumulation input in soils around Wulmi River, except in irrigation farms 2 and 4 which have geo-accumulation input of Pb to be 0.00. Analysis of variance indicates that there is significant difference in pH, concentrations of TDS, Cd, and Co from one sampling point to another throughout the periods of analyses. The data generated will be used to develop a computer based time series model, which can be used to predict the concentrations of the heavy metals in the near future at these sampling points in Wulmi River.

Comment [t1]: Do not write down permissible limit in this section

1 INTRODUCTION

Wulmi, a village in Pankshin local government area of Plateau state is located at longitude 9°24'58.4712''E and latitude 9°18'38.63096''N is noted for rural agricultural practices. The farmers use fertilizers, herbicides etc as farming inputs and the run-off from those farms enter Wulmi River. There are no portable water supplies in the catchment areas of Wulmi, hence the inhabitants of villages along it depend on water sources mainly from the river for domestic, irrigation, and livestock activities.

Of recent, the presence of toxic metals have been a source of worry to environmentalist, government agencies and health practitioners. Hence, contamination of heavy metals in the aquatic environment has attracted global attention owing to its abundance, persistence and environmental toxicity (Ahmed *et al.*, 2015a; Islam *et al.*, 2015a). Both natural and anthropogenic activities are responsible for the abundance of heavy metals in the environment (Wilson and Pyatt, 2007; Kham *et al.*, 2008). However, anthropogenic activities can effortlessly generate heavy metals in soil and water that pollute the aquatic environment (Sanchez – Chardi *et al.*, 2007). The increasing pollution by heavy metals has significant adverse health effects for invertebrates, fish, and humans (Islam *et al.*, 2014; Martin *et al.*, 2015; Islam *et al.*, 2015b,d; Ahmed *et al.*, 2015b). The metal pollution of aquatic ecosystems is increasing due to the effects from urbanization and industrialization (Sekabira *et al.*, 2010; Zhang *et al.*, 2011; Bai *et al.*, 2011; Grigoratos *et al.*, 2014; Martin *et al.*, 2015). During transportation of heavy metals in the riverine system, it may undergo frequent changes due to dissolution, precipitation and sorption phenomena (Abdel-Ghani and Elchaghaby, 2007), which affect their performance and bio availability (Nicolau *et al.*, 2006; Nauri *et al.*, 2011).

Comment [t2]: The

Comment [t3]: The

Comment [t4]: Verify that the verb "generate" really describes a generation process. Otherwise, consider replacing it with "produce".

Comment [t5]: The word "significant" is misused and vague. It might mean statistically significant or significant to the author. Alternatives: "substantial, notable"

The disposal of urban wastes, untreated effluents from various industries and agrochemicals in the open water bodies and rivers has reached alarming situation in many countries which are continually increasing the metals level and deteriorating water quality (Khadse *et al.*, 2008; Venugopal *et al.*, 2009; Islam *et al.*, 2015a,c). Diseases, including asthma, pneumonia, and wheezing, have been found in workers who breathed high levels of cobalt in the air (Arinola and Akiibinu, 2006).

1.1 Geo-accumulation Index (Igeo)

The degree of contamination from the heavy metals could be assessed by measuring the geo-accumulation index (Igeo). The index of geo-accumulation has been widely used for the assessment of soil contamination (Santos *et al.*; 2003; Saleem *et al.*, 2015). In order to characterize the level of pollution in the soil, geo-accumulation index (Igeo) value is calculated using the equation;

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

Where C_n is the measured concentration of metal in the soil and B_n is the geochemical background value of element n in the background sample (Yu *et al.*, 2011; Rhaman and Ishiga, 2012; Islam *et al.*, 2015a). The factor 1.5 is introduced to minimize the possible variations in the background values which may be qualified to lithogenic effects. Geo-accumulation index (Igeo) values are interpreted as: $I_{geo} \leq 0$ = practically uncontaminated; $1 \leq I_{geo} \leq 1$ = uncontaminated to moderately contaminated; $1 \leq I_{geo} \leq 2$ = moderately contaminated; $2 \leq I_{geo} \leq 3$ = moderately to heavily contaminated; $3 \leq I_{geo} \leq 4$ = heavily contaminated; $4 \leq I_{geo} \leq 5$ = heavily to extremely contaminated; and $5 < I_{geo}$ = extremely contaminated.

2 MATERIALS AND METHOD

Reagents

Chart 1 : List of reagents used for the study

Reagents	Manufacturer name	Country
CONC HCl	British Drug house	England
CONC HNO ₃	Sigma Aldrich	Germany
30% H ₂ O ₂	British Drug house	England

Comment [t6]: Do not write the reagent table

Equipment

Atomic absorption spectrophotometer (AAS) with model number Bupk Scientific 210 VGP was used.

Study Area

The study area for this research is in Wulmi River in Pankshin Local Government of Plateau State. The river sites span a wide range of villages and towns. The sampling points along the river are labeled;

S₁ = sampling point 1

S₂ = sampling point 2

S₃ = sampling point 3

S₄ = sampling point 4

S₅ = sampling point 5

Sampling and Sample Collection of Water

The water samples at each sampling point was collected monthly in plastic container previously cleaned by washing in non-ionic detergent, rinsed with deionised water prior to usage. The sample collection was done at an interval of 200m against the direction of the flowing water. During the sampling, the plastic containers were rinsed with sample water at each point three times before collection. The sample bottles were labeled, transported to laboratory and stored at room temperature prior to analysis.

Comment [t7]: What is the method of the samples?

Flow Rate of Water in the River

The average volume of water in meter cube (M³) that flowed pass the river per second was measured by a super water flow meter with model number (ISO 4064 DN 20 CLASS B). The diameter of the flow meter is 20mm. The flow rate is achieved by measuring the differential pressure within the constriction.

Sampling and Sample Collection of Soil Sample

Soil samples were randomly collected at 15cm depth from five irrigation farm lands. Background samples or control were similarly collected 1000m away from each sampling point in the river.

Comment [t8]: The soil...

Soil Preservation

The soil samples from the five irrigation farmlands (F1 – F5) around the study sites were homogenized to make a composite sample. The collected soil samples were then transferred into a black polythene bag and properly labeled before transporting to the laboratory.

After series of coning and quartering, 300g of the soil sample from each of the irrigation farm land were air dried for one week in a well-ventilated space to remove excess moisture and sieved through 2mm mesh to prevent chemical microbial changes and to remove large mineral inclusions and organic debris. The sieved samples were stored in labeled polythene bags and used for subsequent analysis.

Comment [t9]: Temperature????

pH

Electrometric method is used to determine the pH by measuring the electromotive force of the cell comprising an indicator electrode immersed in the test solution and the reference electrode. Contact between the test solution and the reference electrode is got by means of a liquid junction, which forms a part of reference electrode. The electromotive force is measured with pH meter (with model No. HANNA pH 209). The electrode is allowed to stand for 2 minutes to stabilize before taking reading.

Total Dissolved Solids

Total dissolved solids is a measure of the dissolved matter in water that remains after all the water has been evaporated. It is used as an indicator of aesthetic characteristics of drinking water and as an aggregate indicator of the presence of a broad array of chemical contaminants. A known volume of a well-mixed sample is filtered through a standard glass-fiber filter and the filtrate collected. The filtrate is evaporated to a constant weight condition in an oven maintained at a temperature of 180°C to remove mechanically occluded water. The mass of the dried sample is determined and used to calculate the concentration of total dissolved solids in the sample using the formula:

Comment [t10]: This temperature is

$$TDS (mg/l) = \frac{(W_1 - W_2) \times 1000}{\text{volume of sample taken (ml)}} \quad (\text{Biswas, 2015})$$

Where w_1 = final 180°C weight of the dried residue + the tared dish (mg)

w_2 = tared dish weight (mg)

Temperature

The temperature measurement was made by taking the portion of water sample from each sampling point (about 1litre) and a 0.1°C division thermometer was immersed into it for a sufficient period of time (till the reading stabilized) and the reading was taken (Biswas,2015).

Digestion of Water Samples for Heavy Metal Determination

The water samples were digested as follows: 100cm³ of the sample was transferred into a beaker and 5ml concentrated HNO₃ was added. The beaker with the content was placed on a hot plate and evaporated down to about 20ml. The beaker was allowed to cool and another 5ml concentrated HNO₃ was added. The beaker was covered with a watch glass and returned to the hot plate. The heating was continued, and small

portion of HNO_3 was added until the solution appeared light coloured and clear. The beaker and watch glass was washed with distilled water and the sample filtered to remove some insoluble materials that could clog atomizer. The volume was adjusted to 100cm^3 with distilled water (Radojevic and Bashkin, 1999).

The heavy metals determinations were done using Atomic Absorption Spectrophotometer (AAS) with model number Bupk Scientific 210VGP.

Digestion of Irrigated Farm Soil Samples For Heavy Metal Determination

Soil samples were air-dried in the laboratory, any crumbs found in the soils were removed and mixed uniformly by coning and quartering.

Soils were sieved through a 2mm sieve to remove coarse particles. Two grammes of the soil samples were weighed out into acid washed glass beaker. Soil samples were digested by the addition of 20cm^3 of aqua regia (mixture of HCl and HNO_3 , ratio 3:1) and 10cm^3 of 30% H_2O_2 . The H_2O_2 was added in small portions to avoid any possible overflow leading to loss of material from the beaker. The beaker was covered with watch glass and heated over a hot plate at 90°C for two hours.

The beaker wall and watch glass was washed with distilled water and the sample was filtered out to separate the insoluble solid from the supernatant liquid. Blank solution was handled as detailed for the samples. All samples and blanks were stored in plastic containers (Srikanth et al; 1993). The heavy metals were analysed using AAS with model number Bupk Scientific 210 VGP.

Statistical Analysis

SPSS package was used to calculate the mean, standard deviation, weighted means of the metal concentration and physico-chemical properties of the water at each sampling point from Wulmi River. Analysis of variance was determined to find out if there is significant difference in pH, concentrations of TDS, Cd and Co from one sampling point to another throughout the periods of analyses

3 RESULTS

The results of heavy metals concentrations and physico-chemical properties of water at each sampling site in Wulmi River are presented in tables 1–5. Tables 6 and 7 give the weighted means of heavy metals concentrations and physico-chemical parameters in the sampling points in Wulmi River. Tables 8-12 give the heavy metals concentrations and physico-chemical parameters in Pankshin Dam at each sampling point. Tables 13 and 14 provide the weighted means of heavy metals concentration and physico-chemical parameters in Pankshin Dam. Tables 15 and 16 provide the mean concentrations of heavy from five selected irrigation farm lands around Wulmi River and their geo-accumulation index respectively. Tables 17–23 provide the analysis of variance for the heavy metals concentration and physico-chemical parameters under investigation.

Comment [t11]: The

Comment [t12]: The

Comment [t13]: The

Table 1: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) in Wulmi River at Sampling Point S₁

S/No	pH	Temp(^o C)	TDS(mg/l)	Cu	Cd	Pb	Co
M ₁	6.51 ±0.51	28.16 ±2.36	30.67 ±1.53	0.29 ±0.23	1.02 ±0.04	0.36 ±0.26	10.17 ±1.08
M ₂	7.20 ±0.31	25.17 ±4.07	29.40 ±0.69	0.61 ±0.34	0.96 ±0.71	0.19 ±0.03	12.10 ±3.87
M ₃	6.81 ±0.19	26.17 ±1.26	26.51 ±1.77	0.21 ±0.02	1.69 ±0.52	0.13 ±0.11	6.68 ±2.07
M ₄	6.92 ±0.66	26.75 ±0.67	25.57 ±3.01	0.06 ±0.03	1.44 ±0.54	0.11 ±0.02	7.08 ±2.54
M ₅	6.91 ±0.11	23.67 ±3.22	28.23 ±3.84	0.13 ±0.07	1.69 ±0.59	0.09 ±0.06	5.60 ±1.39
M ₆	6.66 ±0.86	23.67 ±2.52	25.00 ±2.65	0.34 ±0.28	0.97 ±0.09	0.11 ±0.04	4.68 ±2.27
M ₇	6.91 ±0.18	26.00 ±1.00	26.43 ±2.06	0.16 ±0.13	0.63 ±0.33	0.29 ±0.23	3.75 ±1.09
M ₈	6.18 ±0.44	24.00 ±1.00	21.87 ±1.58	0.52 ±0.42	0.69 ±0.97	0.13 ±0.12	1.81 ±0.42
USEPA, WHO STD	6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where M1 to M8 are results of monthly samples taken from location S1 from May-December

Table 2: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) from Wulmi River at Sampling Point S₂

S/NO	Water Flow Rate (M ³ /s)	pH	Temp (°C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	1753.33 ±224.80	6.83 ±0.72	29.07 ±1.01	26.71 ±5.73	0.05 ±0.02	1.40 ±0.55	0.03 ±0.02	4.93 ±0.98
M ₂	5027.00 ±1010.43	6.23 ±0.15	28.75 ±1.53	23.48 ±4.70	0.19 ±0.05	0.96 ±0.93	0.08 ±0.03	5.51 ±2.05
M ₃	7724.67 ± 622.22	6.44 ±0.51	26.58 ±0.38	27.27 ±2.05	0.20 ±0.16	1.08 ±0.88	0.12 ±0.09	4.03 ±1.72
M ₄	1090.67 ±1560.17	6.70 ±0.55	25.70 ±0.61	22.68 ±2.11	0.19 ±0.02	1.12 ±1.06	0.05 ±0.04	4.17 ±1.09
M ₅	9738.67 ±1608.00	6.36 ±0.56	25.03 ±1.00	20.72 ±1.53	0.19 ±0.19	1.58 ±0.10	0.05 ±0.04	3.36 ±1.16
M ₆	3000.00 ±1000.00	6.70 ±0.44	25.70 ±0.61	20.37 ±1.55	0.44 ±0.32	2.09 ±0.14	0.09 ±0.11	4.68 ±2.27
M ₇	500.00 ±100.00	6.32 ±0.51	24.73 ±0.55	22.03 ±2.61	0.13 ±0.11	2.25 ±0.10	0.09 ±0.02	2.13 ±0.13
M ₈	60.00 ±10.00	6.64 ±0.56	21.33 ±1.53	16.59 ±3.77	0.13 ±0.12	1.02 ±0.22	0.05 ±0.02	1.84 ±1.24
USEPA/WHO STD		6.5 - 8.5	30	1000	0.05	0.005	0.05	2.00

Where M1 to M8 are results of monthly samples taken from location S2 from May-December

Table 3: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) from Wulmi River at Sampling Point S₃

S/No	Water Flow Rate (M ³ /s)	pH	Tempt(°C)	TDS(mg/l)	Cu	Cd	Pb	Co
M ₁	1753.33 ±224.80	6.96 ±0.14	28.77 ±1.37	17.90 ±3.80	0.35 ±0.09	1.41 ±0.55	0.10 ±0.01	2.81 ±0.81
M ₂	5027.00 ±1010.43	7.03 ±0.33	27.36 ±0.57	10.57 ±1.61	0.32 ±0.29	1.43 ±0.51	0.17 ±0.04	2.86 ±1.21
M ₃	7724.67 ± 622.22	6.66 ±0.64	26.33 ±0.58	9.30 ±0.85	0.18 ±0.09	1.65 ±0.38	0.13 ±0.09	4.32 ±1.30
M ₄	1090.67 ±1560.17	6.60 ±0.47	25.37 ±0.55	6.77 ±0.63	0.09 ±0.11	2.19 ±0.16	0.19 ±0.13	2.24 ±0.28
M ₅	9738.67 ±1608.00	7.01 ±0.10	24.70 ±0.61	9.50 ±0.66	0.12 ±0.12	1.75 ±0.42	0.19 ±0.07	1.77 ±0.53
M ₆	3000.00 ±1000.00	6.77 ±0.26	26.04 ±0.99	7.27 ±1.59	0.19 ±0.08	1.66 ±0.58	0.09 ±0.03	2.50 ±1.08
M ₇	500.00 ±100.00	7.03 ±0.80	24.37 ±0.55	7.05 ±1.83	0.20 ±0.12	2.26 ±0.32	0.14 ±0.11	1.14 ±0.92
M ₈	60.00 ±10.00	6.73 ±0.55	23.33 ±0.58	7.08 ±1.90	0.17 ±0.09	1.69 ±1.33	0.06 ±0.05	0.89 ±0.77
USEPA /WHO STD		6.5- 8.5	30	1000	0.05	0.005	0.05	2.00

Where M1 to M8 are results of monthly samples taken from location S3 from May-December.

Table 4: Physico-chemical and Heavy Concentrations (mg/l) from Wulmi

River at Sampling Point S₄

S/No	Water Flow Rate (M ³ /s)	pH	Temp (°C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	1753.33 ±224.80	6.67 ±0.49	25.87 ±0.71	29.37 ±2.49	0.13 ±0.11	1.13 ±0.13	0.09 ±0.03	6.17 ±0.99
M ₂	5027.00 ±1010.43	6.70 ±1.04	26.10 ±0.60	26.52 ±4.24	0.19 ±0.06	2.09 ±0.06	0.07 ±0.06	8.44 ±1.65
M ₃	7724.67 ± 622.22	6.40 ±0.69	25.53 ±0.55	22.61 ±2.50	0.10 ±0.07	1.78 ±0.63	0.08 ±0.05	6.12 ±0.11
M ₄	1090.67 ±1560.10	6.80 ±0.60	25.50 ±0.87	19.01 ±2.63	0.19 ±0.11	1.71 ±0.62	0.57 ±0.06	4.93 ±0.65
M ₅	9738.67 ±1608.00	6.30 ±0.36	25.67 ±1.07	13.62 ±1.43	0.15 ±0.04	1.48 ±1.05	0.09 ±0.06	4.14 ±0.13
M ₆	3000.00 ±1000.00	6.83 ±0.21	25.80 ±0.92	12.39 ±2.75	0.20 ±0.09	2.08 ±0.04	0.08 ±0.07	3.51 ±0.44
M ₇	500.00 ±100.00	6.70 ±0.60	24.67 ±0.58	9.18 ±0.93	0.18 ±0.06	2.11 ±0.16	0.09 ±0.09	2.02 ±0.04
M ₈	60.00 ±10.00	7.30 ±0.53	23.67 ±0.49	7.34 ±3.95	0.14 ±0.11	1.36 ±0.69	0.01 ±0.01	1.98 ±0.81
USEPA, WHO STD		6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where M1 to M8 are results of monthly samples taken from location S4 from May-December.

Table 5: Physico-chemical Parameters and Heavy Metals Concentrations

(mg/l) from Wulmi River at Sampling Point S₅

S/No	Water Flow Rate (M ³ /s)	pH	Temp (°C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	1753.33 ±224.80	6.97 ±0.06	26.33 ±0.59	28.04 ±1.98	0.05 ±0.02	1.72 ±1.49	0.05 ±0.01	2.06 ±0.08
M ₂	5027.00 ±1010.43	6.67 ±0.49	26.80 ±0.82	18.04 ±1.03	0.18 ±0.04	1.92 ±0.23	0.05 ±0.03	1.36 ±0.56
M ₃	7724.67 ± 622.22	6.43 ±0.58	25.67 ±0.58	25.83 ±4.05	0.10 ±0.10	1.72 ±0.63	0.05 ±0.04	1.91 ±0.63
M ₄	1090.67 ±1560.10	6.63 ±0.46	25.67 ±0.58	16.10 ±3.68	0.08 ±0.03	1.37 ±0.59	0.06 ±0.03	1.83 ±0.49
M ₅	9738.67 ±1608.00	6.53 ±0.45	25.67 ±0.59	15.09 ±2.98	0.11 ±0.02	1.67 ±0.57	0.04 ±0.01	1.41 ±1.01
M ₆	3000.00 ±1000.00	6.60 ±0.26	26.37 ±0.43	11.55 ±1.03	0.08 ±0.02	1.60 ±0.37	0.18 ±0.03	1.13 ±1.00
M ₇	500.00 ±100.00	6.17 ±0.06	25.37 ±0.55	9.28 ±1.23	0.28 ±0.34	1.08 ±0.15	0.17 ±0.08	1.49 ±0.62
M ₈	60.00 ±10.00	6.73 ±0.38	24.67 ±0.58	5.45 ±1.45	0.07 ±0.04	1.81 ±0.51	0.05 ±0.01	1.05 ±0.83
USEPA, WHO STD		6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where M1 to M8 are results of monthly samples taken from location S5 from May-December.

Table 6: Weighted Means of Heavy Metals Concentration (mg/l) in the Five Sampling Points in Wulmi River

Sampling Points	Cu	Cd	Pb	Co
S ₁	0.29 ±0.19	1.17 ±0.39	0.18 ±0.09	6.48 ±3.36
S ₂	0.19 ±0.11	1.44 ±0.49	0.91 ±0.03	3.56 ±1.33
S ₃	0.20 ±0.09	1.76 ±0.31	0.13 ±0.05	2.21 ±1.10
S ₄	0.16 ±0.03	1.71 ±0.37	0.14 ±0.12	4.66 ±2.22
S ₅	0.11 ±0.07	1.62 ±0.28	0.08 ±0.05	1.53 ±0.39
USEPA, WHO STD	0.05	0.005	0.05	2.00

Table7: Weighted Means of Physico-chemical Parameters in the Five Sampling Points in Wulmi River

Sampling Points	pH	Temp ^(°C)	TDS (mg/l)
S ₁	6.84 ±0.20	25.45 ±1.62	26.71 ±2.75
S ₂	6.53 ±0.21	25.92 ±2.31	22.48 ±3.47
S ₃	6.85 ±0.17	25.53 ±1.35	9.43 ±3.90
S ₄	6.71 ±0.30	25.35 ±0.79	17.51 ±8.15
S ₅	6.59 ±0.23	25.82 ±0.67	15.92 ±8.05
USEPA,WHO STD	6.5-8.5	30.00	1000

Table 8: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) in Pankshin Dam at Sampling Point SD₁

S/No	pH	Temp ^t (°C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	7.03 ±0.16	27.33 ±1.53	1191.67 ±137.33	0.60 ±0.02	0.08 ±0.07	0.08 ±0.02	2.18 ±0.58
M ₂	7.20 ±0.36	24.33 ±2.08	1538.67 ±464.78	0.59 ±0.10	0.13 ±0.01	0.09 ±0.06	2.27 ±0.22
M ₃	7.13 ±0.16	22.33 ±2.13	1700.33 ±99.50	0.52 ±0.01	0.19 ±0.05	0.50 ±0.02	2.90 ±0.16
M ₄	7.17 ±0.30	21.33 ±2.22	1536.00 ±55.51	0.35 ±0.16	0.35 ±0.22	0.05 ±0.01	2.90 ±0.15
M ₅	7.00 ±0.17	24.00 ±1.00	1410.67 ±88.64	0.34 ±0.22	0.17 ±0.13	ND	2.20 ±0.16
M ₆	7.05 ±0.14	27.00 ±1.00	1306.33 ±100.00	0.27 ±0.21	0.19 ±0.06	0.04 ±0.03	2.41 ±1.62
M ₇	6.67 ±0.50	20.33 ±1.53	1240.33 ±56.57	0.21 ±0.23	0.19 ±0.18	ND	2.30 ±0.17
M ₈	7.20 ±0.36	18.33 ±2.12	1161.00 ±38.43	0.21 ±0.11	0.20 ±0.01	ND	2.05 ±0.17
USEPA,WHO STD	6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where SD1 is water sample from sampling point 1 at Pankshin dam.

Table 9: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) in Pankshin Dam at Sampling point SD₂

S/No	Ph	Tempt(^o C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	6.33 ±0.58	26.71 ±1.48	1097.00 ±80.73	0.36 ±0.17	1.14 ±0.03	0.09 ±0.06	4.03 ±0.19
M ₂	7.13 ±0.16	25.67 ±0.58	1376.67 ±366.65	0.50 ±0.25	0.85 ±0.10	0.05 ±0.03	4.86 ±2.06
M ₃	6.97 ±0.41	25.67 ±1.32	1602.33 ±521.64	0.49 ±0.16	1.14 ±0.26	0.06 ±0.03	2.67 ±1.96
M ₄	7.29 ±0.28	21.67 ±1.62	1303.67 ±359.08	0.45 ±0.26	0.69 ±0.22	0.02 ±0.01	2.67 ±0.22
M ₅	7.00 ±0.17	25.00 ±1.00	1634.00 ±152.21	0.40 ±1.13	0.34 ±0.62	0.01 ±0.01	2.15 ±1.12
M ₆	7.04 ±0.16	25.33 ±2.09	1634.00 ±152.20	0.38 ±0.02	0.31 ±0.17	0.01 ±0.01	2.55 ±1.92
M ₇	7.07 ±0.38	19.33 ±1.23	1044.00 ±545.56	0.26 ±0.17	0.27 ±0.01	ND	1.89 ±0.22
M ₈	6.90 ±0.26	16.67 ±2.22	1225.67 ±34.43	0.19 ±0.21	0.24 ±0.21	ND	1.87 ±0.68
USEPA,WHO STD	6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where SD₂ is water sample from sampling point 2 at Pankshin dam.

Table 10: Physico-chemical and Heavy Metals Concentrations (mg/l) in Pankshin Dam at Sampling Points SD₃

S/No	Ph	Tempt(^o C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	6.97 ±0.14	27.67 ±1.53	1128.33 ±67.89	0.43 ±0.01	0.26 ±0.03	0.04 ±0.01	2.35 ±0.17
M ₂	6.50 ±0.26	25.67 ±0.58	972.00 ±62.87	0.59 ±0.21	0.23 ±0.21	0.06 ±0.04	4.67 ±0.26
M ₃	7.23 ±0.35	25.67 ±1.01	1116.00 ±90.42	0.48 ±0.22	0.26 ±0.18	0.14 ±0.08	3.90 ±1.16
M ₄	6.98 ±0.02	20.00 ±2.10	1584.67 ±510.00	0.44 ±0.02	0.22 ±0.06	ND	3.90 ±1.96
M ₅	7.04 ±0.16	24.00 ±3.23	1433.67 ±378.02	0.39 ±0.18	0.22 ±0.16	0.01 ±0.01	2.91 ±0.26
M ₆	6.97 ±0.14	25.67 ±1.28	1183.67 ±604.28	0.32 ±0.25	0.20 ±0.10	0.02 ±0.02	2.55 ±0.77
M ₇	6.97 ±0.41	19.00 ±1.00	1504.67 ±106.03	0.27 ±0.11	0.17 ±0.20	ND	2.48 ±0.92
M ₈	6.97 ±0.03	19.33 ±2.30	1345.33 ±60.58	0.24 ±0.86	0.19 ±0.04	ND	1.99 ±0.66
USEPA,WHO STD	6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where SD₃ is water sample from sampling point 3 at Pankshin dam.

Table 11: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) in Pankshin Dam at Sampling Point SD₄

S/No	Ph	Tempt (°C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	6.97 ±0.41	27.83 ±0.47	746.67 ±140.21	0.46 ±0.06	0.31 ±0.10	0.03 ±0.01	3.16 ±1.99
M ₂	7.20 ±0.36	23.00 ±1.00	720.67 ±90.03	0.49 ±0.21	0.28 ±0.02	0.05 ±0.02	2.79 ±0.26
M ₃	7.00 ±0.17	24.33 ±2.01	780.00 ±147.73	0.44 ±0.10	0.41 ±0.16	0.14 ±0.01	2.55 ±0.98
M ₄	7.24 ±0.24	21.00 ±1.20	475.67 ±52.88	0.42 ±0.22	0.37 ±0.22	0.02 ±0.01	2.65 ±0.45
M ₅	7.14 ±0.41	24.00 ±2.03	399.00 ±93.95	0.38 ±0.36	0.29 ±0.18	0.01 ±0.01	2.57 ±0.66
M ₆	6.91 ±0.08	28.00 ±1.73	657.00 ±51.74	0.35 ±0.26	0.27 ±0.17	0.02 ±0.02	2.06 ±0.25
M ₇	7.23 ±0.55	20.67 ±2.30	456.67 ±48.91	0.22 ±0.15	0.25 ±0.24	ND	1.88 ±0.23
M ₈	6.73 ±0.47	18.67 ±1.66	382.00 ±49.67	0.20 ±0.27	0.24 ±0.11	ND	1.84 ±0.66
USEPA, WHO STD	6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where SD₄ is water sample from sampling point 4 at Pankshin dam.

Table 12: Physico-chemical Parameters and Heavy Metals Concentrations (mg/l) in Pankshin Dam at Sampling Point SD₅

S/No	pH	Tempt (^o C)	TDS (mg/l)	Cu	Cd	Pb	Co
M ₁	7.03 ±0.12	28.00 ±1.26	1095.00 ±70.53	0.41 ±0.01	0.30 ±0.19	0.04 ±0.02	1.90 0.21
M ₂	7.17 ±0.30	26.00 ±2.06	970.00 ±60.83	0.48 ±0.02	0.31 ±0.15	0.05 ±0.01	3.58 ±0.77
M ₃	7.03 ±0.14	25.33 ±0.92	1388.67 ±362.47	0.36 ±0.16	0.33 ±0.22	0.07 ±0.03	3.69 ±0.37
M ₄	7.20 ±0.16	22.00 ±2.40	1608.33 ±513.94	0.34 ±0.26	0.28 ±0.16	ND	3.33 ±0.16
M ₅	6.97 ±0.41	25.00 ±1.20	1084.00 ±109.23	0.30 ±0.10	0.26 ±0.16	0.03 ±0.02	2.91 ±0.22
M ₆	7.28 ±0.45	25.33 ±2.32	1599.33 ±406.38	0.28 ±0.01	0.24 ±0.01	0.02 ±0.01	2.34 ±0.86
M ₇	7.03 ±0.20	18.00 ±3.26	1850.33 ±58.83	0.19 ±0.06	0.20 ±0.19	ND	2.19 ±0.21
M ₈	7.07 ±0.38	18.00 ±1.17	1271.67 ±457.61	0.21 ±0.11	0.17 ±0.10	ND	2.01 ±0.19
USEPA, WHO STD	6.5-8.5	30	1000	0.05	0.005	0.05	2.00

Where SD₅ is water sample from sampling point 5 at Pankshin dam.

Table 13: Weighted Means of Heavy Metals Concentrations (mg/l) in the Five Sampling Points in Pankshin Dam

Sampling Points	Cu	Cd	Pb	Co
SD ₁	0.39 ±0.16	0.19 ±0.07	0.04 ±0.03	2.40 ±0.32
SD ₂	0.38 ±0.10	0.62 ±0.39	0.03 ±0.03	2.77 ±0.93
SD ₃	0.39 ±0.12	0.21 ±0.03	0.03 ±0.02	3.09 ±0.94
SD ₄	0.37 ±0.11	0.30 ±0.06	0.03 ±0.01	2.44 ±0.47
SD ₅	0.32 ±0.09	0.26 ±0.06	0.03 ±0.02	2.74 ±0.73
USEPA, WHO STD	0.05	0.005	0.05	2.00

The weighted means of Cu, Cd and Co are all about the permissible unit set by USEPA. However, lead at all the samplings points in Pankshin Dam are within the permissible limit of 0.05 mg/l.

Table 14: Weighted Means of Physico-chemical Parameters in the five Sampling points in Pankshin Dam

Sampling Points	pH	Temp ^(°c)	TDS (Mg/l)
SD ₁	7.05 ±0.19	23.12 ±3.15	1385.63 ±193.16
SD ₂	6.97 ±0.29	23.26 ±3.63	1364.75 ±238.73
SD ₃	6.95 ±0.20	23.38 ±3.41	1283.54 ±215.51
SD ₄	7.05 ±0.18	23.36 ±3.23	577.21 ±165.39
SD ₅	7.09 ±0.11	23.46 ±3.75	1358.42 ±308.56
USEPA, WHO STD	6.5-8.5	30	1000

The pH and temperature at all the sampling points are within the permissible unit of 6.5-8.5 and 30°C respectively.

The total dissolved solids at sampling point SD₄ is also within the permissible limit of 1000mg/l. However, at sampling points SD₁, SD₂, SD₃ and SD₅ the total dissolved solids are all above the permissible limit of 1000mg/l.

Table 15: Mean Concentrations of Heavy Metals from Five Selected Irrigation Farms F1 to F5 around Wulmi River

Sampling Points	Concentrations (µg/g)			
	Cu	Cd	Pb	Co
F1 (John Danboyi farm)	28.05 ±1.99 (1.04)	11.53 ±3.36 (0.81)	6.54 ±0.15 (0.05)	15.62 ±2.41 (1.44)
F2 (Wokji Ndam's farm)	18.32 ±1.80 (0.11)	16.17 ±1.08 (0.07)	9.85 ±1.43 (ND)	27.82 ±2.65 (0.02)
F3 (Rachel Bala's farm)	14.84 ±5.04 (0.21)	5.49 ±3.09 (0.45)	2.24 ±0.02 (0.01)	13.48 ±3.72 (0.11)
F4 (Gowus Dauda's farm)	15.54 ±5.01 (1.06)	17.92 ±2.18 (0.52)	8.24 ±0.23 (ND)	24.28 ±3.37 (0.61)
F5 (Sunday Micheal's farm)	12.27 ±3.46 (0.61)	11.95 ±2.85 (0.58)	2.88 ±0.25 (0.02)	19.79 ±1.48 (1.13)
WHO,2004,USEPA,2002	25µg/g	6µg/g	10µg/g	50µg/g

N= 3,ND=Not detected, values in parentheses are levels in control site

Table 16: Geoaccumulation Indices (Igeo) for the Heavy Metals from Five Irrigation Farm Lands around Wolmi River

Element	Farm1	Farm2	Farm3	Farm4	Farm 5
Cu	1.56	2.35	0.99	1.29	1.43
Cd	1.28	2.49	1.21	1.66	1.44
Pb	2.21	0.00	2.47	0.00	2.28
Co	1.16	3.27	2.21	1.72	1.37

$I_{geo} \leq 0$ = practically uncontaminated

$0 \leq I_{geo} \leq 1$ = uncontaminated to moderately contaminated

$1 \leq I_{geo} \leq 2$ = moderately contaminated

$2 \leq I_{geo} \leq 3$ = moderately to heavily contaminated

$3 \leq I_{geo} \leq 4$ = heavily contaminated

Table 17: Analysis of Variance of pH in Water from Wolmi River

Observation = 8

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	.670	4	.167	3.158	.026
Within Groups	1.856	35	.053		
Total	2.526	39			

Comment [t14]: The results of ANOVA written in summary

There is significant difference between the concentrations ($P < 0.05$)

For pH, the least significant difference value is calculated as

$$LSD = t \sqrt{\frac{2 \times MS}{Ng}}$$

$$LSD = 2.03 \times 0.115 = 0.23$$

$$\bar{X}_{largest} - \bar{X}_{smallest} = 6.85 - 6.53 = 0.32 \text{ (significant difference)}$$

$$\bar{X}_{largest} - \bar{X}_{smallest} = 6.85 - 6.53 = 0.32 \text{ (significant difference)}$$

$$\bar{X}_{2nd largest} - \bar{X}_{smallest} = 6.84 - 6.53 = 0.31 \text{ (significant difference)}$$

$$\bar{X}_{3rd largest} - \bar{X}_{smallest} = 6.71 - 6.53 = 0.18 \text{ (no significant difference)}$$

$$\bar{X}_{4th largest} - \bar{X}_{smallest} = 6.59 - 6.53 = 0.06 \text{ (no significant difference)}$$

Table 18: Analysis of Variance of Temperature in Water from Wulmi River

Observation = 8

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	1.925	4	.481	.221	.925
Within Groups	76.052	35	2.173		
Total	77.977	39			

There is no significant difference between the concentrations, since the p-value (0.925) > 0.05

Table 19: Analysis of Variance of TDS in Water from Wulmi River

Observation = 8

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	1384.807	4	346.202	10.517	.000
Within Groups	1152.161	35	32.919		
Total	2536.968	39			

There is significant difference between the concentrations (p< 0.05)

For TDS, the least significant difference value is calculated as

$$LSD = t \sqrt{\frac{2 \times MS}{Ng}}$$

$$LSD = 2.03 \times 2.87 = 5.82$$

$$\bar{X}_{\text{largest}} - \bar{X}_{\text{smallest}} = 26.71 - 9.43 = 17.28 \text{ (significant difference)}$$

$$\bar{X}_{\text{2nd largest}} - \bar{X}_{\text{smallest}} = 22.48 - 9.43 = 13.05 \text{ (significant difference)}$$

$$\bar{X}_{\text{3rd largest}} - \bar{X}_{\text{smallest}} = 17.51 - 9.43 = 8.08 \text{ (significant difference)}$$

$$\bar{X}_{\text{4th largest}} - \bar{X}_{\text{smallest}} = 16.17 - 9.43 = 6.74 \text{ (significant difference)}$$

Table 20: Analysis of Variance of Copper in Water from Wulmi River

Observation = 8

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	.127	4	.032	2.384	.070
Within Groups	.467	35	.013		
Total	.594	39			

There is no significant difference between the concentrations at (0.05 level of significance)

UNDER PEER REVIEW

Table 21: Analysis of Variance of Cadmium in Water from Wulmi River

Observation = 8					
	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	1.840	4	.460	3.236	.023
Within Groups	4.974	35	.142		
Total	6.814	39			

There is significant difference between the concentrations ($P < 0.05$)

Determining which mean of results differ in Cadmium use least significant difference (LSD)

For an equal number of replicates N_g in each group, the least significant difference is calculated as follows:

$$LSD = t \sqrt{\frac{2 \times MS}{N_g}}$$

The value of t of 2.03 is obtained for the 95% of confidence level and 35 degrees of freedom, $MS =$ Mean square = 0.142, $N_g =$ Number of group = 8

$$LSD = 2.03 \times 0.188 = 0.38$$

We now calculate the differences in means and compare them with 0.38.

$$\bar{X}_{\text{largest}} - \bar{X}_{\text{smallest}} = 1.76 - 1.17 = 0.59 \text{ (significant difference)}$$

$$\bar{X}_{\text{2ndlargest}} - \bar{X}_{\text{smallest}} = 1.72 - 1.17 = 0.55 \text{ (significant difference)}$$

$$\bar{X}_{\text{3rdlargest}} - \bar{X}_{\text{smallest}} = 1.61 - 1.17 = 0.44 \text{ (significant difference)}$$

$$\bar{X}_{\text{4th largest}} - \bar{X}_{\text{smallest}} = 1.44 - 1.17 = 0.27 \text{ (no significant difference)}$$

Table 22: Analysis of Variance of Lead in Water from Wulmi River

Observation = 8

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	.060	4	.015	1.561	.206
Within Groups	.337	35	.010		
Total	.397	39			

There is no significant difference between the concentrations since (p-value 0.206) > 0.05)

UNDER PEER REVIEW

Table 23: Analysis of Variance of Cobalt in Water from Wulmi River

Observation = 8

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	124.805	4	31.201	8.069	.000
Within Groups	135.340	35	3.867		
Total	260.145	39			

There is significant difference between the concentrations ($P < 0.05$)

For cobalt, the least significant difference value is calculated as

$$LSD = t \sqrt{\frac{2 \times MS}{Ng}}$$

$$LSD = 2.03 \times 0.983 = 1.996$$

$$\bar{X}_{\text{largest}} - \bar{X}_{\text{smallest}} = 6.48 - 1.53 = 4.95 \text{ (significant difference)}$$

$$\bar{X}_{\text{2nd largest}} - \bar{X}_{\text{smallest}} = 4.66 - 1.53 = 3.13 \text{ (significant difference)}$$

$$\bar{X}_{\text{3rd largest}} - \bar{X}_{\text{smallest}} = 3.83 - 1.53 = 2.30 \text{ (significant difference)}$$

$$\bar{X}_{\text{4th largest}} - \bar{X}_{\text{smallest}} = 2.32 - 1.53 = 0.79 \text{ (no significant difference)}$$

Plate I: Wulmi River in Pankshin Local Government of Plateau State

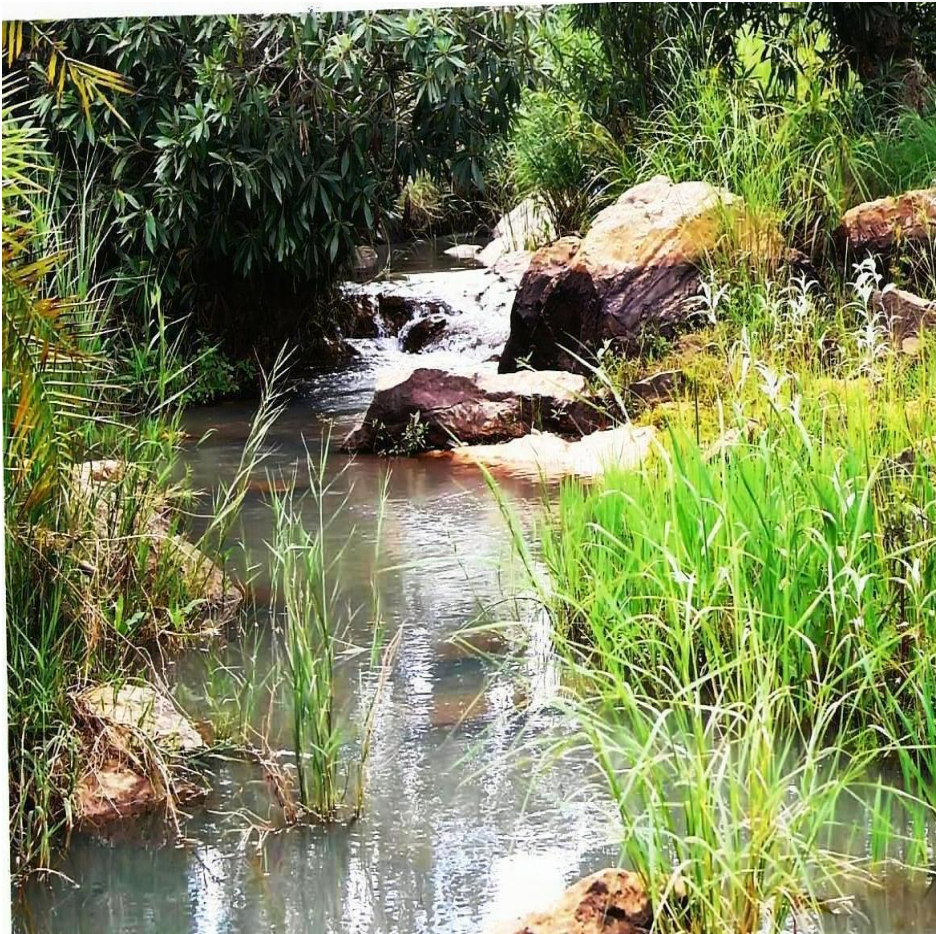


Plate II: The Wulmi River Passes through Pankshin Dam which serves as Reservoir for the Pollutants.



Trends in the Accumulation of the Studied Metals

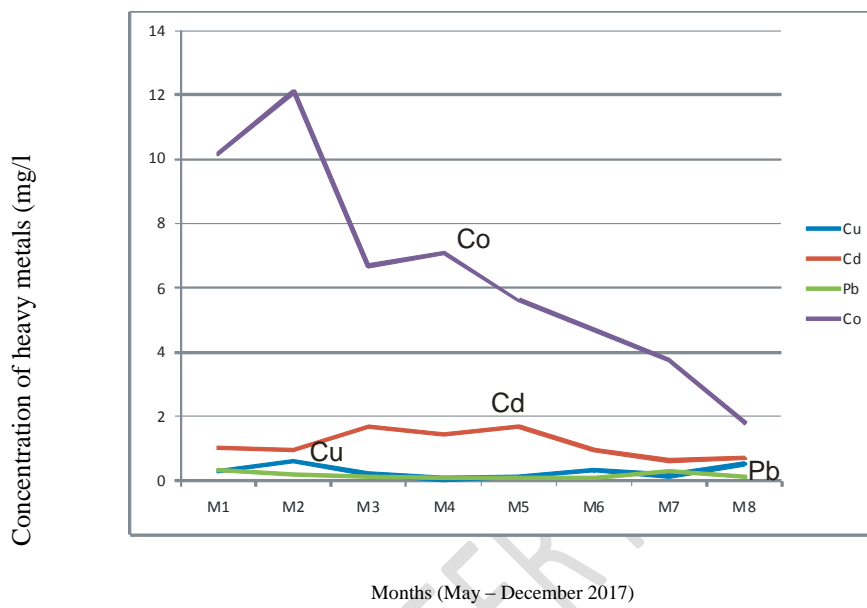


Figure 1. Trend of accumulation of heavy metals at sampling point 1 in Wulmi River

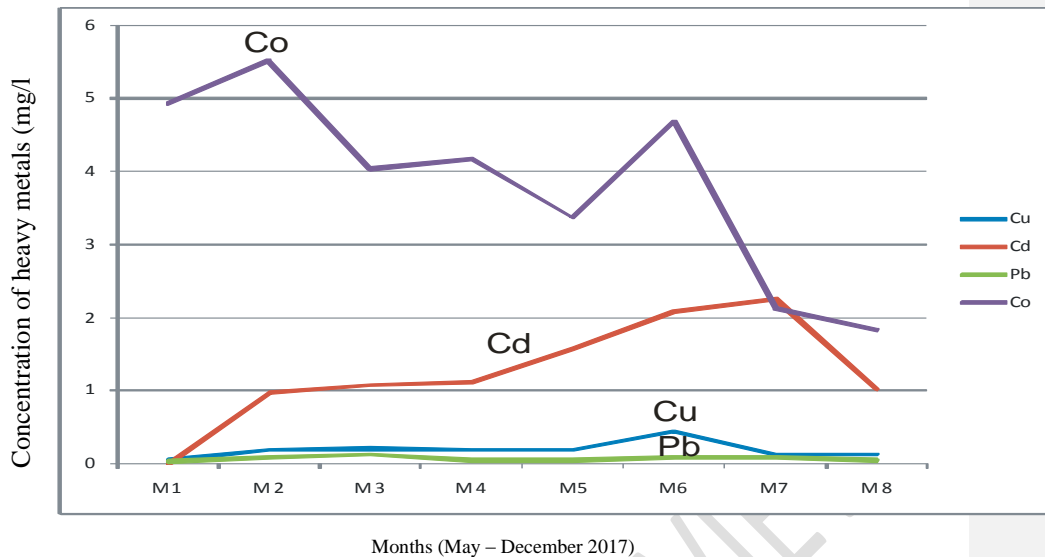


Figure 2. Trend of accumulation of heavy metals at sampling point 2 in Wulmi River

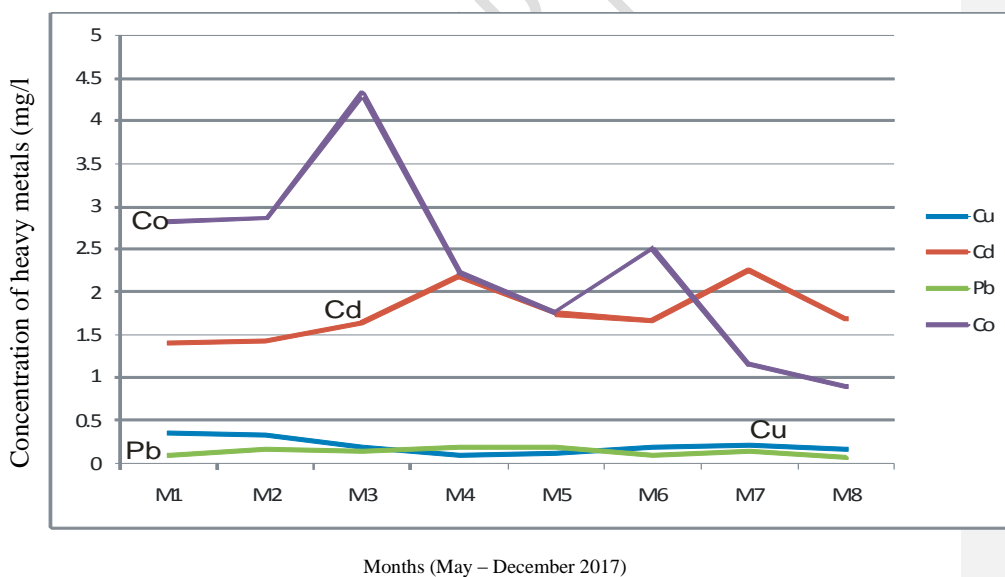


Figure 3. Trend of accumulation of heavy metals at sampling point 3 in Wulmi River

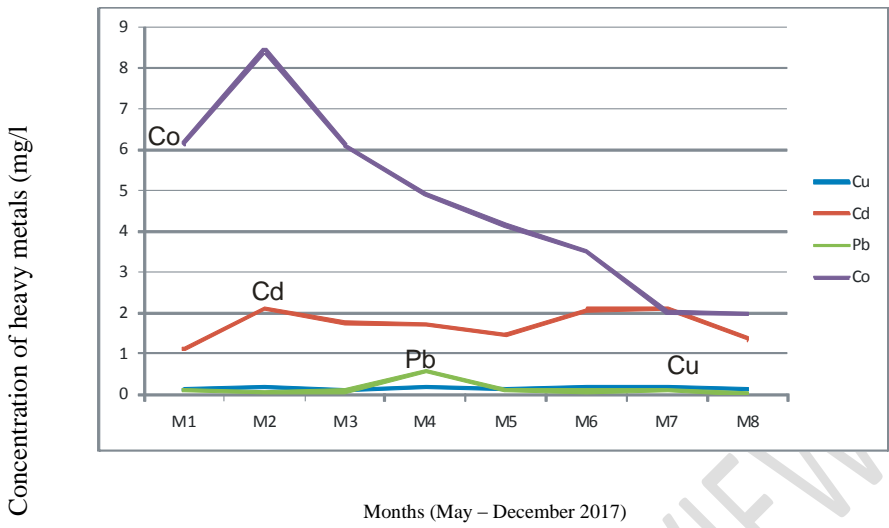


Figure 4. Trend of accumulation of heavy metals at sampling point 4 in Wulmi River

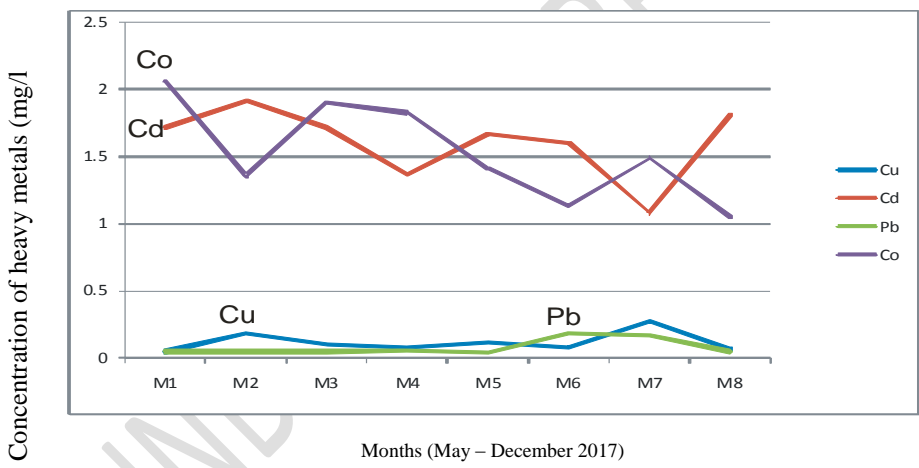


Figure 5. Trend of accumulation of heavy metals at sampling point 5 in Wulmi River

Discussions

From table 6, the levels of Cu (weighted means) in all the sampling points were higher than the WHO permissible limit of 0.05 mg/l. The order of accumulation of Cu (mg/l) was $S_1 > S_3 > S_2 > S_4 > S_5$. The high level

of Cu as seen in the result may be due to the application of fungicides, insecticides and copper compounds added to fertilizers and animal feeds a nutrient to support plant and animal growth on farm lands. Cu is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation (Bai *et al.*, 2011).

The weighted mean concentrations of Cd in all the sampling points were observed to exceed the WHO standard value of 0.005 mg/l. Cd accumulation in all the sampling points was in the order $S_3 > S_4 > S_5 > S_2 > S_1$. The levels of Cd in the water samples from the five sampling points were above the (WHO, 2004) standard values of 0.01 Mg/l for the survival of aquatic organisms.

The weighed mean concentrations of Pb in the water samples ranged between 0.08 ± 0.05 mg/l and 0.91 ± 0.03 mg/l. The concentration of Pb in the water sample from source of these sampling points in Wulmi River exceeded the permissible limit of 0.05 mg/l set by (WHO,2004). The order of accumulation of Pb (mg/l) was $S_2 > S_1 > S_4 > S_3 > S_5$. The level of Pb in the water samples from these portions of Wulmi River might be attributed to heavy agricultural run-off which contains fertilizers, agrochemicals and pesticides (Banat *et al.*, 1998).

In all the sampling points, the weighted mean concentrations of Co exceeded the WHO guideline value of 2.00 mg/l except at sampling point S_5 which is within the permissible limit. Co is an essential element which could be introduced anthropogenically into aquatic ecosystem as run-off from industrial and agricultural activities. The toxicity potential of Co are quite low compared to other heavy metals. However, exposure to very high doses could cause severe health effect.

Water pH is a major factor influencing metal chemistry. The weighted pH value for the sampling sites was in the order; S_3 (6.85) > S_1 (6.84) > S_4 (6.71) > S_5 (6.59) S_2 > (6.53). This therefore suggests that the water at each sampling points are very slightly acidic. Most fish can tolerate pH values of about 5.0 to 9.0 although these small changes in pH are not likely to have a direct impact on aquatic life, they greatly influence the availability and solubility of all chemical forms in the river and may aggravate nutrient problems. The pH values for points $S_1 - S_5$ were within the stipulated values of 6.0 – 9.0 for drinking water and water meant for full contact recreation (DAWF, 1996). Therefore, the parameter does not give cause for concern in this river.

Comment [t15]: The pH of water

The temperature weighted means was slightly higher at sampling point S_2 (25.92°C). And the least value was observed at point S_4 (25.35°C). The weighted mean temperature at sampling point $S_1 - S_5$ are all within the permissible value of 30°C set by WHO.

High temperature reduces the amount of dissolved oxygen in water thereby affecting aquatic lives.

The levels of total dissolved **solid** in Wulmi River fluctuates between 9.43 ± 3.90 mg/l and 26.71 ± 2.75 mg/l. The highest concentration was observed at sampling point S_1 (26.71 ± 2.75 mg/l), while the least

Comment [t16]: solids

value was detected at point S₃ (9.43 ± 3.90 mg/l). The concentration of total dissolved solids was in the order S₁ > (26.71 mg/l) > S₂ (22.48 mg/l) > S₄ (17.51 mg/l) > S₅ (15.92 mg/l) > S₃ (9.43 mg/l). The significant variation between the five sampling points might be due to variation in agricultural activities within the study area. However, the TDS levels recorded in the entire sampling points were below the WHO guideline of 1000 mg/l for the protection of fisheries and aquatic life and for domestic water supply.

The concentrations of Cu, Cd, Pb, Co determined in farms F2, F3, F4 and F5 are all within the permissible limit of WHO (2004) and USEPA (2002) except Cu in farm F1 which is above the standard value of 25 µg/g in the soil. The concentration of copper in all the soil samples ranged between 12.27 ± 3.46 µg/g and 28.05 ± 1.99 µg/g.

The concentration of Cd in soil sample F4 is 17.92 ± 2.18 µg/g which is above the standard value of 6 µg/g in the soil. The Cd concentration ranged between 5.49 ± 3.09 µg/g and 17.92 ± 2.18 µg/g.

Lead has a concentration ranging between 2.24 ± 1.43 which is within the concentration limit of 10 µg/g in the soil.

Cobalt in all the samples are within the acceptable limit of 50 µg/g in the soil. The concentration of cobalt ranged between 13.48 ± 3.72 µg/g and 27.82 ± 2.65 µg/g.

All the metals under investigation have geo-accumulation input in soils around the Wulmi River. However, in irrigation farm 2 and 4, Pb showed no geo-accumulation input. This suggests that these metals are derived mainly from indiscriminate disposal of wastes and agricultural activities in these study sites. The geo-accumulation indices of the metals under investigation are shown in table 16.

Soil samples in all the irrigation farm lands were polluted with Cu but at different degrees. F1 (1.56), F2 (2.35), F4 (1.29) and F5 (1.43) are moderately contaminated by copper. However, in irrigation farm F3 (0.99) was within the range uncontaminated to moderately contaminated.

For cadmium, the accumulation indices values of F1 (1.28), and F3 (1.21), F4 (1.66) and F5 (1.44) fall within the range $1 \leq I_{geo} \leq 2$ which means that those irrigation farm lands are moderately contaminated by cadmium. However, in farm F2 which has an accumulation index value of 2.49 falls within the range $2 \leq I_{geo} \leq 3$ which means that the pollution level of cadmium in this farm land ranges from moderately to heavily contaminated.

For lead, the accumulation indices values for F1 (2.21), F3 (2.47) and F5 (2.28). This clearly shows that soil from those farms are moderately and heavily contaminated with lead because the geoaccumulation indices values of those farms fall within the range $2 \leq I_{geo} \leq 3$. However, farms F2 and F4 both have geo-accumulation indices of 0.00 which means those farm lands are practically uncontaminated by lead.

Soil from farm F1, F4 and F5 have geo-accumulation indices that fall within the range $1 \leq I_{geo} \leq 2$, which means that those farms are moderately contaminated with cobalt. Farm F2 with geo-accumulation index value of 3.27 means the soil is heavily contaminated by cobalt. Farm F3 which has geo-accumulation index value of 2.21 falls within the range $2 \leq I_{geo} \leq 3$ which means the soil from that farm land is moderately or heavily contaminated by cobalt.

Analysis of variance in table 17 indicates, $p = 0.026 < 0.05$ shows that there is significant difference in pH from one sampling point to another in water from Wolmi River throughout the periods of analyses.

Comment [t17]: $P < 0.05$

Analysis of variance in table 18 indicates $P = 0.925 > 0.05$ shows that there is no significant difference in temperature from one sampling point to another in water from Wolmi River throughout the periods of analyses.

Comment [t18]: $P < 0.05$

Analysis of variance in table 19 indicates $p = 0.00 < 0.05$ shows that there is significant difference in TDS concentrations from one sampling points to another in water from Wolmi River throughout the periods of analyses.

Comment [t19]: $P < 0.05$

Analysis of variance in table 20 indicates $P = 0.07 > 0.05$ shows that there is no significant difference in copper concentrations from one sampling point to another in water from Wolmi River throughout the periods of analyses.

Comment [t20]: $P > 0.05$

Analysis of variance in table 21 indicates $P = 0.02 < 0.05$ shows that there is significant difference in cadmium concentrations from one sampling point to another in water from Wolmi River throughout the periods of analyses.

Comment [t21]: $P < 0.05$

Analysis of variance in table 22 indicates $P = 0.26 > 0.05$ shows that there is no significant difference in lead concentrations from one sampling point to another in water from Wolmi River throughout the periods of analyses.

Comment [t22]: $P > 0.05$

ANOVA table 23 also reveals $P = 0.00 < 0.05$ means there is significant difference in cobalt concentrations from one sampling point to another in water from Wolmi River throughout the periods of analyses.

Comment [t23]: $P < 0.05$

CONCLUSION

The study showed that the concentrations of the heavy metals in all the sampling points studied are high when compared with WHO standard, except for the level of cobalt at sampling point S₅. These high levels

Comment [t24]: This

of metals in water at these sampling points would have a negative impact on the surrounding, posing health risks.

UNDER PEER REVIEW

REFERENCE

- Abdel-Ghani, N.T., Elchaghaby, G.A. (2007). Influence of Operating Conditions on the Renewal of Cu, Zn, Cd, and Pb Ions from Waste Water by Adsorption. *International Journal of Environmental Science Technology* **4**: 451-456.
- Ahmed, M.K., Baki, M.A., Islam, M.S., Kundu, G.K., Sarkar, S.K., Hossain, M.M., (2015a). Human Health Risk Assessment of Heavy Metals in Tropical Fish and Shell Fish Collected from the River Buringanga, Bangladesh. *Environmental Science Pollution* . Htt://elx.doi.org/10.1007/s11356-015-4813-z.
- Ahmed, M.k., Shaheen, N., Islam, M.S., Al-Mamun, M.H., Islam, S., Mohiduzzaman, M., Bhattacharjee, L. (2015c). Dietary Intake of Trace Element from Highly Consumed Cultured Fish (*Labeorohita*, *Pengasius* and *Oreochromis Massambicus*) and Human Health Risk Implication in Bangladesh. *Chemosphere* **128**:284-292.
- Arinola, O.G., Akiibinu, M.O. (2006). The Level of Antioxidants and some Trace Metals in Nigerians that are Occupationally Exposed to Chemicals. *India Journal of Occupational and Environment Medicine*. **10**(2):65-68.
- Asaah, V.A., Abimbola, A.F., Such, C.E. (2005). Heavy Metals Concentration And Distribution in Surface Soils of the Bassa Industries Zone, Douala, Cameroon. Tyani, M. and Onodera, S. (2009). Hydro Geochemical Assessment of Metal Contamination in an Urban Drainage System: A case Study of Osogbo Township, SW-Nigeria. *Journal of Water Resource and Protection*. **1**(3):164-173.
- Bai, J., Xiao, R., Cui B., Zhang, K., Wang, Q., Liu, X., M Gao, H., Huang, L (2011). Assessment of Heavy Metals Pollution in Wetland Soils from the Young and Old Reclaim Regions in the Pearl River Estuary, South China. *Environmental Pollution*. **159**: 817-824.
- Banat, I M., Hassan, E. S, El-shahawi, M.S., and Abu-hilal, A.H. (1998) "Postgulf-war Assessment of Nutrients, Heavy Metal Ions, Hydrocarbons, and Bacterial Pollution Levels in the United Arab Emirates Coastal Waters." *Environment International*. **24**:109 -116.
- Biswas, J. (2015). Assessment of physicochemical quality of food waste water of Raipur area. *International Journal of Engineering Research*. **3**(1): 2-7.
- DAWF, "South Africa Water Quality Guideline (1996). **Domestic Water Use**". 2nd Edition, Department of Water Affairs and Forestry, Pretoria.
- Grigoratos, T., Samera, Voutsas, D., Manoli, E., Kouras, A. (2014). Composition and Mass Closure of Ambient Coarse Particles at Traffic and Urban Background Side in Thessaloniki. *Greece Environmental. Science. Pollution*. **21**:7708-7722.
- Islam, M.S., Ahmed, M.K., Habibullah-a-Al-Mamun, M., Islam, K.N., Ibrahim, M., Masunaga, S. (2004). Arsenic and Lead in Foods: A Potential Threat to Human Health in Bangladesh Food Addit. *Contaminant. Part A* **31**(12). 1982-1992.
- Islam, M. S., Ahmed, M. K., Habibulla-Al-Mamun, M., Hoque, M. F (2015a). Preliminary Assessment of Heavy Metal Contamination in Surface Soils from a River Bangladesh. *Environmental. Earth Science*. **73**, 1837-1848.
- Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Haabibulla-Al-Mamun, M., Masunaga, S. (2015b). Metal Speciation in Soil and their Bioaccumulation in Fish Species of three Urban Rivers in Bangladesh. *Environmental Contamination Toxicology* **68**: 92-106.
- Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Habibullah – Al – Mamun, M., Islam, M.K. (2015c). Heavy Metal Pollution in Surface Water and Soil: A Preliminary Assessment of an Urban River in a Developing Country. *Ecological Indices*. **48**:282 – 291.
- Islam, M.S., Ahmed, M.K., Raknuzzaman, M., Haabibulla-Al-Mamun, M., Masunaga, S. (2015d). Assessment of Trace Metals in Fish Species of Urban Rivers in Bangladesh and Health Implication. *Environmental Toxicology Pharmacology*. **39**: 347-357.

- Khadse, G.K., Patni, P.M., Kelkar, P.S., Devotta, S. (2008). Qualitative Evaluation of Kanhan River and its Tributaries Flowing Over Central Indian Plateau. *Environmental Monitoring Assessment*. **147**: 83 – 92.
- Khan, S., Cao, Q., Zhen, Y.M., Huang, Y.G., (2008). Health Risk of Heavy Metals in Contaminated Soil and Food Crop Irrigated with Waste Water in Beijing, China. *Environment Pollution* **152**:686-692.
- Lasat, M.M. (2002) Phytoremediation of Toxic Metals: A Review of Biological Mechanisms. *Journal of Environmental Quality*, **31**:109 – 120.
- Loska, K., Danuta, W., (2003). Application of Principal Component Analysis For Estimation of Source of Heavy Metal Contamination in Surface Soils from the Rybnik Reservoir. *Chemosphere* **51**:723-733.
- Marchiol, L., Assolaris, S., Sacco, P., Zerb., G. (2004). Phyto – Extraction of Heavy Metals by Canola (*BrassilaNapus*) and Radish (*RaphanusSativus*) Grown on Multi-contaminated Soils. *Environmental Pollution* **132**:21 – 27.
- Martin, J. A.R., Arana, C.D., Ramos-Miras, J.J., Gil, C., Boluda R. (2015). Impact of 70 Years Urban Growth Associated with Heavy Metals Pollution. *Environmental Pollution* **196**:156-163.
- Mohuddeen, K.M., Zakir, H.M., Otomo, K., Sharmin, S., Shikazono, N. (2010). Geochemical Distribution of Trace Water Pollution in Water and Soil of Downstream of an Urban River. *International Journal of Environmental Science Technology*, **7**(1):17-28.
- Nicolau, R., Galera, C.A., Lucas, Y. (2006). Transfer of Nutrient and Labile Metals from the Continent to the Sea by a Small Mediterranean River. *Chemosphere*. **63**:469-476.
- Nor, W.A.Z.N., Syakirah, A.M., Saffaatul, H.I., Wan, A.A.W.A. (2012). Assessment of Heavy Metal in Soil due to Human Activities in Kangor, Perlis, Malaysia. *International Journal of Civil and Environmental Engineering*, **12**(6): 28 – 33.
- Nauri, J., Lorestani, B., Yousefi, N., Khorasani, N., Hasani, A.H., Seif, S., Cheraghi, M. (2011). Phyto-remediation Potential of Nature Plants Ground in the Vicinity of Abangaram Lead-zinc mine (Hemedan, Iran). *Environmental Earth Science* **62**:639-644.
- Nwuiche, C.O. and Ugoji, E.O. (2008). Effect of heavy metals pollution on the SoilMicrobialActivity. *International Journal of Environmental Science Technology*., **2**(3) 409-4141.
- Parven, N., Bashar, M.A., Quraishi, S.B. (2009). Bioaccumulation of Heavy And Essential Metals Tropic Level of Pond Ecosystem. *Journal of Bangladesh Academy of Science*. **33**(1): 131-137.
- Radojevic, M., and Bashikin, V.N (1999). “Practical Environmental Analysis”. The Royal Society of Chemistry, Cambridge, Pp 466.
- Rhaman, M.A., Ishiga, H. (2012). Trace Metals Concentrations in Tidal Flat Coastal Soils Yamaguchi Prefecture, Southwest Japan. *Environ. Monit. Assess.* **184**:5755-5771.
- Saleem, M., Iqbal, J., Shah, M.H. (2015). Geochemical Speciation, Anthropogenic Contamination, Risk Assessment and Source Identification of Selected Metals in Fresh Water Soils, a Case Study from Mangla Lake, Pakistan. *Environ. Nanotechnology. Monitoring Management*. **4**: 27-36.
- Sanchez-Chardi, A., Lopez-Fuster, M.J., Nadal., (2007). Bioaccumulation of Lead, Mercury and Cadmium in Greater White-Toothed Shrew, *CrociduraRussula* from Ebro Delta (NE Spain): Sex and Age-dependent Variation. *Environmental Pollution* **145**: 7-14.
- Santos Bermejo, J.C., Beltrom, R., Gomez Ariza, J.L. (2003). Spatial Variations of Heavy Metals Contamination in Soils from Odiel River (Southwest Spain). *Environmental International* **29**:69-67.
- Sekabira, K., OryemOriga, H., Basaamba, T.A., Mutumba, G., Kakudidi, E.

- (2010). Assessment of heavy water pollution in the Urban Stream Soils and its tributaries. *Literature of Journal of Environmental Science Technology* 7(4):435-446.
- Singh, K. P. Malik, A., Sinha, S., Singh, V.K., Murthy, R.C., (2005) Estimation of Source of Heavy Metal Contamination in Soils of Gomti River (India) Using Principal Component Analysis. *Water Air Soil Pollution* 166:321-341.
- Srikanth, R., Rao, A.M., Kumar, C.S., Khanum, A. (1993). Lead, Cadmium, Nickel and Zinc Contamination of Ground Water around Hussain Sugar Lake, Hyderabad, India. *Pollution of Environmental Contamination and Toxicology*, 50: 138-143.
- Tomilson, D.L., Wilson, J., Harris, C.R., Jeffrey, D.W. (1980). Problem in Assessment of Heavy Metals in Estuaries and the formation of Pollution Index. *Helgol. Wiss. Meeresunter*. 33: 566-575.
- USE PA (1999). "Volunteer Laka Monitoring: A methods Manual" EPA 440/4 – 91-002. Office of Water US Environmental Protection Agency, Washington DC.
- Venugopal, T. Giridharan, L., Jayaprakash, M., Velmurugan, P.M. (2009). A Comprehensive Geochemical Evaluation of the Water quality of River Adyar India. *Bull. Environmental Contamination Toxicology* 82:211 – 217.
- Victor, A. A., Akinlolu, F.A., Cheo, E.S. (2006). Heavy Metal Concentrations And Distribution in Surface Soil of the Bassa Industrial Zone 1, Douala, Cameroon. *The Arabian Journal for Science and Engineering*, 31 (2A): 148 – 158.
- WHO (2004), "World Health Organization Standard for Drinking Water," Guidelines for Drinking Waters Quality Volume 1, Recommendation France, Pp 181.
- Wilson, B., Pyatt, F.B., (2007). Heavy Metals Dispersion Persistence, and Bioaccumulation around an Ancient Corps Mine Situated in Anglesey. UK. *Ecotoxicology of Environmental Safety*. 66:224-231.
- Yan, Z. P., Lu, W.X., Long, Y.Q., Ban, X.H., Yang, Q.C. (2011). Assessment Of Heavy Metals Contamination in Urban Topsoil from Changchun City, China. *Journal of Geochemical. Exploration* 108(1): 27 – 38.
- Yit, Y., Yeing, Z., Zhang, S. (2011). Ecological Risk Assessment of Heavy Metals in Soil and Human Health Risk Assessment of Heavy Metals in Fishes in the Middle and Lower Reaches of the Yangtze River Basin. *Environmental Pollution* 159: 2575-2587.
- Yu, G.B., Liu, Y., Yu, S., Wu, S. C., Leung, A.O.W., Luo, X. S., Xu, B., Li, H.B., Weng, M.H. (2011). Inconsistently and Comprehensiveness of Risk Assessment for Heavy Metals in Urban Surface Soils. *Chemosphere* 85:1080-1087.
- Zauro, S.A., Dabai, M.U., Tsafe, A.I., Umar, K.J., Lawal, A.M. (2013). Extent Of some Heavy Metals Contamination in Soil of Farmlands around Sokoto Metropolis. *European Scientific Journal*, 9(3): 30-36.
- Zhang, C., Qiao, Q., Piper, J.D.A., Huang, B. (2011). Assessment of Heavy Metals Pollution from a Fe-smelting Plant in Urban River Soil using Environmental Magnetic and Geochemical Methods. *Environmental Pollution* 159:3057-3070.
- Zhenli, L.H., Xiaoe, E.T., Peter, J. S. J. 9(2005). Trace Elements Medication *Biology* 19:125.