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

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Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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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 (S_1-S_5) 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. 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

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were in the range 6.53±0.21 - 6.85±0.17 for pH. 25.35±0.79 ^{0}C - 25.92±2.31^{0}C for temperature which is within the permissible limit of 30^{0}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 [1] 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.

Keywords: Heavy metals concentrations; Wulmi River; urbanization; industrialization.

1. INTRODUCTION

Wulmi, a village in Pankshin local government area of Plateau state is located at longitude 9^{o}24'58.4712''E and latitude 9^{o}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, the 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 [2,3]. Both natural and anthropogenic activities are responsible for the abundance of heavy metals in the environment [4,5]. However, anthropogenic activities can effortlessly introduce heavy metals in soil and water that pollute the aquatic environment [6]. The increasing pollution by heavy metals has enormous adverse health effects for invertebrates, fish, and humans (Islam *et al.,* 2014; [7,8] Ahmed et al., 2015b. The metal pollution of aquatic ecosystems is increasing due to the effects from urbanization and industrialization [9,10,11,12,7]. 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) [13] which affect their performance and bio availability [14,15].

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 [16,17,18].

Diseases of the lungs, including asthma, pneumonia, and wheezing, have been found in workers who breathed high levels of cobalt in the air [19].

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 [20,21]. In order to characterize the level of pollution in the soil, geo-accumulation index (Igeo) value is calculated using the equation;

$$Igeo = \log 2\left(\frac{C_n}{1.5B_n}\right)$$

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 [22,23,3]. 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: Igeo≤ 0 = practically uncontaminated; 1 ≤Igeo≤ 1= uncontaminated to moderately contaminated; 1 ≤Igeo≤ 2 = moderately contaminated; 2 ≤Igeo≤ 3= moderately to heavily contaminated; 3 ≤ 4 = heavily contaminated; 4 ≤Igeo≤ 5 = heavily to extremely contaminated; and 5 <Igeo = extremely contaminated.

2. MATERIALS AND METHODS

2.1 Reagents

Chart 1. List of reagents used for the study

Conc. HCl (British drug house, England)
Conc, HNO3 (Sigma Aldrich, Germany)
30%H2O2 (British drug house, England)

2.2 Equipment

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

2.3 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;

S_1 = sampling point 1
S_2 = sampling point 2
S_3 = sampling point 3
S_4 = sampling point 4
S_5 = sampling point 5

2.4 Sampling and Sample Collection of Water

The water samples at each sampling point were 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 sterile sample bottles were labeled, transported to laboratory and stored at room temperature prior to analysis.

2.5 Flow Rate of Water in the River

The average volume of water in meter cube (M^3) 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.

2.6 Sampling and Sample Collection of Soil Sample

The 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.

2.7 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 at room temperature (25^{o}C) 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.

2.8 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.

2.9 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 110°C 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:

$$TDS\ (mg/l) = \frac{(W1-W2)x1000}{volume\ of\ sample\ taken(ml)} \quad [24]$$

Where

w_1= final 180°C weight of the dried residue + the tared dish (mg)
w_2= tared dish weight (mg)

2.10 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 [24].

2.11 Digestion of Water Samples for Heavy Metal

2.11.1 Determination

The water samples were digested as follows: 100cm^3 of the sample was transferred into a beaker and 5ml concentrated HNO_3 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 HNO_3 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.

2.12 Digestion of Irrigated Farm Soil Samples for Heavy

2.12.1 Metal Determination

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

The Soils were sieved through a 2mm sieve to remove coarse particles. Two grammes of the soil samples were weighed out into acid watched glass beaker. The 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;).[25] The heavy metals were analysed using AAS with model number Bupk Scientific 210 VGP.

2.13 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. Tables17–23 provide the analysis of variance for the heavy metals concentration and physico-chemical parameters under investigation.

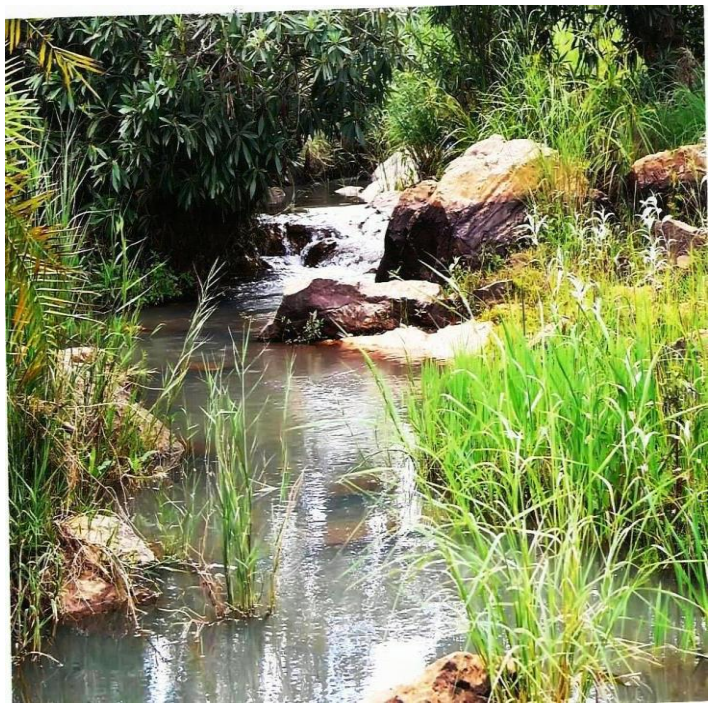

Plate 1. Wulmi river in pankshin local government of Plateau State

Plate 2. The Wulmi river passes through pankshin dam which serves as reservoir for the pollutants

Table 1. Physico-chemical parameters and heavy metals concentrations (mg/l) in Wulmi river at sampling point S_1

S/No	pH	Tempt(^{0}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 S_2

S/NO	Water Flow Rate (M^3/s)	pH	Tempt (^{o}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 S_3**

S/No	Water Flow Rate (M^3/s)	pH	Tempt(^{o}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

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

3.1 Trends in the Accumulation of the Studied Metals

Trends in the Accumulation of the Studied Metals shown in Fig. 1.

Table 4. Physico-chemical and heavy concentrations (mg/l) from Wulmi river at sampling point S_4

S/No	Water Flow Rate (M^3/s)	pH	Tempt (^oC)	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 S_5

S/No	Water Flow Rate (M^3/s)	pH	Tempt (^0C)	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	Tempt(^OC)	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 SD_1

S/No	pH	Tempt(^{0}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 SD_2

S/No	Ph	Tempt(^{0}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 SD_3

S/No	Ph	Tempt(^{0}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 SD_4

S/No	Ph	Tempt(^{0}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 SD_5

S/No	pH	Tempt (°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	1.900.21
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 1382hysic-chemical parameters in the five sampling points in Pankshin Dam

Sampling Points	pH	Tempt (^{0}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

Table 15. Mean concentrations of heavy metals from five selected irrigation farms F1 to F5 around Wulmi River

	Concentrations (μg/g)			
Sampling Points	**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 Wulmi 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

Igeo≤0 = Practically uncontaminated
0≤Igeo≤ 1 = Uncontaminated to moderately contaminated
1 ≤Igeo≤ 2 = Moderately contaminated
2 ≤Igeo≤ 3 = Moderately to heavily contaminated
3 ≤Igeo≤ 4 = Heavily contaminated

Table 17. Analysis of variance of pH in water from Wulmi 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**			

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

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)

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)

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)

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-value0.206) > 0.05)

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)

4. DISCUSSION

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 [11].

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) [1] 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) [1]. 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 [26].

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.

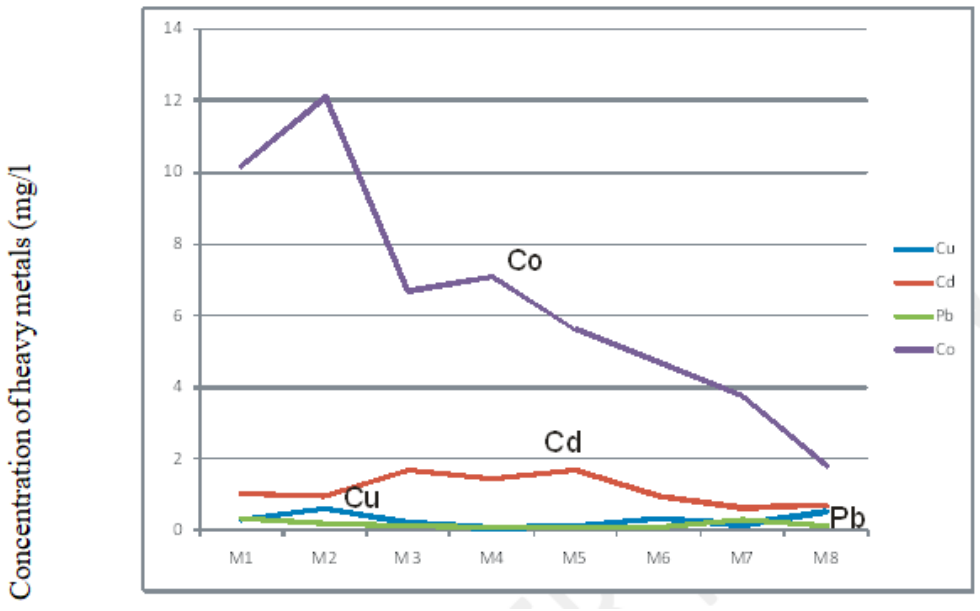

Fig. 1. Trend of accumulation of heavy metals at sampling point 1 in Wulmi River
Months (May – December 2017)

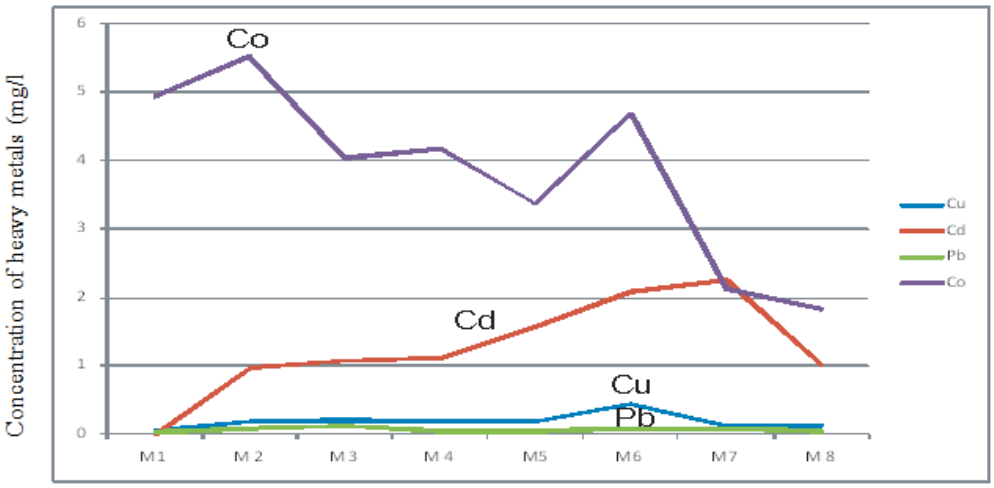

Fig. 2. Trend of accumulation of heavy metals at sampling point 2 in Wulmi River
Months (May – December 2017)

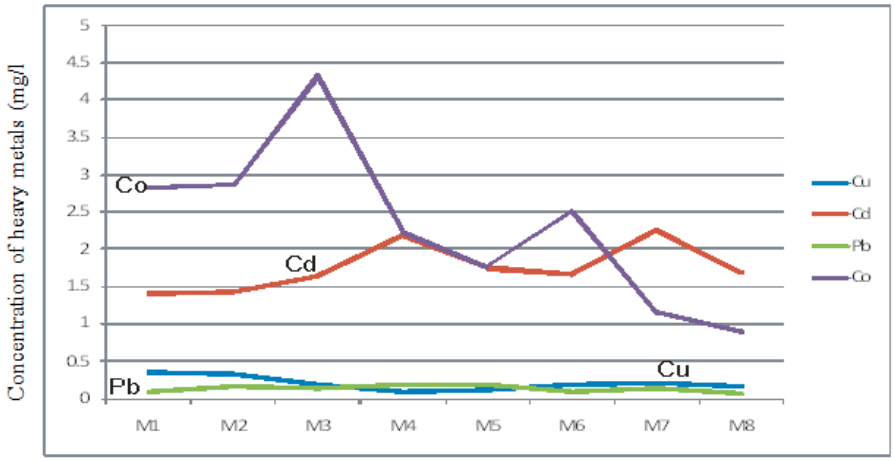

Fig. 3. Trend of accumulation of heavy metals at sampling point 3 in Wulmi River
Months (May – December 2017)

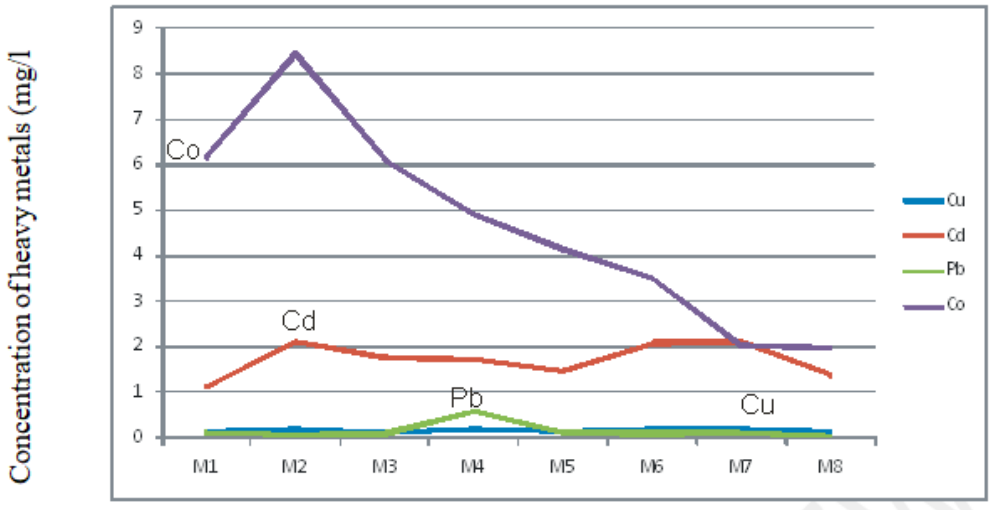

Fig. 4. Trend of accumulation of heavy metals at sampling point 4 in Wulmi River
Months (May – December 2017)

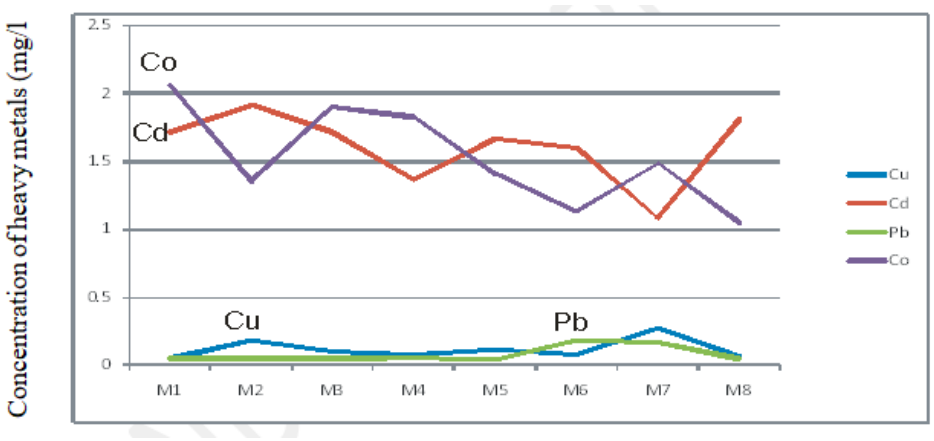

Fig. 5. Trend of accumulation of heavy metals at sampling point 5 in Wulmi River
Months (May – December 2017)

The pH of Water 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 [27]. Therefore, the parameter does not give cause for concern in this river.

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

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

The levels of total dissolved solids 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 value was detected at point S_3 (9.43 ± 3.90 mg/l). The concentration of total dissolved solids was in the order S_1> (26. 71 mg/l) >S_2 (22.48 mg/l) >S_4 (17.51mg/l) >S_5 (15.92 mg/l)>S_3 (9.43mg/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 where 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) [1] and USEPA (2002) except Cu in farm F1 which is above the standard value of 25µg/g in the soil. The concentration of copper in all the soil sample 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 6µg/g in the soil. The Cd concentration ranged between 5.49 ± 3.09 µg/g and 17.92 ± 2.18 µg/g.

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

Cobalt in all the samples are within the acceptable limit of 50µg/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≤Igeo≤ 2 which means that those irrigation farm lands are moderately contaminated by cadmium. However, in farm F2 which has accumulation index value of 2.49 falls within the range 2 ≤Igeo≤3 which means that 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 ≤Igeo≤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≤Igeo≤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≤Igeo≤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 Wulmi River throughout the periods of analyses.

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 Wulmi River throughout the periods of analyses.

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 Wulmi River throughout the periods of analyses.

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 Wulmi River throughout the periods of analyses.

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 Wulmi River throughout the periods of analyses.

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 Wulmi River throughout the periods of analyses.

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 Wulmi River throughout the periods of analyses.

5. CONCLUSION

This 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 S_5. These high levels of metals in water at these sampling points would have a negative impact on the surrounding, posing health risks.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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