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Variations in the Level of Trace Metals in Three Different Irrigation Farmlands at Galga Village of Gubi Dam Area, Bauchi State, Nigeria

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Abstract Trace elements pollution in agricultural soils has attracted scientific attention in recent time due to its effect's agricultural productivity and human health. In this study, the concentrations (mg/kg) of trace metals in the soils of three different farmlands (Farmlands A, B, C and Control) obtained at Galga village of Gubi Dam area were analyzed using Atomic Absorption Spectrophotometry. The mean values of metals varied with the sampling sites with higher values of Pb at all the farms including the control sampling site and the lowest mean value was for Cd and Hg in all the three farmlands. The levels of each metal in all the farmlands and control are significantly different as revealed by one-way analysis of variance (ANOVA) and least significant difference test (LSD). The levels of metals at the control sites are found to be higher compared to the levels in the other three farm locations except Pb and Cr. Pearson coreelqation analysis results revealed a strong positive correlation between Pb and Cr; Cd, As, Fe, and Hg; and a strong negative relationship between Pb and Hg; Fe and Zn; There was, however, no correlation exist between Pb, Cd and As; Cd, Cr and Zn; Cr and As as well as Hg and Zn. This study highlights the importance regular monitoring and assessment of trace elements in agricultural soils in order protect the environment and safeguard the public health.

Keywords Heavy metals, Atomic Absorption Spectroscopy, Galga Village, Gubi Dam

Introduction

Heavy metals are naturally occurring elements having atomic number greater than 20, atomic weight between 63.50 and 200.50 and a specific elemental density greater than 5.00 g/cm3(Fonge *et al.,*, 2021). Regarding their roles in biological systems, they are classified as essential and non-essential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentration. However, non-essential metals have no known biological role in living organism. Examples of essential heavy metals includes Mn, Fe, Cu, Zn and Mo while Cd, Pb, Hg and As are toxic and are regarded as biologically non-essential (Hassan *et al.,*, 2020; Badamasi *et al.,*, 2022).

Sources of heavy metals in environment can be both natural/geogenic/lithogenic and anthropogenic. The natural or geological source of heavy metals in the environment is weathering of metal bearing rocks and volcanic eruptions. The anthropogenic sources of heavy metals in the environment are mining, industrial and agricultural activities. These metals are released during mining and extraction of different elements from their respective ores. Heavy metals that are released to the atmosphere during mining, smelting and other industrial processes return to the land through dry and wet deposition. Discharge of waste-water such as industrial effluents and domestic sewage adds heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic inputs of heavy metals in the environment (Shen *et al.,*, 2019).

Mines are deep cut into the earth purposely for precious materials like metals, gemstones and fossil fuels can be extracted. Common materials that are mined include coal, copper, nickel, diamond and uranium. People have been mining for thousands of years and the process of mining can have a detrimental effect on environment and health of individuals. Most miners suffer from various respiratory and skin diseases such as asbestosis, silicosis or black lung disease. Furthermore, one of the biggest subsets of mining that affects humans are the pollutants that end up in the water which results in poor water quality (Olfat, 2020; Badamasi *et al.*,, 2022). Mining activities produce potential toxic element (PTE) accumulation, which lead to unnatural enrichment, ecological pollution and environmental degradation. The ecological resources impeded by the PTEs cause serious abnormalities in the population through dermal contact, inhalation and digestion. Anthropogenic activities such as mining are well-known causes of contamination of ecological resources (Abdul, *et al.*,, 2020).

This study highlights the importance regular monitoring and assessment of trace elements in agricultural soils in order protect the environment and safeguard the public health.

2. Materials and Methods

2.1 Materials / Equipment

All materials of analytical standard were used and the instrument used in the determination of availability of trace metals in the samples was Atomic Absorption Spectrophotometer (Model AA32ON Shanghai General Analytical Instrument).

2.1.1 Reagents and solutions

Reagents (a mixture of concentrated acids: HCl, HNO_3 and $HClO_4$) of analytical purity were used in the digestion of all the samples and distilled water was also used throughout the experiment.

2.2 Sample Collection and Preparation

2.2.1 Sampling of soil

Sub-soil samples were collected at Galga village of Gubi Dam area (Fig.1) from three different irrigation farmlands (of the same zone) designated as: Farmland A, B, C and Control (of different zone) at a depth of 1-10 cm to allow for the determination of heavy metals levels. The soil samples were collected in clean polyethylene bags and labeled. The soil samples from each farmland were separately homogenized to form a composite sample and air-dried. The samples were ground, sieved to pass through a mesh (2 mm) and preserved for chemical analyses.

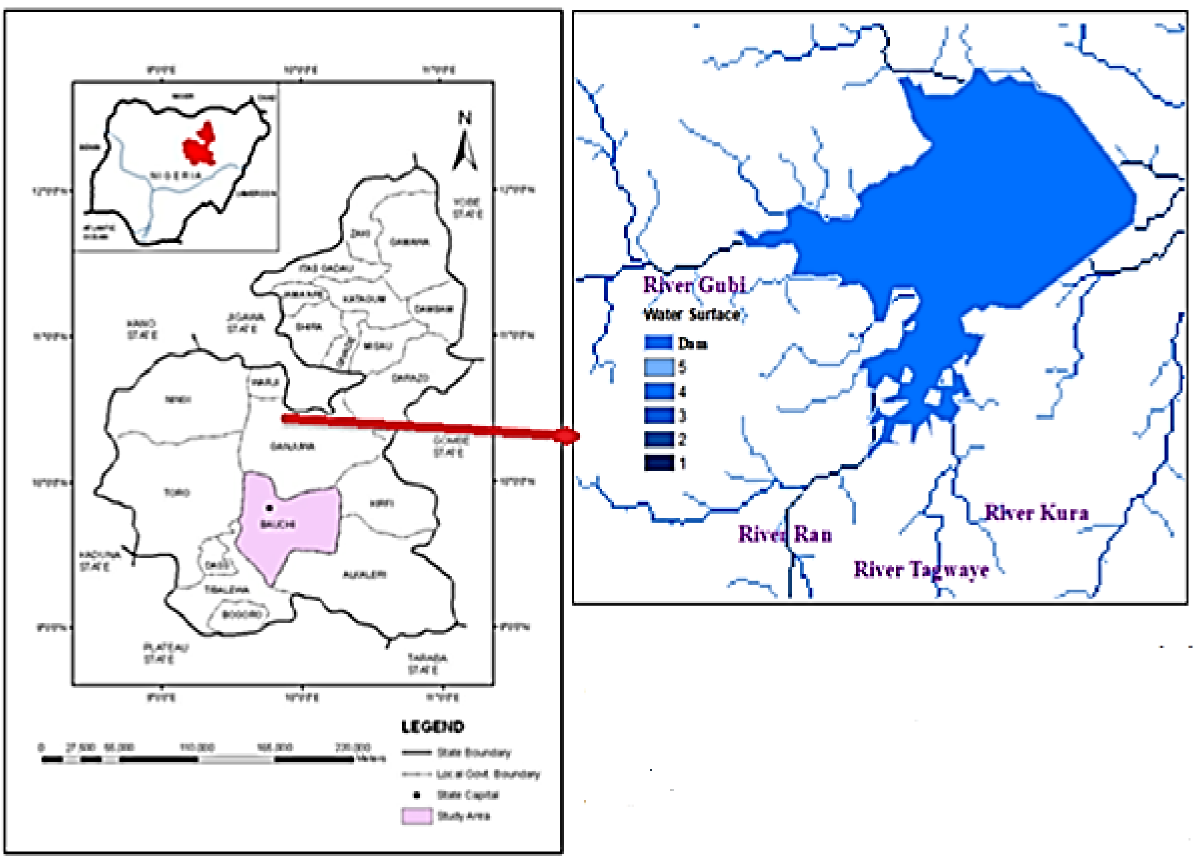

Figure 1: Map Showing the Study Area

2.3 Digestion Procedure

2.3.1 Digestion of soil

For heavy metal extraction, 5.00 g of soil sample was weighed in a 250 cm^3 conical flask and digested using a tri-acid mixture (15.00 cm^3) in a volume ratio of 5:1:1 of HNO_3, H_2SO_4 and $HClO_4$ respectively at 70 ºC until a transparent solution was formed. The resulting solution was filtered using Whattman filter paper No. 41 into a 100 cm^3 volumetric flask and made to volume with distilled water for elemental analysis (Tukura *et al.,*, 2012).

2.4 Statistical Analysis

The data generated in this analysis are means and standard deviation as evaluated by AAS instrument (AA32ON Shanghai General Analytical Instruments). The data generated for levels of heavy metals in the soil samples were subjected to One-way Analysis of Variance (ANOVA) and Least Significant Difference (LSD) to test for variations.

3. Results and Discussion

3.1 Results

3.1.1 Levels of Trace Metals (mg/kg) in Soil Samples

Table 1: The concentration of trace metals (mg/kg) found

Heavy metals	Farm A	Farm B	Farm C	Control
Pb	10.32c ± 0.11	9.37b ± 0.04	14.08a ± 0.14	7.13d ± 0.02
Cd	0.27b ± 0.03	0.54c ± 0.00	1.93d ± 0.00	4.11a ± 0.03
Cr	7.56d ± 0.00	4.44c ± 0.02	10.36a ± 0.10	4.11b ± 0.07
Hg	0.30c ± 0.00	0.31b ± 0.00	0.20d ± 0.00	8.21a ± 0.14
As	4.60d ± 0.00	1.73b ± 0.03	4.37c ± 0.04	6.51a ± 0.02
Fe	4.91d ± 0.02	6.50b ± 0.02	5.71c ± 0.01	9.48a ± 0.00
Zn	1.43d ± 0.02	8.65a ± 0.00	2.49c ± 0.10	5.75b ± 0.01

Values are mean ± standard deviation (n= 3). Values on the same row with different superscript letters are significantly different as revealed by one-way ANOVA and least significant difference (LSD) test ($p \leq 0.05$), while those with same superscript letters are significantly the same. The superscript letters a, b, c and d represents level of significance.

Table 1 shows the concentration of trace metals (mg/kg) found in Galga village at three different farm locations (Farmlands A, B, C and Control). The level of Cd in farm A was found to be the lowest (0.27 mg/kg), while that of Pb was found to be the highest (10.32 mg/kg). The levels of other metals (As, Cr, Hg, Fe and Zn) in the same farmland fell between the extreme values. In farm B, the level of Hg was found to be the lowest (0.31) and that of Pb was found to be highest (9.37). The levels of other metals (Cd, As, Cr, Fe and Zn) in the same farmland fell between the extreme values. In farm C, the level of Pb was also found to be the highest (14.08 mg/kg) compared with other two farmlands. The lowest was Hg with the level (0.20 mg/kg). The levels of other metals analyzed fell between the extreme values. In the control soil sample, the levels of all the trace metals analyzed were greater than what was obtained in three different farmlands (9.48, 8.21, 6.51, 5.75 and 4.11 mg/kg) for Fe, Hg, As, Zn and Cd respectively. The only exception was that of Pb and Cd with the levels 7.13 and 4.11 mg/kg lower than what was obtained at the three irrigated farmlands.

The concentration of lead (mg/kg) was found to be at the range of 7.13 (control) to 14.08 (farm C). The concentration at farms A and B fell within the lowest and highest values obtained. The observed values of' lead are compared with 3.11 to 13.91 mg/kg which was obtained in Owerri metropolis (Ogoko, 2015) and much lower than 36.60 to 525.00 µg/g (36.60 - 525.00 mg/kg) found in Garki Area Council of Abuja soil (Kabiru *et al.,*, 2018). The experimental values were also found to be higher than 0.34 mg/kg (Dass-Bununu road network) and 3.67 mg/kg (Dass-Mball road network) with 1.83 to 2.17 mg/kg (Dass-Zwall road network) to (Bauchi Road network) as reported by Hassan *et al.,* (2020). Also, the reported values were lower than the threshold limit of Pb (100 mg/kg). It is therefore evident that the levels of Pb in all the farms with the control were within the permissible limit (WHO, 2007). The levels (mg/ kg) as determined in the present study at the different farmlands with the control are found to be statistically different as revealed by one-way ANOVA and LSD (Table 1). High dose of Pb can lead to coma, seizure, encephalopathy (irreversible brain damage) and death if not taken care of instantly (Hassan *et al.,*, 2020). The percentage contributions of heavy metals levels in the soil are shown in Figure 2.

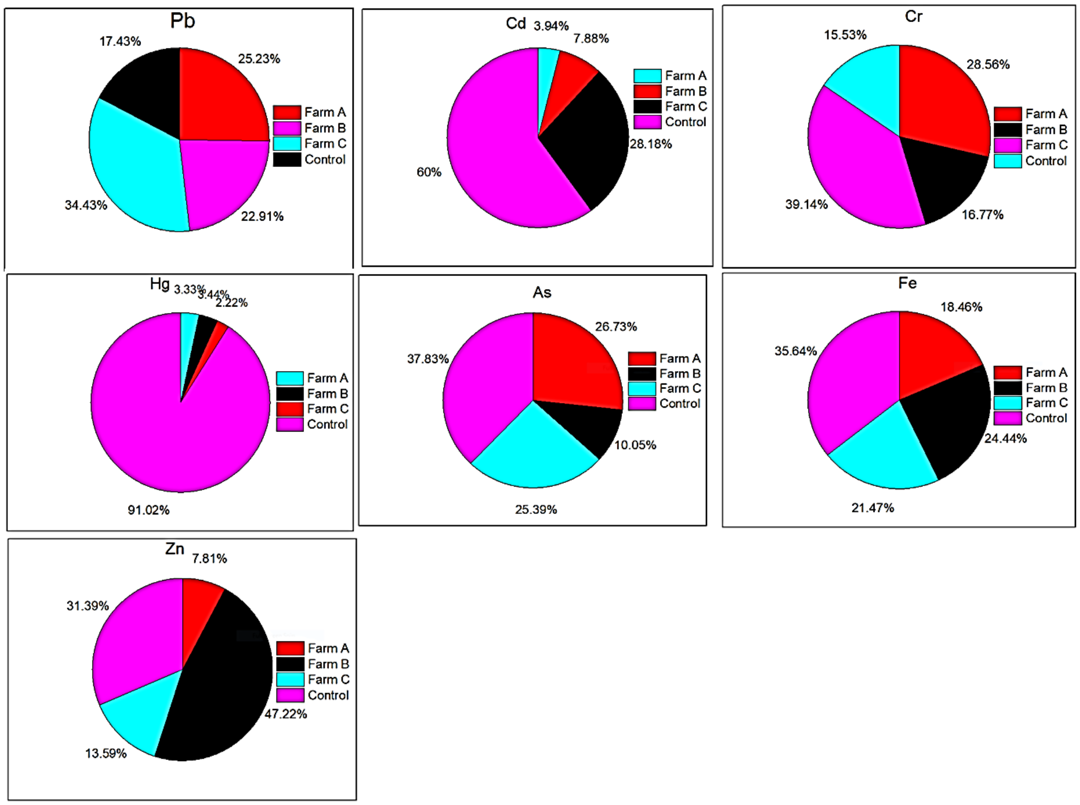

Figure 2: Percentage contributions of heavy metals in the soil

Table 2: Treatment Means Difference of Lead in Three Different Farmlands with the Control ($LSD_{0.05}$=1.80)

	Farm C: 14.08	Farm A: 10.32	Farm B: 9.37	Control: 7.13
Farm C: 14.08	-	3.76	4.71	6.95
Farm A: 10.32	-	-	-	3.19
Farm B: 9.37	-	-	-	2.24

(-) indicates no significant difference

The concentration (mg/kg) of cadmium determined spread from 0.27 (farm A) to 4.ll (control). The level of the metal at farm B and C are 0.54 and 1.93 respectively. These values obtained are compared well with the levels of Cd (2.70 - 5.80 mg/kg) found in soil samples of Owerri metropolis (Ogoko, 2015) and 0.33 mg/kg to 0.67 mg/kg found in roadside soil sample of Dass LGA of Bauchi State. The values of the present study were also compared with 3.67 to 4.00 mg/kg of Cd in roadside soil samples of Bauchi (Hassan *et al.*,, 2019a). The experimental values of 0.27, 0.54 and 1.93 (mg/kg) at all the farmlands were lower than the tolerable limit of 3.00 mg/kg (WHO, 2014) except at the control soil with 4.11 mg/kg of cadmium which exceeded the threshold limit. Statistical significant difference exists in the levels of the metals at all the farmlands as revealed by one-way ANOVA and LSD. Among the effects of Cd include: osteomalacia, temporary gastro-intestinal hemorrhage (Gimler *et al.*,, 2002). Cd is a toxic metal and it is said to be carcinogenic.

Table 3: Treatment Means Difference of Cadmium in Three Farmlands with the Control ($LSD_{0.05}$= 0.20)

	Control: 4.11	Farm C: 1.93	Farm B: 0.54	Farm A: 0.27
Control: 4.11	-	2.18	3.57	3.84
Farm C: 1.93	-	-	1.39	1.66
Farm B: 0.54	-	-	-	0.27

(-) indicates no significant difference

Minimum and maximum mean values of Chromium (Cr) were found to be at the range of 4.11 to 10.46 mg/kg at farm C and the control soil sample. The observed chromium levels are higher than 0.50 mg/kg of the metal found in Dass-zwall road side soil (Hassan *et al.,* 2020) and 0.234 to 1.577 mg/kg found in agricultural soils of Tehran (Delbari and Kulkami, 2011). Similarly, the observed Cr levels were lower than 16.73 mg/kg found in soil sample of Yargalma (Tsafe *et al.,* 2012). The Cr levels determined at farm A, B, C and control were comparatively lower than 50.00 mg of the metal per kilogram of soil according to WHO (2001) as reported by Lente *et al.,* 2014. The concentration values at farm B and control are statistically the same whereas at farm A and C are statistically different as shown in table 6. Chromium is an essential trace and mineral that improves the sensitivity of insulin and enhances the metabolism of lipids, carbohydrates and proteins (Devlin, 2006).

Table 4: Treatment Means Difference of Chromium in Three Different Farmlands with the Control ($LSD_{0.05}$= 0.20)

	Control: 4.11	Farm C: 1.93	Farm B: 0.54	Farm A: 0.27
Control: 4.11	-	2.18	3.57	3.84
Farm C: 1.93	-	-	1.39	1.66
Farm B: 0.54	-	-	-	0.27

(-) indicates no significant difference

The concentrations (mg/kg) of mercury (Hg) in all the sampling locations were found to be 0.30, 0.31, 0.20 and 8.21 at farm A, B, C and Control sample respectively. The level (8.21mg/kg) at control site was found to be highest. The observed levels were compared with the available literature. Reta *et al.,* 2020 reported the Hg level (6.26 and 7.30 mg/kg) under tomato and cabbage cultivation soil collected at Mojo area farmlands in central Ethiopia. The experimental results of Hg in all the sampling locations were found to be statistically different as shown in table 1.

Table 5: Treatment Means Difference of Mercury in Three farmlands with the Control ($LSD_{0.05}$ = 0.40)

	Control: 8.21	Farm B: 0.31	Farm A: 0.31	Farm C: 0.20
Control: 8.21	-	7.90	7.91	8.01
Farm C: 0.31	-	-	0.01	0.11
Farm B: 0.30	-	-		0.10

(-) indicates no significant difference

The levels of Arsenic (As) in the soil samples studied spread from 1.73 mg/kg (farm B), 4.37 mg/kg (farm C), and 4.60 mg/kg (farm A) to 6.51 mg/kg (control) respectively. The concentrations are higher than 0.10 to 0.18 mg/kg of arsenic reported by Ogoko, 2015 in the soil of Owerri metropolis. Higher levels of as of up to 27,000 mg/kg were reported in soils contaminated with mine or smelter wastes (USEPA, 1982). Also, the experimental levels were much higher than the recommended limit of arsenic (0.10 mg/kg) set by FAO/WHO (2007). Among the acute health effect of as (arsenic poisoning) includes vomiting, abdominal pain and diarrhea. These are followed by numbness and tingling of the extremities, muscle cramping and death in extreme cases. The long-term effect/exposure to high levels of inorganic arsenic (for examples, through drinking water and food) are usually observed in the skin, and include pigmentation changes, skin lesions and hard patches on the palms and soles of the feet (hyperkeratosis). Statistically, the different plant parts were found to accumulate different amount (mg/kg) of trace metals as assessed by one-way ANOVA and LSD.

Table 6: Treatment Means Difference of Arsenic in Three Different Farmlands with the Control ($LSD_{0.05}$ = 0.42)

	Control: 6.51	Farm A: 4.60	Farm C: 4.37	Farm B: 1.73
Control: 6.51	-	1.91	2.14	4.78
Farm A: 4.60	-	-	-	2.87
Farm C: 4.37	-	-	-	2.64

(-) indicates no significant difference

The levels of zinc (mg/kg) in three different irrigation farmlands (soil) with the control sample ranging from 1.43 (farm A) to 8.65 (farm B). Other values in farm C and control site fell within the minimum and maximum values. Comparatively, the observed values are lower than what was reported by Hassan *et al.,* 2020 on the level of Zn

(57.83- 79.83 mg/kg) in major road network of Dass soil samples and Ogoko (2015) reported 67.26 - 137.87 mg/kg in the soil of Owerri metropolis. The levels of zinc determined are lower than 300 mg/ kg threshold limit in soil (WHO, 2014). Zinc is regarded as relatively non-toxic since the oral lethal dose is approximately 3.00 g/kg body mass. Zinc is an essential micronutrient that is relevant in biological processes particularly in the proper functioning of proteins in all living organisms (35). The experimental values are statistically different ($p < 0.05$) at all the three farmlands as revealed by one-way analysis of variance (ANOVA) and least significant difference test (LSD).

Table 7: Treatment Means Difference of Zinc in Three Different Farmlands with the Control ($LSD_{0.05}$=1.80)

	Farm C: 14.08	Farm A: 10.32	Farm B: 9.37	Control: 7.13
Farm C: 14.08	-	3.76	4.71	6.95
Farm A: 10.32	-	-	-	3.19
Farm B: 9.37	-	-	-	2.24

(-) indicates no significant difference

The levels of iron (mg/kg) determined in all the farmlands and the control site ranged from 4.91 (farm A) to 9.48 (control). The concentrations of 5.71 (farm C) and 6.50 (farm B) fell in between the lowest and highest observed values. Comparatively, the levels of iron in samples obtained at Dass roadside soil was found to be at the range of 108.33 to 455.00 mg/kg as reported by Hassan *et al.,* 2020. Another literature for iron value in desert soil sample was 4.60 µg/g (4.60 mg/kg) reported by Abdul *et al.,* 2009 of Kuwait governorates. The iron values in the present study is much lower than that of Dass road side soil and compared favorably well with the sample obtained in Kuwait, also much lower than 50,000 mg/kg permissible limit (WHO 2014). Statistical significant difference ($p \leq 0.05$) was found to exist in the levels of iron in all the farms and the control soil (Table 1). Among the effects of high dose of iron in living beings include: hostility, gut damage, headache, metabolic acidosis, liver damage, anorexia, arthritis, increased oxidative stress, heart disease and cancer (Hassan *et al.,* 2020).

Table 8: Treatment Means Difference of Iron in Three Different Farmlands with the Control ($LSD_{0.05}$= 0.87)

	Control: 9.48	Farm B: 6.50	Farm C: 5.71	Farm A: 4.91
Control: 9.48	-	2.98	3.77	4.57
Farm A: 6.50	-	-	-	1.59
Farm B: 5.71	-	-	-	1.14

(-) indicates no significant difference

3.1.2 Correlation Analysis of Trace Metals in Soil Samples

To investigate any potential connections or associations between trace metals, a Pearson correlation study was conducted, and the results are presented in Table 10. A correlation coefficient value (r) greater than ± 0.6 is considered strong; those that lie between 0.4 and 0.6 are considered moderate; and those in the range of 0.2–0.4 are regarded as weak (Gulan *et al.,* 2017). In the present study, a strong positive correlation exists between Pb and Cr (r = 0.94) and a strong negative relationship exists between Pb and Hg, Fe, and Zn (r = -0.72, -0.72, and -0.54, respectively). Cd displays a strong association between Hg (r = 0.91), As (r = 0.76), and Fe (r = 0.88), while Cr shows a negative correlation with Hg (r = -0.58), Fe (r = -0.68), and Zn (r = -0.78). Hg shows a strong positive correlation with as (r = 0.74) and Fe (r = 0.95), while no correlation exists between Hg and Zn. As displays a positive relationship with Fe (r = 0.51) and a moderate relationship with Zn (r = -0.41), while Fe shows a positive relationship with Zn (r = 0.52). There is, however, no correlation between Pb, Cd, and As; Cd, Cr, and Zn; Cr and As; as well as Hg and Zn. Metals that show strong positive and negative correlations with one another indicate that they are of similar origin, and an increase in the level of one metal will lead to an increase in the other, and vice versa. However, those metals that show weak or no correlation with one another demonstrate that they might have originated from different sources, and the increase in the level of one metal may have no effect on the concentration of another metal.

Table 9: Correlation Analysis of Trace Metals in Soil Samples

	Pb	Cd	Cr	Hg	As	Fe	Zn
Pb	1.00						
Cd	-0.37	1.00					
Cr	**0.94**	-0.26	1.00				
Hg	**-0.72**	**0.91**	**-0.58**	1.00			
As	-0.25	**0.76**	0.03	**0.74**	1.00		
Fe	**-0.72**	**0.88**	**-0.68**	**0.95**	**0.51**	1.00	
Zn	**-0.54**	0.12	**-0.78**	0.24	-0.46	**0.52**	1.00

Conclusion

Based on the findings of this research, the three irrigated farmlands were found to have varied levels of heavy metals. The research revealed that the mean concentrations of Pb, Cd, Cr, Hg, As, Fe and Zn varied with the sampling sites with higher values of Pb at all the farms and the control sampling sites and the lowest Cd and Hg in all the three farmlands. The levels of each metal in all the farmlands and control are significantly different as revealed by one-way analysis of variance (ANOVA) and least significant difference test (LSD). The levels at the control sites are found to be higher compared to the levels in the other three farmlands locations. This may be due to either dispersion of metals downstream /downslope, surface run-off or absorption by plants roots. Based on the correlation analysis, some metals show strong positive and negative correlations with one another which demonstrated similar pollution source, while those metals that shows weak or no correlation with one another indicated that they might have originated from different sources.

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