

Assessment of Heavy Metals Concentrations in Some Irrigated Soils of Dadin-Kowa Dam, Gombe State, Nigeria

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Abstract

This study assessed heavy metals concentration in some irrigated soils of Dadin Kowa Dam, Gombe State Nigeria. The soils were collected along transect lines (different sampling points) within the farms and samples were taken to the laboratory for analysis. The analysis was conducted using (Thermo Fisher Scientific) Energy Dispersive X-ray Fluorescence Spectroscopy. The results give the following metals with their mean concentrations: Mo (8.200 and 8.926), Zr (432.990 and 440.236), Sr (204.358 and 87.142), Rb (47.642 and 42.533), Zn (44.165 and NA), Cu (42.161 and NA), Fe (43090.640 and 24846.236), Mn, (992.881 and 397.248), Cr (140.456 and 88.054), V (56.842 and 27.159), Ti (2403.982 and 1421.486), Ca (3344.789 and 982.722), K (4706.758 and 3172.047), S (466.152 and 310.510), Ba (933795.090 and 959675.238) and Nb (26.285 and 24.964) were obtained from the onion and cabbage farms soils samples respectively (Values in part per millions (ppm)). The degree of pollution of the soils studied were ascertained and compared with literature toxicity data. Other pollution indices like Enrichment factor, Clarke ratio, Coefficient of variation, Contamination factor, Metal Pollution Index and Geo-Accumulation Index were assessed also and found out that the contamination level for the soils is tolerable for irrigation. At $\alpha = 0.01$ significant level, positive correlation exists between Fe and Cu, Zn and Ca while Zn and Rb; Ca and Rb have significantly negative correlation between them. By implications, these results showed that the complexes of some elements within the soil strata could influence the presence of other given elements. Therefore, Dam irrigation area soils studied showed relatively low state of pollution for the elements determined.

Key words: Heavy metals, X-ray Fluorescence Spectroscopy, Soil samples, irrigation areas, Dadin Kowa dam

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INTRODUCTION

Soil is a mixture of sand and organic materials that serves as natural medium for plants growth. To date, most research in aquatic systems has been concerned with the form of contaminants present, rather than the amount of potential toxic material bound up in the soils. The low concentration elements are undoubtedly the most difficult to study because background levels are always present in the environment masking their presence, and a small perturbation on an ecosystem could bring about rapid increase in the rates of synthesis of these heavy metals (Seydou, 2008)

Heavy metals are naturally occurring elements, and are present in varying concentrations in all ecosystems. Heavy metals have atomic densities higher than 4 g/cm^3 , and these include lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), copper (Cu), iron (Fe), and platinum (Pt). (Onakpa *et al.*, 2018, Ghaderpoori *et al.*, 2018 and Ugonna *et al.*, 2020)

Heavy metals in soil may dissolve in water and be up taken by plants and vegetation to enter the food chain. The high level of food contamination by these metals is dangerous because their uptake by plants and subsequent accumulation in food crops consumed by humans and animals is delaterious to health. (Sadovska, 2012; Ihedioha *et al.*, 2017 and Zhou *et al.*, 2019).

The main activities of people in Dadin Kowa village is animal husbandry and farming which includes irrigation. Consequently, assessment of elements concentrations in soil samples collected from the study area can educate the public on the contamination level of the soils. Conclusion can be drawn, when the results obtained is compared with the limit set by the standard regulatory bodies.

The aim of this work is to assess heavy metals concentrations in farm soils where onions and cabbages will be cultivated through irrigation near Dadin Kowa Dam, Gombe Sate, Nigeria.

MATERIALS AND METHOD

Description of the Study Area

Dadin Kowa Dam is located in Dadin Kowa. A village in Yamaltu-Deba Local Government Area of Gombe State in the north east of Nigeria. Which is about 35kilometres to the east of Gombe town. It provides drinking water for the neighboring villages and Gombe metropolis. The Dam was completed by Federal Government in 1984, with the goal of providing irrigation and electricity for the planned Gongola sugar plantation project. The coordinates for the study area are $10^{\circ} 19' 19'' \text{ N}$, $11^{\circ} 28' 54'' \text{ E}$ and has the total capacity of eight hundred million metre cube ($800,000,000 \text{ m}^3$). Tables 1 and 2 give the farms location with the referencing coordinates and sample codes with description respectively.

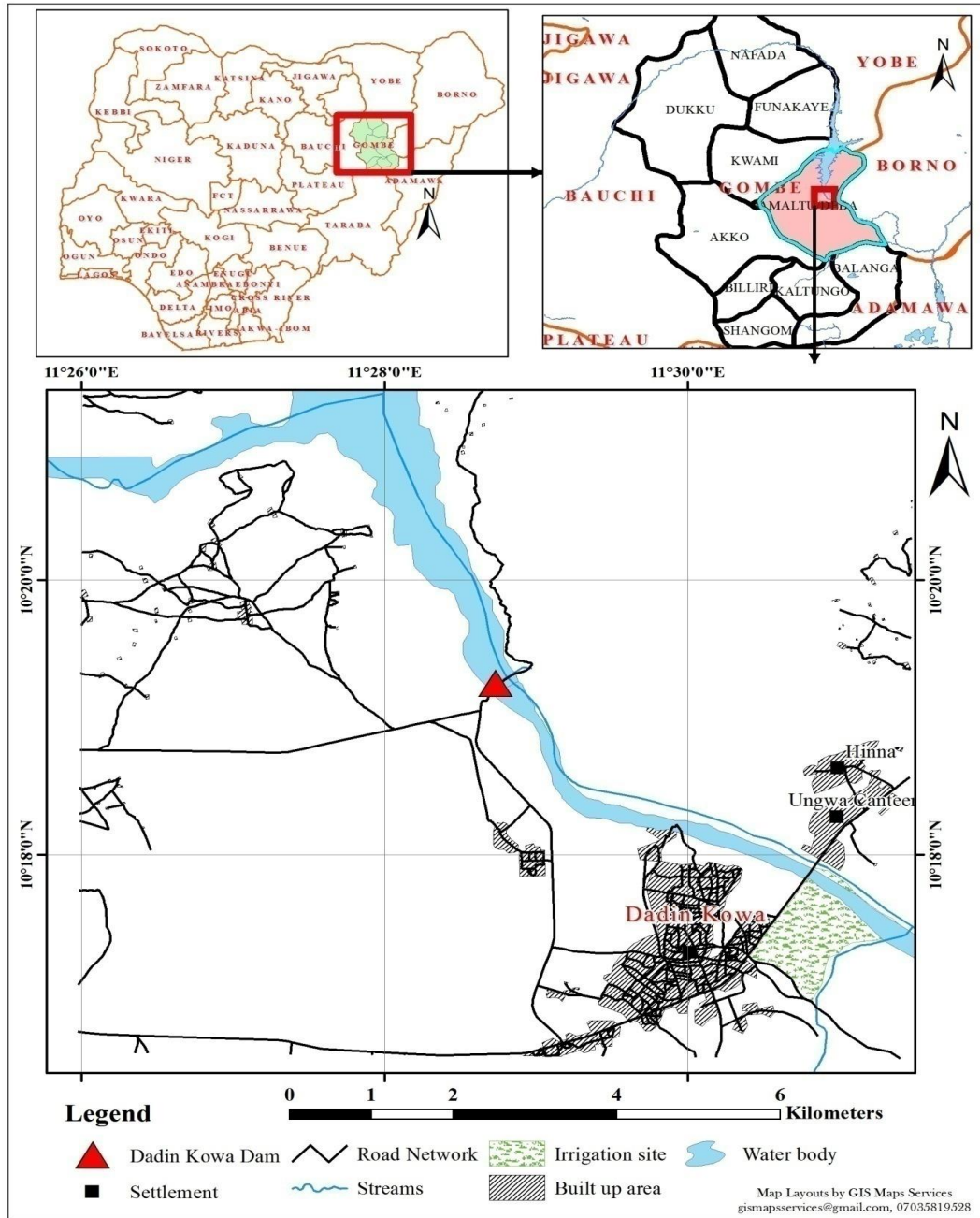


Figure 1: Map of the study area (GIS Maps Services Gombe) (Andrew,2021)

Table 1: Farms locations with their geo-referencing coordinates.

| S/N | FARM LOCATIONS | LATITUDE | LONGITUDE | ALTITUDE |
|-----|----------------|------------------|-----------------|----------|
| 1 | Onion Farm | 10° 17' 35.49" N | 11°30' 40.60"E | 210.12m |
| 2 | Cabbage Farm | 10° 17' 50.19" N | 11° 30' 43.9" E | 210.25m |

Table 2: Sample codes and their descriptions

| S/N | SAMPLE CODES | SAMPLE CODES DESCRIPTION |
|-----|--------------|--------------------------|
| 1 | ONSPA | Onion Soil Point A |
| 2 | ONSPB | Onion Soil Point B |
| 3 | ONSPC | Onion Soil Point C |
| 4 | ONSPD | Onion Soil Point D |
| 5 | ONSPE | Onion Soil Point E |
| 6 | CBSPA | Cabbage Soil Point A |
| 7 | CBSPB | Cabbage Soil Point B |
| 8 | CBSPC | Cabbage Soil Point C |
| 9 | CBSPD | Cabbage Soil Point D |
| 10 | CBSPE | Cabbage Soil Point E |

Sample Collection and Preparation

The soil samples were collected along transect lines (Melville and Welsh, 2001). Five samples of the top soil were taken along each of the transect line. Soils samples were collected from five positions at a depth of 15 cm. 0-15 cm depth was considered to represent the plough layer and average root zone for nutrients uptake and heavy metals burden by vegetables (Eddy *et al.*, 2006; Odai *et al.*, 2008). The soil samples were then air dried, crushed, passed through a sieve, put in clean labeled polythene bags and stored at room temperature for EDXRF analysis.

Data Analysis and Evaluation

Heavy metals in soil samples were determining using energy dispersive x-ray Fluorescence Spectroscopy (EDXRF) system in the laboratory. The trend distribution of the elements was assessed by various statistical analysis tools after determining the heavy metals in the soil samples collected from the study sites. The pollution indices and statistical analysis includes: Enrichment Factor (EF), Clarke Ratio (CR), Coefficient of Variation (CV), Contamination Factors (CF), Metal Pollution Index (MPI), and Geo-Accumulation Factor. The statistical software SPSS (Statistical Package for Social Science) was used to obtain a descriptive interpretation of the Pearson correlation of the elements found in the vegetables.

Enrichment Factors

The enrichment factor of an element in the soil relative to its abundance in the earth’s crust is termed Crustal Enrichment: usually known as Clarke Enrichment (Gluskoter, *et al.*, 1977). The enrichment ratios of trace elements determined for each of the deposits studied along the course of the farms soils, were calculated relative to the concentration of titanium in the samples, since titanium is always present in the earth’s crust.

Enrichment factor as defined in this work is thus:

$$EF_{(crustal)} = \frac{[X]_s / [Ti]_s}{[X]_c / [Ti]_c} \tag{1}$$

where, EF denoted the Enrichment Factor:

$[X]_s$ = Concentration of the element X in the sample.

$[Ti]_s$ = Concentration of Titanium in the sample.

$[X]_c$ = Concentration of the element X in the earth’s crust.

$[Ti]_c$ = Concentration of the Titanium in the earth’s crust.

Other normalizing elements like Fe, Sc, and Si has been discussed by Pardue, *et al.*, (1988), Adetunji and Ong (1989), and Seydou (2011) respectively. But with some limitations for the soil in the case of iron.

Clarke Ratio (CR)

Clarke ratio is defined as the ratio of concentration of element in the sample to the mean global concentration of the same element in the earth's crust. Clarke Ratio tends to throw some light on the modification of elemental concentration in the soil depositions. It shows the magnitude of the variation of an element in a given location with respect to a geochemically accepted and globally fixed value called the 'Clarke Value (Seydou,1998).

Clarke Ratio as defined in this work is thus:

$$R = [X_s / X_c] 100 \quad (2)$$

where X_s = Concentration of element in the sample

X_c = Clarke Value for the given element

Coefficient of Variation (CV)

The Coefficient of Variation is the ratio of the standard deviation of the concentration of a given element in the sample at a given site with respect to the average concentration of the element in the farms soils for all the sites determined, expressed as percentage.

Coefficient of Variation as defined in this work is:

$$CV = [S.D / X] 100\% \quad (3)$$

where S.D = Standard deviation of the element concentration in the sample for different sites

X = Mean concentration of the element determined for a given site along the river course.

The evaluation of CV for each element gives an assessment of how each element varies along the farm course. The variation could be either due to depletion or enrichment that could arise due to various physico-chemical or geochemical factors. It could also be used to assess pollution along the farms if all the factors responsible for pollution are rightly assessed (Seydou,1998).

Contamination Factor (CF)

The term contamination factor refers to the degree of presence of strange substances apart from the original composition of the sample of interest (onion and cabbage). It can be obtained by taking the ratio of concentration of each metal in the samples (onion and cabbage) to that of the background (concentration in unpolluted onions and cabbage). It can be determined by the following equation (Lenntech,2004)

$$CF = \frac{(C)_{Heavy\ metal}}{(C)_{Background}} \quad (4)$$

where, $(C)_{heavy\ metal}$ is the concentration of heavy metal in the sample and $(C)_{Background}$ is the background value for the same metal.

Metal Pollution Index (MPI)

Metal pollution index (MPI) index was calculated using equation 3.2 given by (Ureso *et al.*,1997; Seydou and Auwal,2019; Seydou and Jibrin,2020), which is the geometrical mean of concentrations of all the metals in the corresponding onions and cabbage samples. The MPI value of greater than 1 signifies that the sample is polluted, and that of less than 1 indicates that the sample only baseline pollutants level.

$$MPI = \sqrt[n]{CF1 \times CF2 \times CF3 \dots, CFn} \quad (5)$$

where, CF is the contamination factor, n is the number of heavy metals.

Correlation Analysis

The measure of similarity between paired data is termed correlation analysis. The degree of inter relation between variables can be estimated with the help of correlation coefficient (r) without any influence by measurement units. Correlation is the ratio of covariance (joint variation of two variables about their common mean) of two variables to the product of the standard deviation (Davis, 1973; Seydou, 2008).

Correlation Coefficient being a ratio is a dimensionless number and covariance may equal but can never exceed the product of the standard deviation of its variables. Correlation ranges from +1 to -1. A correlation of +1 is an indication of a perfect direct relationship between two variables. While that of -1 indicates that one variable changes inversely in relationship to the other. A spectrum of less than perfect relationship lies between the two extremes including zero which indicates the lack of any linear relationship.

The Geo Accumulation Index

The Geo Accumulation Index indicates the level of contamination of soils in the study area. An index of geo accumulation (I_{geo}) was originally defined by Muller (1969), and can be calculated by the following equation

$$I_{geo} = [C_s / (1.5 \times C_b)] \tag{7}$$

where C_s is the measured concentration of the examined heavy metal in sample; 1.5 is the background matrix correction due to terrigenous effect or is introduced to minimize the effect possible variations in the background and C_b is the geochemical background concentration or reference value of the metal or background value of the heavy metal in the uncontaminated sample

Table 3: Geo Accumulation Index and Pollution Category (Seydou and Jibrin,2020)

| Geo accumulation index | Pollution |
|------------------------|-----------------------|
| $I_{geo} \leq 0$ | Unpolluted |
| $0 < I_{geo} \leq 1$ | Unpolluted/Moderately |
| $1 < I_{geo} \leq 2$ | Moderately |
| $2 < I_{geo} \leq 3$ | Moderately/Heavily |
| $3 < I_{geo} \leq 4$ | Heavily/Extremely |
| $4 < I_{geo} \leq 5$ | Extremely |

RESULTS AND DISCUSSION

Trace Element

The following metals (Mo, Zr, Sr, Rb, Th, Pb, Zn, Cu, Fe, Mn, Cr, V, Ti, Ca, K, S, Ba, and Nb) with their concentrations were obtained in the samples collected and their results were as shown in Table 4 and Table 5. Therefore, the results obtained in Table 6 from the farms' soils in this work will be discussed in terms of Enrichment factor (EFs), Clarke ratio, Co-efficient of Variation (CV), Contamination factor (CFs), Metal Population Index (MPI), and Geo Accumulation Index (I_{geo})

Table 4: Trace elements in the soil samples from onion farm (Values in ppm)

| Elements | ONSPA | ONSPB | ONSPC | ONSPD | ONSPE |
|----------|------------|------------|------------|------------|------------|
| Mo | 6.031 | 6.739 | 10.248 | 9.068 | 8.915 |
| Zr | 471.390 | 336.074 | 515.068 | 391.524 | 450.892 |
| Sr | 207.081 | 207.016 | 226.767 | 191.884 | 189.044 |
| Rb | 44.119 | 42.039 | 63.349 | 45.240 | 43.461 |
| Th | NA | NA | 16.855 | NA | NA |
| Pb | NA | NA | 24.850 | NA | NA |
| Zn | NA | NA | 44.165 | NA | NA |
| Cu | 54.283 | NA | 30.038 | NA | NA |
| Fe | 49512.254 | 44147.176 | 46773.707 | 40084.285 | 34935.777 |
| Mn | 1318.617 | 1092.891 | 820.905 | 1091.514 | 640.480 |
| Cr | 166.796 | 143.620 | 126.437 | 126.858 | 138.561 |
| V | 73.211 | 65.270 | 67.147 | 40.321 | 38.262 |
| Ti | 2905.866 | 2590.296 | 3155.602 | 1593.939 | 1774.186 |
| Ca | 3931.248 | 3752.677 | 4844.439 | 2133.259 | 2062.316 |
| K | 5394.094 | 4971.378 | 6298.826 | 3069.302 | 3800.188 |
| S | 376.690 | 476.393 | 670.233 | 458.721 | 348.721 |
| Ba | 924504.930 | 930887.938 | 930029.000 | 939458.625 | 944095.000 |
| Nb | 26.525 | 25.140 | 25.660 | 25.660 | 28.441 |

NA = not available

Table 5: Trace elements in soil samples from cabbage farm (Values in ppm)

| Elements | CBSPA | CBSPB | CBSPC | CBSPD | CBSPE |
|----------|------------|------------|------------|------------|------------|
| Mo | 7.854 | 8.540 | 11.026 | 10.190 | 7.022 |
| Zr | 447.104 | 449.617 | 427.184 | 450.200 | 427.075 |
| Sr | 94.551 | 101.341 | 86.348 | 75.285 | 77.546 |
| Rb | 44.032 | 50.355 | 39.098 | 35.958 | 43.221 |
| Fe | 25087.455 | 29166.145 | 22333.754 | 22478.271 | 25165.553 |
| Mn | 265.719 | 561.665 | 382.401 | 372.312 | 404.142 |
| Cr | 108.824 | 111.713 | 12.056 | 115.257 | 92.419 |
| V | 32.654 | 37.634 | 14.084 | 24.362 | 27.061 |
| Ti | 1389.735 | 2027.910 | 512.862 | 1475.680 | 1701.245 |
| Ca | 1281.080 | 1956.730 | 437.287 | 1238.515 | NA |
| K | 3066.020 | 4477.749 | 1529.578 | 2915.727 | 3871.160 |
| S | 351.936 | 264.325 | 411.132 | 263.470 | 261.686 |
| Ba | 958715.188 | 951932.250 | 967657.000 | 962219.563 | 957852.188 |
| Nb | 25.664 | 25.342 | 24.427 | 23.169 | 26.218 |

NA= not available

Table 4 and Table 5 gives the report of the abundance of the elements determined for all trace elements detected from the two farms soils (i.e. onion and cabbage farms) of this work. Some of the concentrations are reported as “less than” values because they are below the limit of quantitative accuracy but above zero (Gluskoter, *et al.*, 1977) several researchers for example Valkovic (1983), Seydou (2011), and Amour (2014) reported that less values do not alter much the statistics of the population notably where the total population is not in size with total member of such data sets. Most of the elements determined could be affected by the deposition rates since other factors could account for the variation. The dry season irrigation of the study area calls for intensive usage of the slowly moving debris-load of the farms land that happens to be used during irrigation. These factors determined the concentrations of the elements and could either lead to enrichment or depletion of the elements determined.

Table 6: Mean concentrations of the individual elements from the two farms' soils (in ppm)

| Elements | Mean for Onion farm soil ± SD(n=5) | Mean for Cabbage farm soil ± SD(n=5) |
|----------|---------------------------------------|---|
| Mo | 8.200 ± 1.7534 | 8.926 ± 1.653 |
| Zr | 432.990 ± 70.0785 | 440.236 ± 12.021 |
| Sr | 204.358 ± 15.0563 | 87.142 ± 11.065 |
| Rb | 47.642 ± 8.8567 | 42.533 ± 5.453 |
| Th | 16.855 ± 3.613 | NA |
| Pb | 24.850 ± 4.904 | NA |
| Zn | 44.165 ± 7.902 | NA |
| Cu | 42.161 ± 19.152 | NA |
| Fe | 43090.640 ± 5733.7 | 24846.236 ± 2772.26 |
| Mn | 992.881 ± 112.9120 | 397.248 ± 121.9340 |
| Cr | 140.456 ± 16.4988 | 88.054 ± 43.376 |
| V | 56.842 ± 16.3044 | 27.159 ± 8.926 |
| Ti | 2403.982 ± 689.99 | 1421.486 ± 564.703 |
| Ca | 3344.789 ± 1211.59 | 982.722 ± 550.29 |
| K | 4706.758 ± 4706 | 3172.047 ± 1114.48 |
| S | 466.152 ± 136.4140 | 310.510 ± 81.9060 |
| Ba | 933795.090 ± 7859.80 | 959675.238 ± 5796.145 |
| Nb | 26.285 ± 1.3037 | 24.964 ± 1.19539 |

NA = not available

Table 6 reports the mean concentrations of the abundance trace elements in onion farm soil and cabbage farm soil. Concentrations in ppm or as indicated.

Enrichment Factor

Enrichment Factor (EFs) of each element were determined for onion and cabbage farms soils deposits investigated along the course of the study area as in Table 7. Where most of the elements enrichment factors were found to be low.

Table 7: Enrichment Factor for elements determined from the two farms' soils

| Elements | Onion farm soil EFs | Cabbage farm soil EFs |
|----------------|--------------------------|--------------------------|
| M _o | 5.013x10 ⁻⁰³ | 9.229 x10 ⁻⁰³ |
| Z _r | 7.027 x10 ⁻⁰⁴ | 1.208 x10 ⁻⁰³ |
| S _r | 1.399x10 ⁻⁰⁴ | 1.009 x10 ⁻⁰⁴ |
| R _b | 1.606x10 ⁻⁰⁴ | 2.424 x10 ⁻⁰⁴ |
| Z _n | 1.530 | 0.000 |
| C _u | 2.019 | 0.000 |
| V | 1.099x10 ⁻⁰⁴ | 8.879 x10 ⁻⁰⁵ |
| F _e | 1.821 | 1.776 |
| C _a | 0.189 | 1.174 |
| K | 0.673 | 0.767 |
| C _r | 3.693x10 ⁻⁰⁴ | 3.915 x10 ⁻⁰⁴ |
| N _b | 3.455x10 ⁻⁰⁴ | 5.551 x10 ⁻⁰⁴ |

A summary of Clarke enrichment factor for the two farms soils is as given in Table 8

Table 8: Summary of Clarke enrichment factors for the two farms' soils

| Clarke Enrichment Factor Ranges | Elements for onion farm soil | Elements for cabbage farm soil |
|---------------------------------|-------------------------------------|---------------------------------|
| <1 | Mo, Zr, Sr, Rb, V, Ca, K, Cr and Nb | Mo, Zr, Sr, Rb, V, K, Cr and Nb |
| >1 | Fe, Zn and Cu | Fe and Ca |

From Table 8, elements like Fe, Zn and Cu with enrichment factor greater than 1 in onion farm soil and Ca, are known to be toxic to some extent (Bowen, 1979; Seydou, 2008), even though useful in some cases. Among depleted elements (Ca, K, Zr, Sr, Rb, Zn, V, Cr and Nb) some are toxic while others are relatively harmless to all organisms. Calcium is known to be harmless to all organism (Bowen, 1979; Seydou, 2008). Though Zn and Cu were not available in cabbage farm soil samples but, Fe and Ca were also found to have an enrichment factor greater than 1.

Toxicity

Table 9 shows that the toxicity of some elements obtained in both onion and cabbage farms soils with comments on their toxicity as reported by (Bowen, 1979 and Seydou, 2008) it's clearly shown that Ca, Fe, K, and Zn are probably essential to all plants. This could be used to the seasonal crops grown in the study area. Element like Ti is relatively harmless and essential to some group, not necessary for all. Rb, K, Sr, and Ca are known to have a very high toxicity, which only arises when a large proportion of the essential ion has been replaced. Fe, V, and Zn are moderately toxic while Ca, K, Rb, and Sr are only toxic to very high concentrations, Table 9 clearly shows that they are scarcely toxic. Zr was found to be toxic while element like Nb moderately toxic. Molybdenum (Mo) is a requirement for nitrogen assimilation via nitrate, as this enzyme reduces nitrate to ammonium before assimilation in to biochemical pathways. Mo is an essential compound of two major enzymes in higher plants, nitrate reductase and nitrogenase which is present in nodulated legumes and required in the N fixation process but found to be toxic in this work.

Zinc is the element most frequently concerned with plants damage from industrial emissions, e.g. on mine wastes, near smelters, sewage sludge, river dredging, near galvanized steel buildings and where rubber tyres are burnt (Patterson, 1971; Barrow and Weber 1972; Seydou, 2011). The onion farm soil Zn was found to be in only ONSPC sampling point and the concentration was found to be 44.165ppm as shown in Table 4.1 which was less than 900ppm maximum limit for animals (Jenett *et al.*, 1980). Among the elements reported to be enriched in soil are Fe, Ti, V, and Zr (Bowen, 1979). In this work Fe, K, Ca and Ti was found to be enriched, while the remaining elements under study were depleted.

Table 9: Toxicity of elements from the two farms' soils (Values in ppm or as stated)

| Elements | Values from onion farm soil | Values from cabbage farm soil | Reported toxicity by Bowen (1979) | Remarks on toxicity in onion and Cabbage farm soils |
|----------|-----------------------------|-------------------------------|-----------------------------------|---|
| Mo | 8.200 | 8.926 | 0.2 - 5 ppm | Toxic |
| Zr | 0.433 | 0.440 | 250-700mg/day lethal to rats | Not toxic |
| Sr | 204.358 | 87.142 | Scarcely toxic to plants | Scarcely toxic |
| Rb | 47.642 | 42.533 | Scarcely toxic to plants | Scarcely toxic |
| Zn | 44.165 | ... | 60-400ppm toxic to plants | Expected to be toxic |
| Cu | 42.161 | ... | 50 - 140 ppm toxic to plants | Expected to be toxic |
| V | 56.842 | 27.159 | 10-40ppm toxic to plants | Toxic |
| Ti | 2403.982 | 1421.486 | Relatively harmless | Relatively harmless |
| Ca | 3344.789 | 1279.944 | Relatively harmless | Relatively harmless |
| K | 4706.758 | 3172.047 | Scarcely toxic | Scarcely toxic |
| Nb | 26.285 | 24.964 | Moderately toxic to mammals | Moderately toxic |
| Fe | 43090.640 | 24846.236 | 10-200ppm toxic to plants | Toxic |
| Cr | 140.456 | 88.054 | 14 - 70 ppm toxic to plants | Toxic |

Onion and cabbage farms soils' Clarke Ratio as defined in chapter three was calculated and the results were shown in the Table 10.

Table 10: Clarke Ratio for Trace Elements from the two Farms' Soils

| Elements | Clarke ratio for onion farm soil | Clarke ratio for cabbage farm soil |
|----------|----------------------------------|------------------------------------|
| Mo | 8.200 | 8.926 |
| Zr | 267.278 | 271.751 |
| Sr | 53.218 | 22.693 |
| Rb | 61.080 | 54.530 |
| Zn | 58.112 | 00.000 |
| Cu | 76.656 | 00.000 |
| V | 41.796 | 19.970 |
| Cr | 140.456 | 88.054 |
| Ti | 37.975 | 22.468 |
| Fe | 69.277 | 39.952 |
| Ca | 7.189 | 2.640 |
| K | 25.598 | 17.228 |
| Nb | 131.425 | 124.820 |

Table 11: Clarke ratio summary for farms soils

| Clarke ratio ranges | | Elements for onion farm soil | Elements for cabbage farm soil |
|---------------------|----------|---------------------------------|----------------------------------|
| R < 10 | | Mo and Ca | Mo and Ca |
| 10 < R < 100 | Depleted | Sr, Rb, Zn, Cu, V, K, Ti and Fe | Sr, Rb, Cr, Ca, V, K, Ti and Fe, |
| 100 < R < 1000 | Enriched | Zr, Nb and Cr | Zr, and Nb |

The summary of Clarke ratio is given in Table 11 above and shows that elements like Mo, Fe, Sr, Rb, Zn, Cu, Ca, Ti, K and V were depleted. While Zr, Cr and Nb, are enriched in the onion farm soil. In the case of the cabbage farm soil, Zr and Cr were enriched while the remaining elements remained depleted as in the case of onion farm soil. Therefore, we will conclude that

Ti is a good normalizing element as the enrichment factor results are in good agreement with the Clarke ratio results.

The trace elements concentrations were found within the range 0 to 224. Six elements namely Nb, Sr, Fe, Cr, Zr and Rb show low coefficient variation (<20), while Nb, Fe, Rb, Zr, Sr and Mo show low coefficient of variation (<20). This could be probably due to low deposition, high washout or that the elements exist in highly soluble forms. The other elements that had high coefficient variation ranging from 20 to 224, could be due to high deposition and low washout which suggests that elements might have come from external sources, there by polluting the farm soil. This sources could be from fertilizers, pesticides, herbicides, laundry wastes, sewage sledges or any other way suspected of causing pollution.

Metal Pollution Index

For us to calculate metal pollution index we first calculate contamination factor (Table 12). CF was calculated as stated in chapter three. The background Concentrations (Conc.background) of the individual heavy metals Mo, Zr, Sr, Rb, V, K, Ca, Cr, Nb, Fe, Cu, Ti, and Zn sets by regulatory bodies are 0.43, 220, 87.62, 85.46, 63.9, 740, 4.6, 100, 92.906, 0.3, 1.0, 0.014, and 0.001 mg/kg respectively, (GEMS/FOOD,2000) and (WHO,2001). The background concentrations above are used to calculate the contamination factors of each of the elements from the five (5) sampling points of the two (2) farms.

Table 12: Contamination factor for the trace elements from farms soils

| Elements | CF for onion farm soil | CF for cabbage farm soil |
|----------|------------------------|--------------------------|
| Mo | 19.070 | 20.759 |
| Zr | 1.968 | 2.000 |
| Sr | 2.332 | 0.993 |
| Rb | 0.557 | 0.498 |
| Zn | 8.833 | 0.000000 |
| Cu | 16.864 | 0.000000 |
| Fe | 14.364 | 8.282 |
| Ti | 17.171 | 10.154 |
| Ca | 0.073 | 0.0214 |
| K | 0.000636 | 0.000428 |
| V | 0.890 | 0.425 |
| Cr | 1.405 | 1.098 |
| Nb | 0.283 | 0.269 |

Table 12 shows the mean contamination factor of each element from onion farm soil and cabbage farm soils where most of the elements from the two farms soil were within limit set by the regulating agencies. Only Mo showed higher value.

Metal pollution index as defined in chapter three was calculated and the results were shown in Table 13

Table 13: Metal pollution index of the trace elements obtained from farms soils

| Elements | MPI for onion farm soil | MPI for cabbage farm soil |
|----------|-------------------------|---------------------------|
| Mo | 21.835 | 22.781 |
| Zr | 7.014 | 7.071 |
| Sr | 7.635 | 4.983 |
| Rb | 3.732 | 3.529 |
| Zn | 14.860 | 0.000 |
| Cu | 20.533 | 0.000 |
| Fe | 0.1895 | 0.1438 |
| Ti | 0.2072 | 0.1593 |
| Ca | 0.01348 | 0.0073 |
| K | 0.00126 | 0.00104 |
| V | 4.717 | 3.260 |
| Cr | 5.927 | 5.239 |
| Nb | 2.660 | 2.593 |

The MPI for elements like Mo, Zr, Sr, Rb, Zn, Cu, V, Cr and Nb were found to be above one in both the farms. Though Zn and Cu were not detected in cabbage farm soil. The remaining elements (Fe, Ti, Ca and K) in both farms were found to have MPI values less than one. The MPI value of greater than 1 signifies that the sample is polluted, and that of less than 1 indicates that the sample is within baseline pollutants level (Ureso *et al.*, 1997 and Esmaeilzadeh *et al.*, 2019). So, it was concluded that, elements like Mo, Zr, Sr, Rb, Zn, Cu, V, Cr and Nb found from the two farms soil indicate pollution while the remaining were within the baseline pollutants level.

Table 14: Comparison of this work mean values of farms soils with other related Works (Values in ppm or as stated)

| Elements | Onion Farm Soil | Cabbage Farm Soil | Seydou (2011) | Amour (2014) | World Value(2001) |
|----------|-----------------|-------------------|---------------|--------------|-------------------|
| Zr | 432.990 | 440.236 | 712.64 | - | (32 - 850) |
| Sr | 204.358 | 87.142 | 66.13 | - | 53.4 |
| Rb | 47.642 | 42.533 | 117.17 | - | (18 - 116) |
| Fe(%) | 4.309 | 2.485 | 1.16 | 6.6454 | 0.0426 |
| Zn | 44.165 | - | 107.17 | 629.89 | 300 |
| V | 56.842 | 27.159 | 27.14 | BDL | 100 |
| Nb | 26.285 | 24.964 | 28.15 | - | 12 |
| Cr | 140.456 | 88.054 | - | 57.08 | 44.5 |
| Mo | 8.200 | 8.926 | - | - | 5 |
| Cu | 42.161 | - | - | 70.71 | 50 - 140 |
| Ti(%) | 0.240 | 0.142 | 0.45 | - | 0.46 |
| Ca(%) | 0.335 | 0.123 | 0.38 | 0.0011 | 1.37 |
| K(%) | 0.471 | 0.317 | 2.36 | 0.0002 | 1.4 |

BDL = Below Detection Limit

Table 14 shows the comparison of this work mean values for onion and cabbage farms soil with other related material. Zr, Rb, and Nb in cabbage farms soil were found to have lower concentrations in comparison with the reported literature values. Sr, Fe, and V in this work was found to be higher concentrated than Sr, Fe and V reported by Seydou, (2011). While Zn and Cu was not found in cabbage farm soil. Also Cr was found to be higher concentrated

compared to that of Amour, (2014). Ca and K in cabbage farm soil happen to be lower than that of Seydou, (2011) but lower than that of Amour, (2014). Ti in this work was found to have lower concentration than Ti reported by Seydou, (2011) but was not detected by Amour.

In the case of onion farm soil, it shows that Zr, Rb, and Nb in onion farms soil were found to be lower in concentration compared to the literature values. Sr in this work was found to be higher concentrated than Sr reported by Seydou, (2011). While Zn was found to be lower than the literature values. Fe from farms soil in this work was found to be higher than that of Seydou, (2011) but lower than that of Amour, (2014) reports. Cu in onion farm soil was found to be lower concentrated than what was reported by Amour (2014). Ca and K in onion farm soil happen to be lower than that of Seydou, (2011) but higher than that of Amour, (2014). Ti in this work was found to be higher concentrated than Ti reported by Seydou, (2011) but not detected by Amour, (2014).

Table 14 also shows the comparison of the mean concentration from the two (2) farm soils in this work with the world values. Where Zr, Zn, V, Cu and Rb in both the farms were found to be within the average world values of the stated elements in the soil. While Mo, Sr, Fe, Nb, and Cr were found to be above the world values of the same elements. Also Ti, Ca, and K were found to be very high concentrated in onion farm soil than the average world value.

Table 14 finally shows the comparison of this work mean values of the two (2) farms soil (onion and cabbage farm). Mo, Ti, Ca, K and Zr in onion farm soil were found to be lower concentrated compared to cabbage farm soil values. And Sr, Rb, Fe, V, Nb and Cr were found to be higher concentrated than reported values from cabbage farm soil. While Zn and Cu were found only in onion farm soil.

Geo accumulation Index (I_{geo}) of the two farms soils was calculated as defined above and the results were shown in the Table 15.

Table 15 shows the geo accumulation index of the two farms. Where Sr, Rb, V, Nb, Ca, K, Cr, Cu, Fe, Zn, and Ti were found to be greater than zero but less than one showing unpolluted level. While Zr shows moderate pollution level, because is greater than one but less than two in both the farm soils. Mo was greater than five so, is extremely polluted.

Table 15: Geo accumulation Index (I_{geo}) for farms soils

| Element | I_{geo} for onion farm soil | I_{geo} for cabbage farm soil |
|---------|-------------------------------|---------------------------------|
| Mo | 12.7132 | 13.8387 |
| Zr | 1.7819 | 1.8117 |
| Sr | 0.3548 | 0.1513 |
| Rb | 0.4072 | 0.3635 |
| V | 0.2786 | 0.1331 |
| Nb | 0.8762 | 0.8321 |
| Fe | 0.4619 | 0.2663 |
| Cu | 0.2044 | - |
| Zn | 0.0775 | - |
| Cr | 0.9364 | 0.5870 |
| Ti | 0.2536 | 0.1500 |
| Ca | 0.0479 | 0.0141 |
| K | 0.1705 | 0.1149 |

Pearson’s Correlation matrices among the studied metals (Mo, Zr, Sr, Rb, Zn, Cu, Fe, Ti, Ca, K, Ba, and Nb) in soil samples were obtained using SPSS Version 25 (IBM Corp., USA) software and the results are shown in Table16. However, at ($\alpha = 0.05$) positive correlation exist between K with Sr, Rb, Zn and Fe. Ti with Sr, Rb, Zn, and Fe. Ca with Rb, Zn and Cu. Negative correlation only exist between Ba with Fe. At ($\alpha = 0.01$) Ca with Sr, Fe,Ti and K. Fe with Sr, Ca, Ti and K all has significantly positive correlation between each other. While Ba with Fe, Sr, Ti, Ca and K has negative correlation exist between them. By implications, these results shows that the complexes of some elements within the soil strata could influence the presence of other given element.

Table 16: Person's correlation matrices between variable parameters in the farms soils samples

| | Mo | Zr | Sr | Rb | Zn | Cu | Fe | Ti | Ca | K | Ba | Nb |
|----|--------|--------|---------|--------|--------|--------|---------|---------|---------|---------|--------|----|
| Mo | 1 | | | | | | | | | | | |
| Zr | 0.305 | 1 | | | | | | | | | | |
| Sr | -0.225 | 0 | 1 | | | | | | | | | |
| Rb | 0.11 | 0.529 | 0.501 | 1 | | | | | | | | |
| Zn | 0.358 | 0.58 | 0.452 | .863** | 1 | | | | | | | |
| Cu | -0.313 | 0.531 | 0.544 | 0.397 | 0.407 | 1 | | | | | | |
| Fe | -0.386 | 0.032 | .956** | 0.515 | 0.428 | .695* | 1 | | | | | |
| Ti | -0.455 | 0.242 | .743* | .640* | 0.554 | .689* | .851** | 1 | | | | |
| Ca | -0.335 | 0.184 | .860** | .665* | .634* | .695* | .928** | .963** | 1 | | | |
| K | -0.433 | 0.296 | .681* | .711* | 0.596 | .641* | .786** | .985** | .932** | 1 | | |
| Ba | 0.46 | -0.015 | -.941** | -0.499 | -0.388 | -.673* | -.992** | -.886** | -.934** | -.824** | 1 | |
| Nb | -0.403 | 0.154 | 0.471 | 0.258 | 0.009 | 0.217 | 0.389 | 0.286 | 0.265 | 0.329 | -0.419 | 1 |

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

CONCLUSION

In the farms, soil samples studied showed that most of the elements identified were heavy metals of environmental concern. The elements studied include: Mo, Zr, Sr, Rb, Zn, Cu, Fe, Ti, Ca, K, Ba, and Nb. Among these elements, only Fe was found to be enriched, while the remaining elements are depleted. The depletion showed by certain elements could be due to dilution if the elements had existed in highly soluble form, while the enrichment could be attributed to high sedimentations rates of the derivative complexes of the elements in solution.

Sr, Rb, V, Nb, Ca, K, Cr, Cu, Fe, Zn, and Ti showed absence of pollution while Zr was found moderate

The enrichment, contamination as well as high coefficient of variation could be as a result of the contamination from external sources of pollutants such as fertilizers from farmlands within the vicinity, pesticides, herbicides, or any other wastes capable of polluting the farmlands as a result of human activities. In next work concentration of heavy metals from onion and cabbage plantations will be considered vis á vis the determination of heavy metals intake.

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