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Silicon as a reference element for determining zinc enrichment and depletion in contaminated farming soils of Nigeria

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Abstract

Zinc (Zn) content was evaluated of the arable soils in the vicinity of mining and dumping sites in Nigeria. Its content the arable soils assayed by means of atomic absorption spectrophotometry (AAS) ranged from 48.3 to 280.4mg/kg. The enrichment factor (EF) calculated by using silicon as a crustal reference element fell within a range of 0.57 – 2.90. The mean values of the enrichment factor of 1.40 classified the soil as depletion to minimal enrichment with zinc. Anthropogenic activities contribute significantly to the level of zinc in the studied areas.

Keywords: Zinc, Arable soils, Enrichment, Depletion, Enrichment factor

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1. Introduction

Zinc is an essential plant micronutrient, indispensable to the proper growth of plants. Nearly 200 zinc – containing enzymes have been identified, including many dehydrogenases, aldolases, peptidases, polymerases and phosphatases, and hence, take part in the metabolism of carbohydrates, proteins, and phosphorus compounds; affect auxins synthesis, control ribosomes formation, affect the permeability of cell membrane; and increase plant resistance (O’Dell, 1984; Kobata-Pendias and Pendias, 1999). Zinc deficiency hinders plant growth, causes interveinal chlorosis and yellowing on young leaves, and reduces leaf size (Kabata-Pendias and Pendias, 1999). Soluble zinc forms are easily taken in by plants from soil, the extent of which depends on a plant type and prevailing soil conditions (soil pH and composition) (Dudka and Chlopecka, 1990; Rudd et al., 1988). Zinc is one of the most mobile elements in soil (Bergkvist et al., 1989; Tyler and McBride, 1982). The factors that affect its increase are weathering of matrix, wet and dry atmospheric precipitation, decomposition of living matter, and use of waste water in soil fertilization. At the same time, the enrichment processes are accompanied by leaching ones, which decreases zinc concentration in soil. The reduction may also result from its uptake by plants during a vegetation cycle (Goldschmidt, 1954). Although, many metals are essential, all metals are toxic at higher concentration, because they cause oxidative stress by formation of free radicals. Another reason why metals may be toxic is that they can replace essential metals in pigments or enzymes disrupting their functions. Thus, metals render the soil unsuitable for plant growth and destroy the biodiversity (Ghosh and Singh, 2005). The property of an element in soil (i.e., the evaluation of its accumulation or depletion) may be confirmed by collating contents of a trace element with a reference element (Kabata-Pendias and Pendias, 1999). The result obtained is described as an enrichment factor (EF), and the equation used to calculate it is as follows:

$$EF = \frac{C_n / C_{ref}}{B_n / B_{ref}}$$

In which C_n is content of the examined element in the soil, C_{ref} is content of the examined element in the Earth’s Crust, B_n is content of the reference element in the soil, and B_{ref} is content of the reference element in the Earth’s Crust. A reference element is “preservative” that is, the one that concentration in samples emanates almost only from the Earth’s Crust. The most commonly used reference elements in publications as noted by as noted by Özbaş (2011) are aluminum (Al), Zirconium (Zr), Iron (Fe), Scandium (Sc), and Titanium (Ti) (Blaser et al., 2000; Reimann and de Carital, 2000; Schiff and Weishberg 1999; Schropp et al., 1990) although there are also attempts at using other elements e.g., manganese (Mn) (Loska et al., 1979), Chromium (Cr) (McMurtry et al., 1995), and Lithium (Li) (Loring, 1990). Usually, the enrichment factor is used to evaluate soil contamination (enrichment), and its explanation is as follows (Sutherland, 2000):

EF < 2 – depletion to minimal enrichment

EF 2 < 5 – moderate enrichment

EF 5 < 20 – significant enrichment

EF $20 < 40$ – very high enrichment

EF > 40 – extremely high enrichment

Enrichment Factor can also be used to evaluate element depletion in soil (Blaser et al., 2000). All EF values less than one may indicate that leaching and consumption of an element take precedence over its accumulation in soil. This work is aimed to evaluate zinc enrichment and depletion of arable soil in the vicinity of mining and dumping sites, on the basis of enrichment factor. The samples tested were collected from farming soils in the vicinity of mining and dumping sites, in North-West, North-Central and South-East geopolitical zones of Nigeria. The results were expected to explain which processes, accumulation, or leaching is dominant in the area. The research also attempted to analyze the relationships between enrichment and depletion of the surface layer of soil and parameters such as soil pH and humus content.

2. Materials and methods

2.1. Locations of the research

The study areas are within latitude 4° and 14° North and longitude 3° and 15° East, Nigeria. These include:

- Yargalma farming soil, near local gold ore mining site in Bukkuyum, Zamfara State, North West, Nigeria.
- Dareta arable soil, near gold/lead ores mining site in Anka, Zamfara State, North West, Nigeria.
- Itakpe farming soil, near iron ore mining site in Okene, Kogi State, North Central, Nigeria.
- Ray Field Resort farming soil near tin ore mining site in Jos South, Plateau State, North Central, Nigeria.
- Udi farming soil, near coal mining site in Enugu East, Enugu State, South East, Nigeria.
- Chalawa arable soil in the vicinity of tannery waste dumping site in Kumbotso, Kano State, North West, Nigeria.
- Court Road farming soil, near general dumping site in Kumbotso, Kano State, North West, Nigeria. The dominant formations in the area are carboniferous deposits with layers from the Tertiary and Quaternary Periods. The predominant types of soils in the study areas are arenosols and ultisols. In small areas, histosols occur. The study areas are agricultural, industrial and mining communities. The farmland covers over 65% of the study areas. The farming activity in the study areas deals mainly with crop growing such as yam, cassava, maize, pepper, okra, leafy vegetables, cocoyam, rice, millet, guinea corn, tomatoes, carrot, lettuce and onions. The areas are dominated by extensive agriculture, industrial and mining activities.

2.1.1. Sample collection and analytical procedure

The surface soil layer to a depth of 0 – 20cm (ploughing layer) was sampled with a sharp edged plastic spatula and directly transferred the soil sample into labeled polyethylene homogenization container, and

mixed thoroughly to obtain a homogenous sample representative of the entire sampling interval. Each sample from equi-spaced sample station was a composite of 30 sub-samples from a distance of 20 meters per a sub-sample. When compositing was completed, the labeled homogenization polyethylene bags were closed tightly and returned same to the laboratory for pretreatment and analysis (Mason, 1983; Barth and Mason, 1984).

The farming soil samples were air dried under laboratory conditions for two weeks, ground, sieved through a 2-mm polyethylene sieve and dried to constant mass in an oven at 75°C, and kept in a desiccator for further analysis. 0.25g of the oven dried soil samples were weighed into platinum crucibles. The digestions were conducted with a mixture of 3cm³ of conc. HNO₃, 2cm² of conc. HF and 1cm³ of 40% H₂O₂ solution. The mixture was digested on a sandbath at a temperature of 200 – 230°C and the acids were evaporated to dryness. After the acids had been digested and evaporated, 20cm³ of 0.25MHNO₃ was added, warmed for 10 minutes and transferred and filtered into 50cm³ plastic container and filled to volume with the 0.25MHNO₃ solution. The digested soil samples, the reagent blank and standard solutions were analyzed using Atomic Absorption Spectrometer, model BULK Scientific UPG 210. The zinc content was calculated by using the straight line equation from the calibration curve plotted. Silica was determined gravimetrically by sodium carbonate fusion and silicon evaluated from the silica stoichiometrically. Soil pH was measured potentiometrically in 1MKCl with a soil/extractant ratio of 1:5 in three replicates per sample. The organic carbon was determined by Tiurin method. It was oxidized to carbon dioxide with potassium dichromate in the presence of conc. Sulphuric acid. The unreacted potassium dichromate was titrated with ammonium iron (ii) Sulphate. Considering that the average content of carbon in soil organic matter was equal to 58%, the conversion factor 1.724 was used to calculate the percentage of organic matter from the content of organic carbon.

When the enrichment factor was calculated, silicon was used as a reference element. Silicon is one of the main components of the earth's crust and its concentration in soil is connected mainly with the matrix. When the enrichment factor was calculated, C_{ref} and B_{ref} denoted Zn and Si concentrations in the earth's crust of 79mg/kg and 270000mg/kg, respectively (Taylor and McLennan, 1995).

3. Results

The studied areas include Figures 1-6. The pH of the soils (Figure 8) tested ranged from 4.1 – 8.1, indicating acidic, neutral and slightly alkaline. Humus content (Figure 9) ranged from 0.6% - 4.6%. Zinc distribution skewed towards high frequency of low concentration (Figure 7). It had a wide range of 48.3 – 280.4mg/kg, the highest number of values being found in 74 – 98mg/kg range. Zinc concentrations increased considerably with increasing humus content and vice versa. An increase in pH also affected significantly zinc increase.

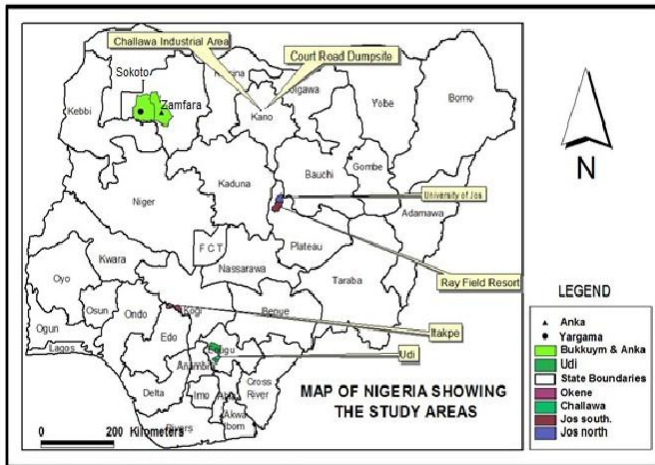


Figure 1. Map of Nigeria Showing the Study Areas

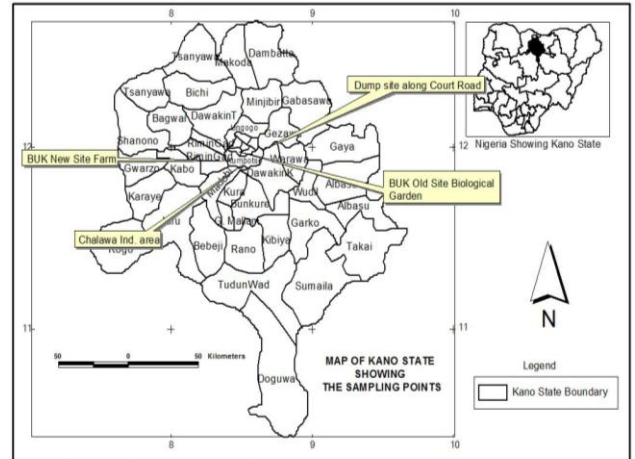


Figure 4. Map of Kano State Showing the Sampling Points

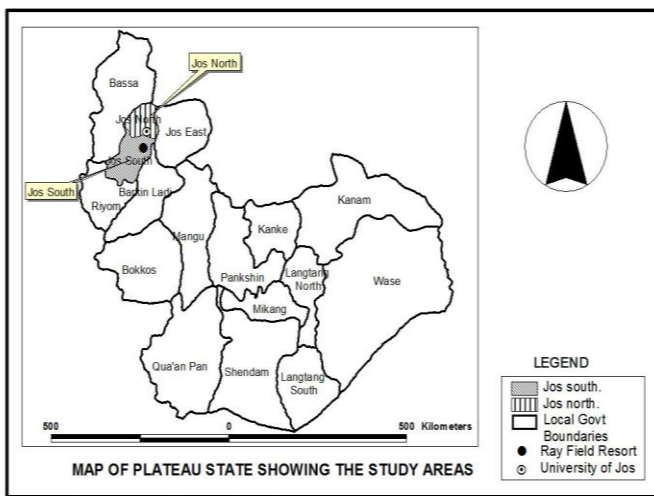


Figure 2. Map of Plateau State Showing the Study

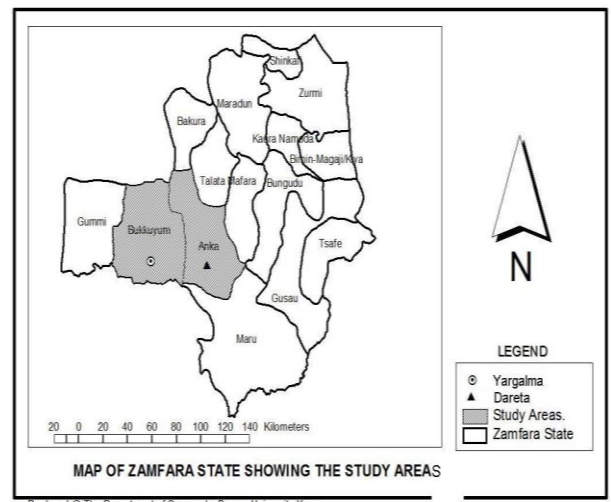


Figure 5. Map of Zamfara State and the Study Areas

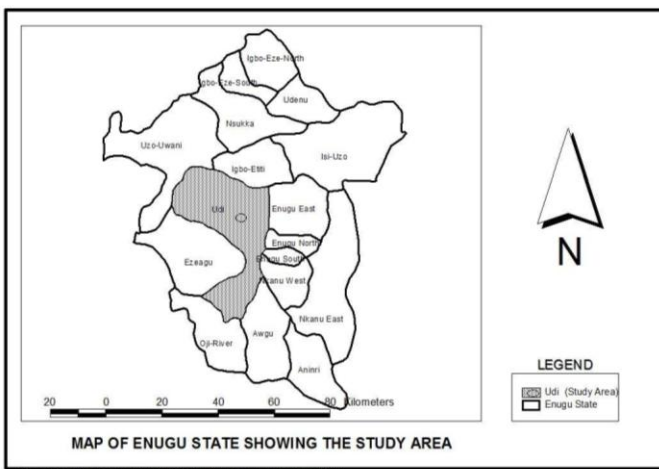


Figure 3. Map of Enugu State Showing the Study

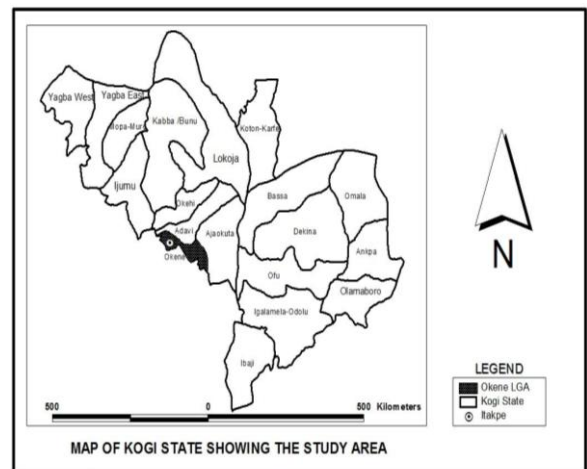


Figure 6. Map of Kogi State Showing the Study Area

The enrichment factors for the soil samples ranged over 0.57 – 2.90, indicating depletion to minimal enrichment. The mean enrichment factor of 1.40 classified the soil as depletion to minimal enrichment (Figure 10). There was zinc depletion in some of the soil samples evaluated.

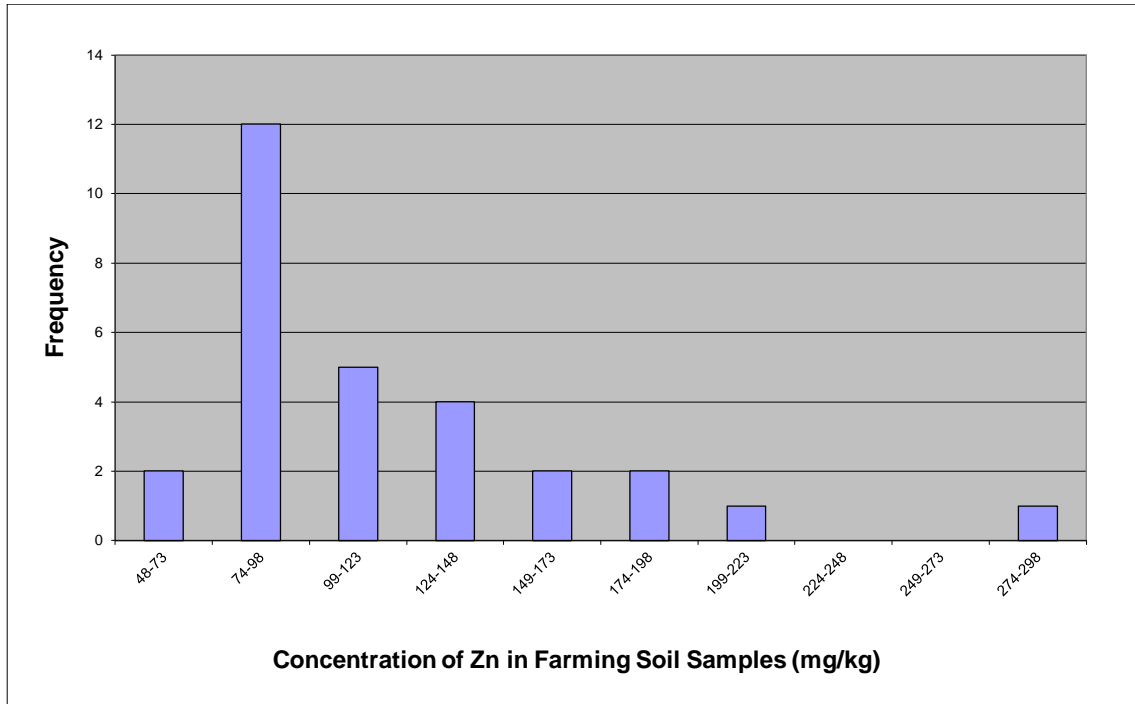


Figure 7. Frequency Distribution Pattern for Concentration of Zn in Farming Soil Samples

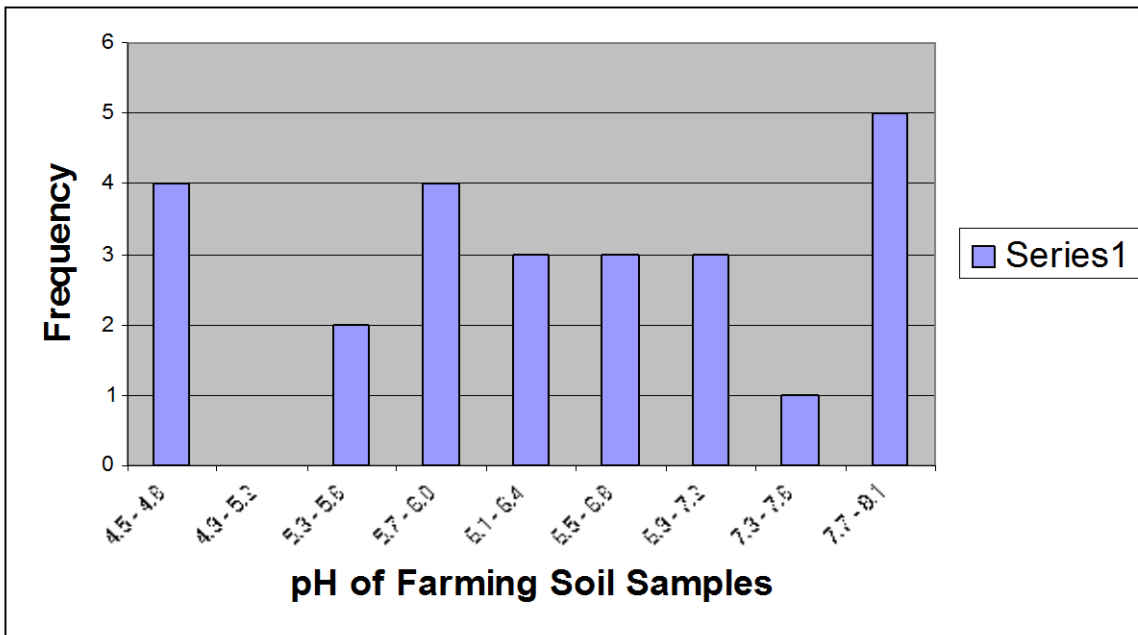


Figure 8. Distribution Pattern for pH in Farming Soil Samples

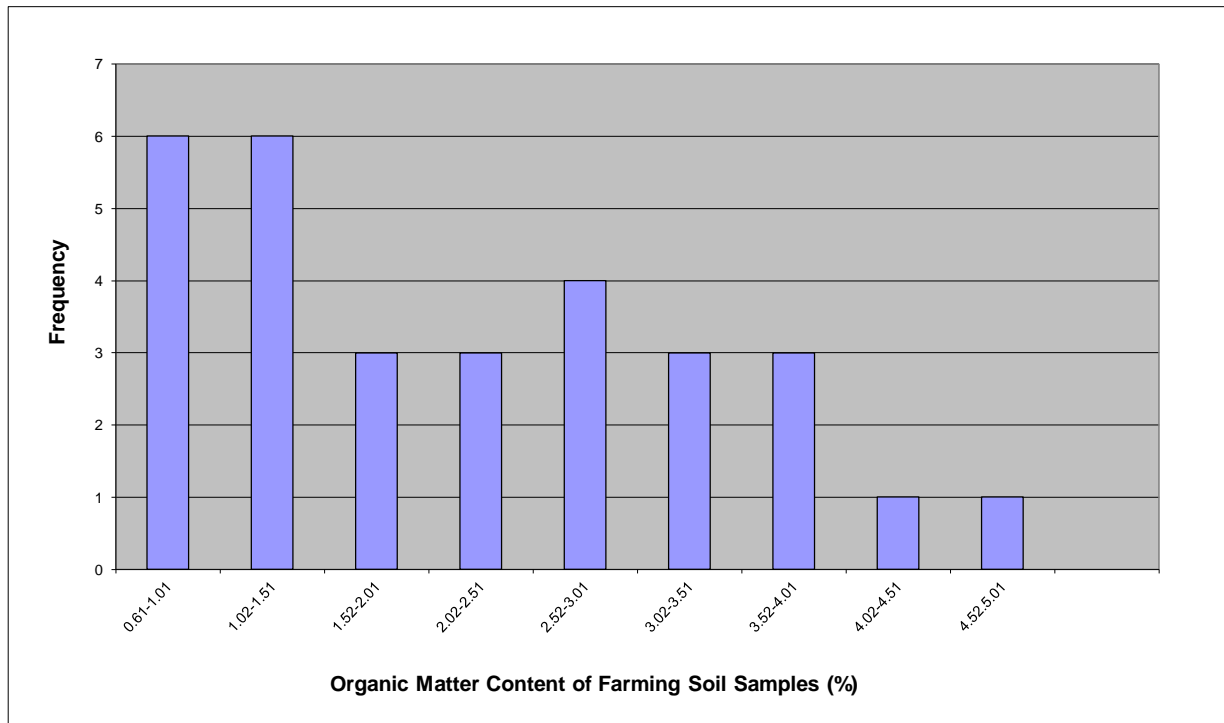


Figure 9. Frequency Distribution Pattern for Organic Matter Content of Farming Soil Samples

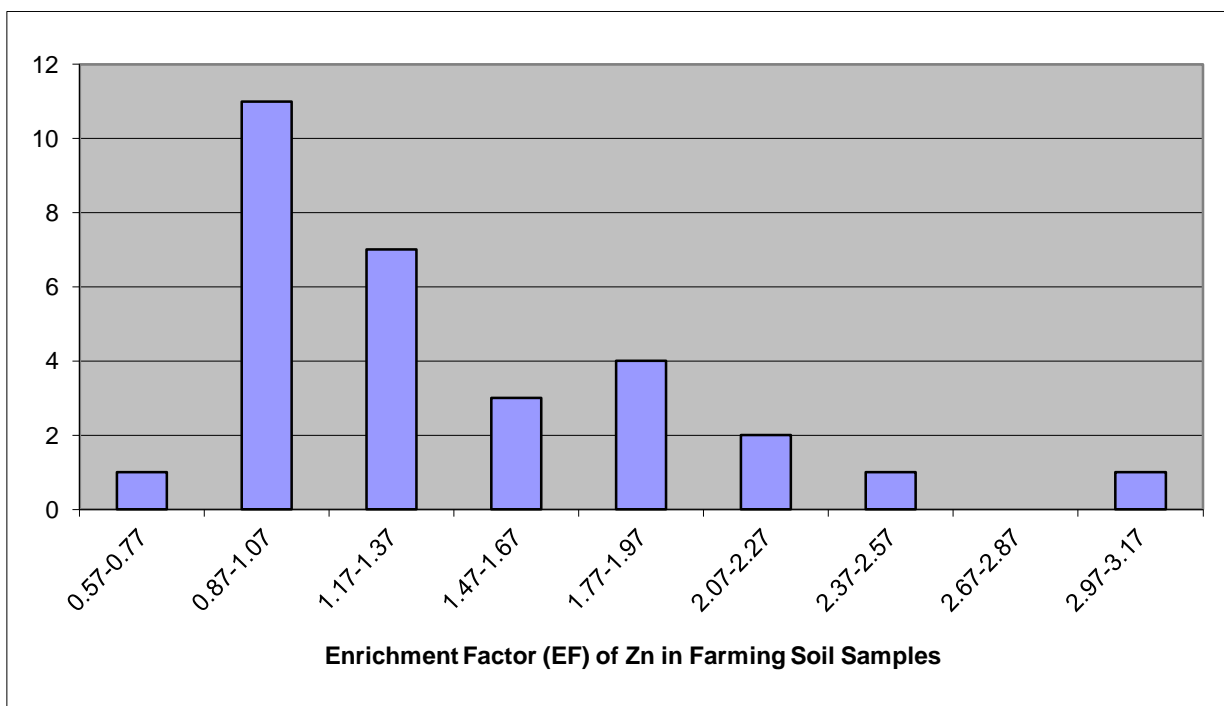


Figure 10. Frequency Distribution Pattern for Enrichment Factor of Zn in Farming Soil Samples, Using Si as a Crustal Reference Element

4. Discussion

The EFs obtained pointed to depletion to minimal enrichment. The mean enrichment factor of 1.40 classified the soil as depletion to minimal enrichment with zinc. The EFs obtained pointed to both zinc enrichment and depletion in arable soil. It was approximately 23% of the samples that contained the amount of zinc that may indicate depletion. This might have been caused by the fact that sampling took place at the end of vegetation season, in addition, the area consisted of farmland mainly characterized by intensive plant growth and consequently, increased demand for traced elements. The fact that most of the soils were acidic should also be taken into consideration. Zinc leaching in such soil is greater than alkaline soil (Kalbasi et al., 1978). Most of the farmers make extensive use of fertilizers, cow dungs and tannery sludge as soil amendment materials. Accumulation of zinc in soils takes place in the surface layers using organic matter (Kabata – Pendias and Pendias, 1999), which is composed of simple organic compounds and humus (i.e., large-molecular, dark-colored organic bonds). Humus, like simple organic compounds, readily accumulates metals, including zinc.

An increase in soil pH, on the other hand, results in an increase in EF. Thus, the increase in pH affects greatly zinc binding in soil and hinders its leaching. Humus content had a smaller effect on soil enrichment and depletion than pH. Nigeria is one of the countries in West Africa most exposed to desert dust because of its proximity to the main emission source area and its location with regard to the dominant winds (Rutherford et al., 1999). Studies have shown that harmattan dust which deposits on vegetations and farmland contains varying degrees of metal concentrations including zinc (Sunnu et al., 2008).

According to the Nigerian Federal Ministry of Environment (FME), there were 14 tanning industries around Challawa, one of the studied areas in Kano State by the year 2001, that discharge their liquid and solid wastes into the immediate environment (consisting of land and water bodies). Imamul Huq (1998), stated that different chemicals are employed during the soaking, tanning and post tanning activities of hides and skins. The major chemicals used are sodium sulphite and basic chromium sulphate and also non-ionic wetting agents, bactericides, soda ash, CaO, ammonium sulphide, ammonium chloride and enzymes. Also used are sodium bisulphate, sodium chlorite, NaCl, H₂SO₄, formic acid, sodium formate, sodium bicarbonate bicarbonate, vegetable tannins, syntans, resins, polyurethane, dyes, fat emulsions, pigments, binders, waxes, lacquers and formaldehyde. (Tudunwada, 2007). Several forms of processes and finishing solvents and ancillaries are used as well. It has been reported that only about 20% of the large number of chemicals used in the tanning process is absorbed by leather, the remaining is released as waste (UNIDO, 2005). Tanneries have been found to discharge not only Cr which is an intrinsic product of the tanning process but also enormous quantities of Zn, Mn, Cu and Pb, have been observed at the main waste disposal points surpassing the permissible level in soils (Imamul Huq, 1998). This anthropogenic activities, contribute significantly to the level of Zn in the studied area.

5. Conclusion

The soil is the sink for macro and micro nutrients including toxic trace metals and the enrichment level of Zn is varying depending on its contamination index and it is presumed that crops/plant uptake of Zn along with

other nutrients during its growth has effectively removed Zn metal from the soil. Heavy metals are generally more mobile at $\text{pH} < 7$ than at $\text{pH} > 7$ in other words, metal concentration in soil decreases with increasing acidity but increases with increasing salkalinity of the soil. Zn depletion in the studied areas due to its plant uptake is more of interest agriculturally because it is essentials plant micronutrient, indispensable to the proper growth of plants.

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