

Manganese as a Reference Element for the Assessment of Zinc Enrichment and Depletion in Selected 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 280.4 mg/kg. The Enrichment Factor (EF) calculated by using manganese as a crustal reference element fell within a range of 16.3-161.2. The mean values of the enrichment factor of 59.41 classified the soil as extremely high enrichment with zinc. Anthropogenic activities contribute significantly to the elevated level of zinc in the studied areas.

Keywords: Anthropogenic activities, arable soils, depletion, enrichment, enrichment factor, zinc

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 behavior of a given element in soil (i.e., the determination of its accumulation or leaching) may be established by comparing concentrations 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:

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

where,

C_n = Content of the examined element in the soil

C_{ref} = Content of the examined element in the Earth's Crust

B_n = Content of the reference element in the soil

B_{ref} = Content of the reference element in the Earth's Crust

A reference element is "conservative" (i.e., the one that content in samples originates almost exclusively from the Earth's Crust. The most common reference elements in the Literature are Aluminum (Al), Zirconium (Zr), Iron (Fe), Scandium (Sc) and Titanium (Ti) (Blaser *et al.*, 2000; Reimann and De Caritat, 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).

Generally, the enrichment factor is used to assess soil contamination (enrichment) and its interpretation is as follows:

- 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 (Sutherland, 2000)

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 study 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.

MATERIALS AND METHODS

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.
- Daretar 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.

Sample collection and analytical procedure: The surface soil layer to a depth of 0-20 cm (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-sapced sample station was a composite of 30 sub-samples from a distance of 20 m 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 2 weeks, ground, sieved through a 2-mm polyethylene sieve and dried to constant mass in an oven at 75°C and kept in a desicator for further analysis.

(0.25 g) of the oven dried soil samples were weighed into platinum crucibles. The digestions were conducted with a mixture of 3 cm³ of conc. HNO₃, 2 cm² of conc. HF and 1 cm³ of 40% H₂O₂ solution.

The mixture was digested on a sand bath at a temperature of 200-230°C and the acids were evaporated to dryness. After the acids had been digested and evaporated, 20 cm³ of 0.25 MHNO₃ was added, warmed for 10 min and transferred and filtered in to 50 cm³ plastic container and filled to volume with the 0.25 MHNO₃ 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.

Soil pH was measured potentiometrically in 1 MKCl 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, manganese was used as a reference element. Manganese 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 Mn concentrations in the earth's crust of 79 and 1100 mg/kg, respectively, (Taylor and McLennan, 1995).

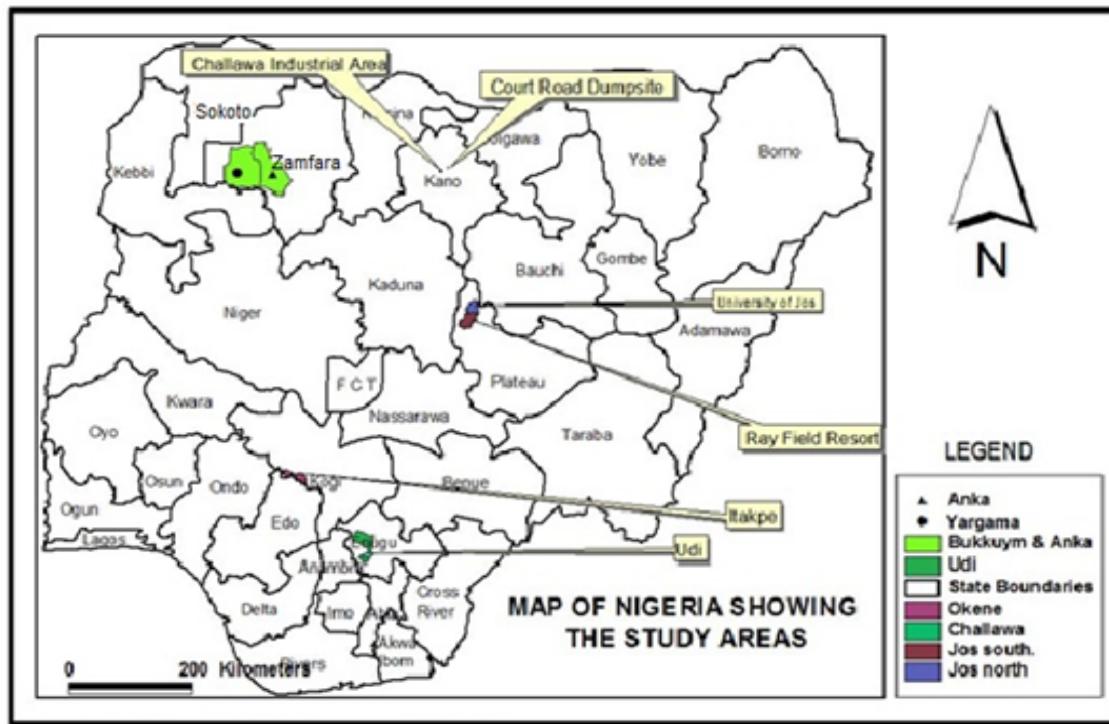


Fig. 1: Map of Nigeria showing the study areas

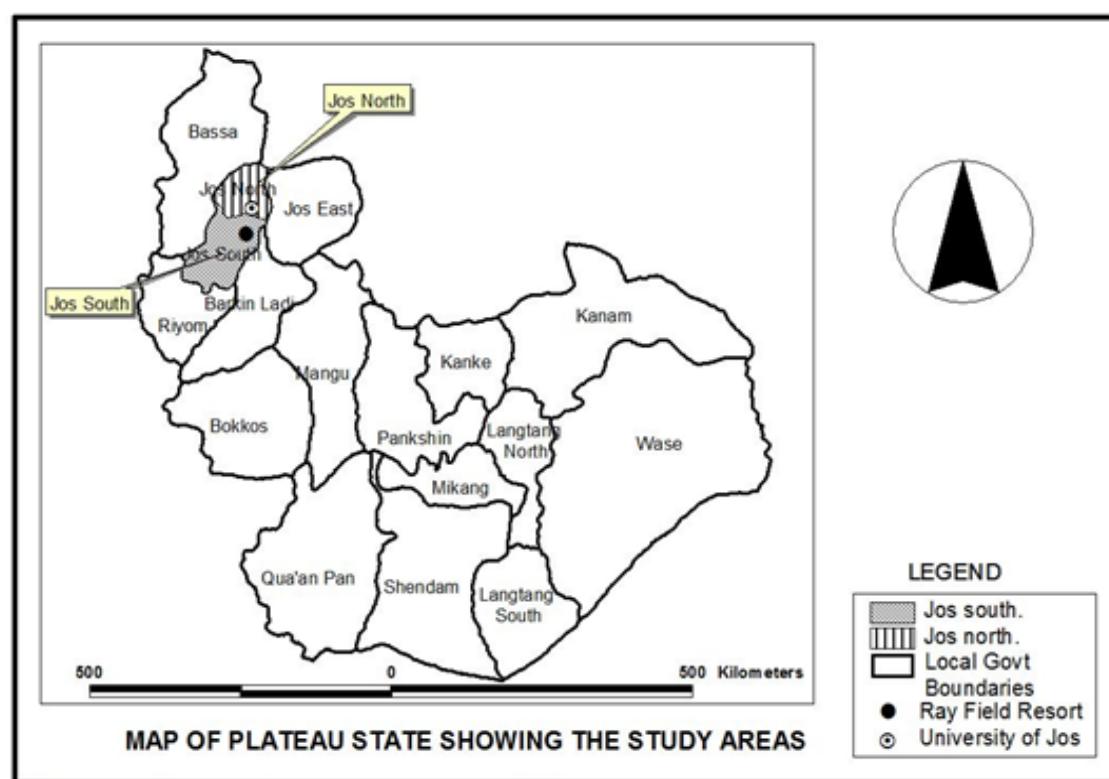


Fig. 2: Map of Plateau state showing the study areas

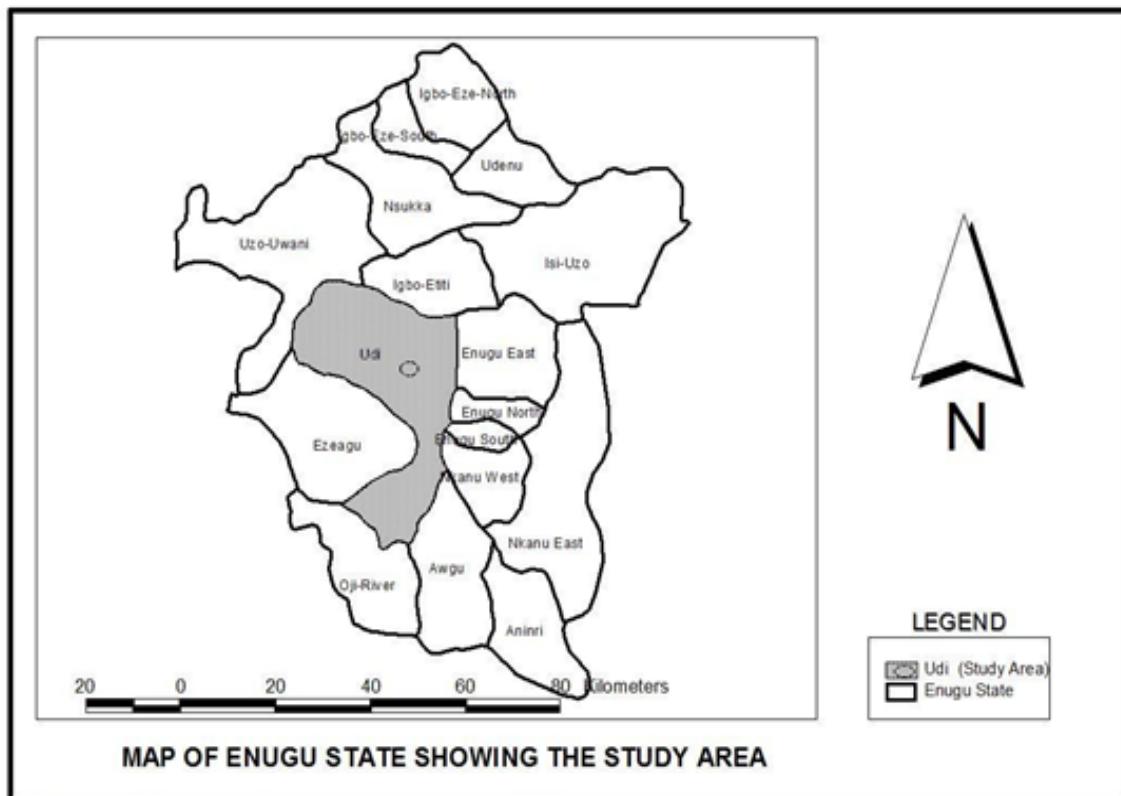


Fig. 3: Map of Enugu state showing the study areas

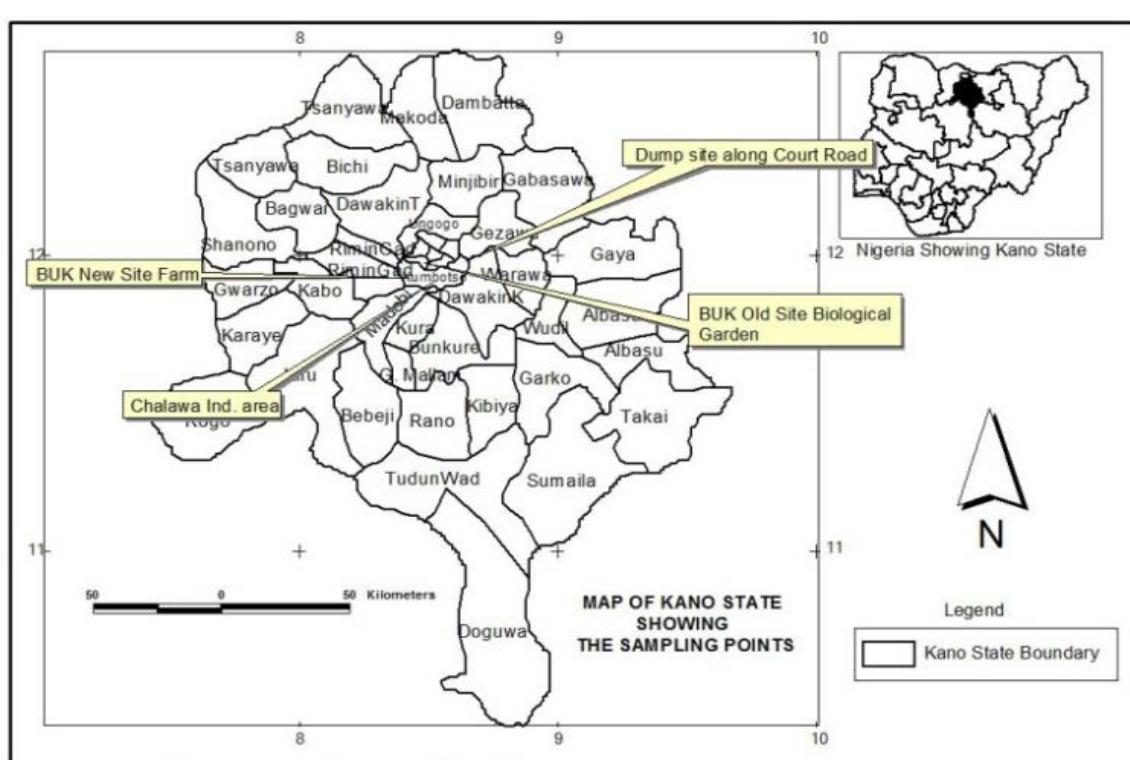


Fig. 4: Map of Kano state showing the sampling points

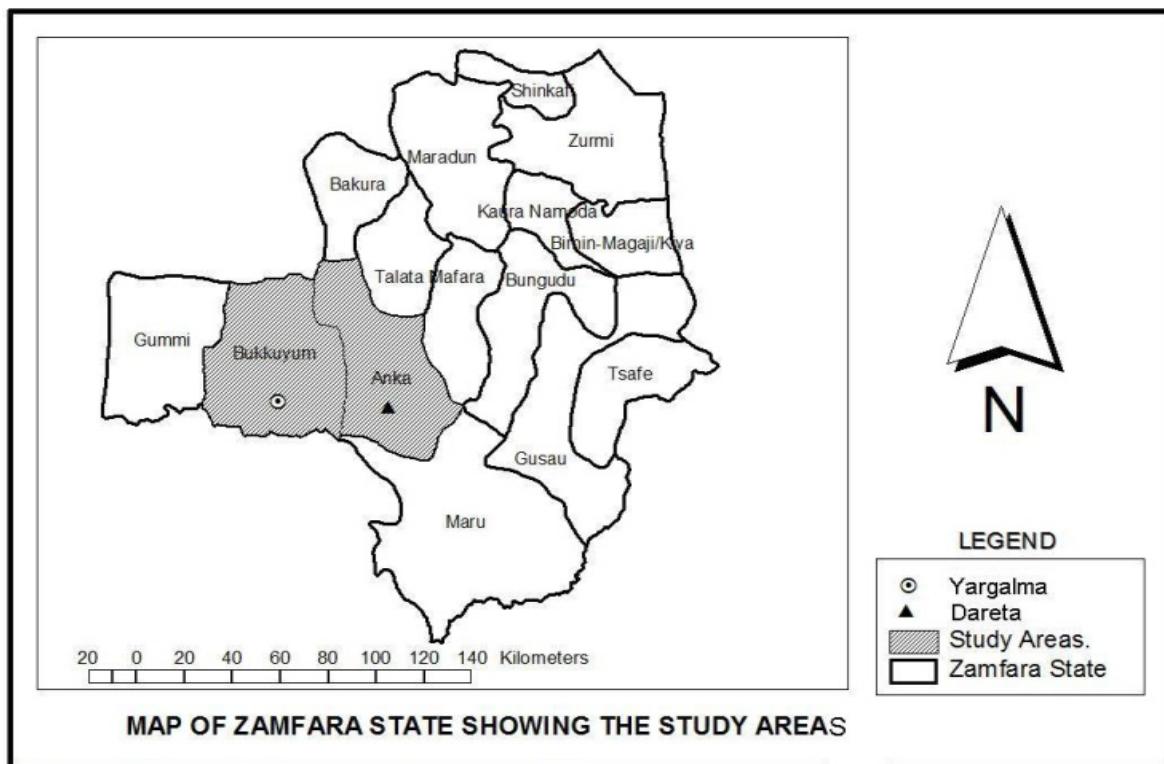


Fig. 5: Map of Zamfara state showing the study areas

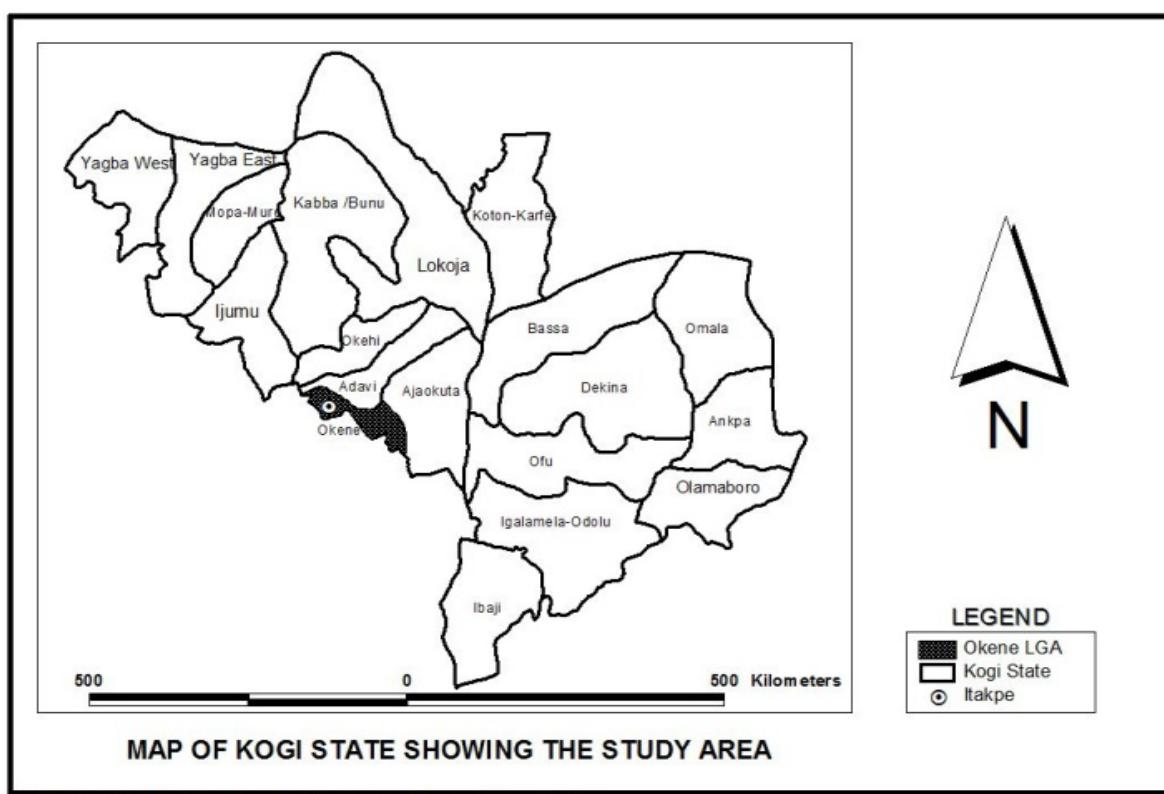


Fig. 6: Map of Kogi state showing the study area

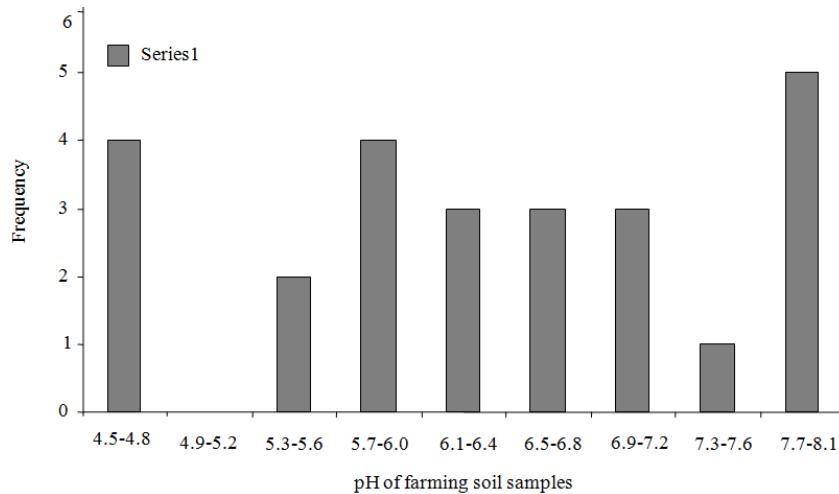


Fig. 7: Distribution pattern for pH in farming soil samples

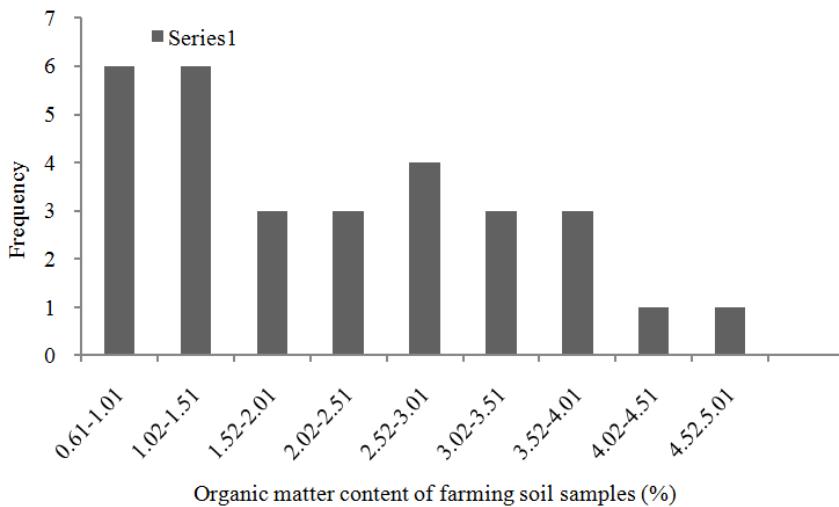


Fig. 8: Frequency distribution pattern for organic matter content of farming soil samples

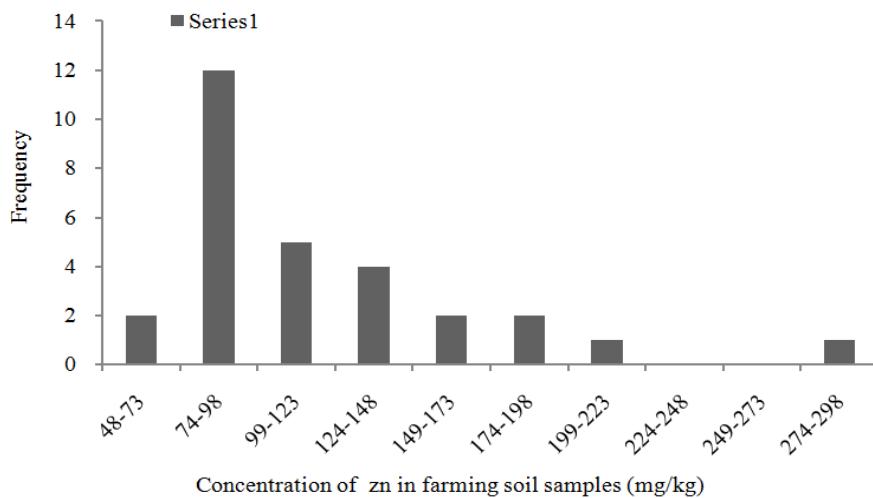


Fig. 9: Frequency distribution pattern for concentration of Zn in farming soil samples

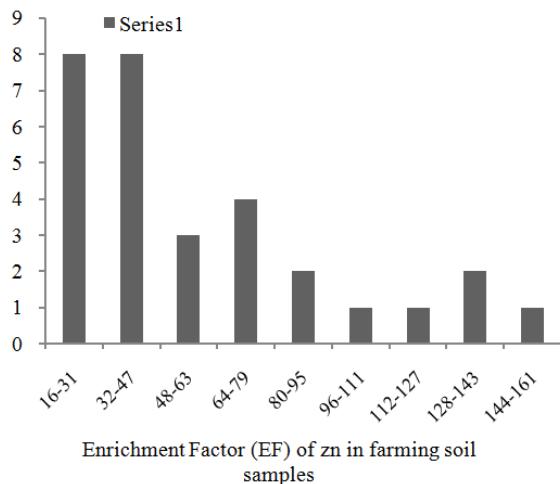


Fig. 10: Frequency distribution pattern for enrichment factor of Zn in farming soil samples, using Mn as a crustal reference element

RESULTS

The studied areas include Fig. 1 to 6. The pH of the soils (Fig. 7) tested ranged from 4.1-8.1, indicating acidic, neutral and slightly alkaline. Humus content (Fig. 8) ranged from 0.6-4.6%. Zinc distribution skewed towards high frequency of low concentration (Fig. 9). It had a wide range of 48.3-280.4 mg/kg, the biggest number of values being found in 74-98 mg/kg range. Zinc concentrations increased considerably with increasing humus content and vice versa. An increase in pH also affected significantly zinc increase. The enrichment factors for the soil samples ranged over 16.3-161.2, indicating very high to extremely high enrichment. The mean enrichment factor of 59.41 classified the soil as extremely high enrichment (Fig. 10). There was no zinc depletion in all the soil samples evaluated.

DISCUSSION

The EFs obtained pointed to very high to extremely high enrichment. The mean enrichment factor of 59.41 classified the soil as extremely high enrichment with zinc. The accumulation of zinc in these study areas is essentially due to anthropogenic influence. 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. The soils tested showed a distinct increase in zinc concentrations with increasing humus.

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 various chemicals are used during the soaking, tanning and post tanning processing of hides and skins. The main chemicals used include sodium sulphite and basic chromium sulphate including non-ionic wetting agents, bactericides, soda ash, CaO, ammonium sulphide, ammonium chloride and enzymes. Others are sodium bisulphite, sodium chlorite, NaCl, H₂SO₄, formic acid, sodium formate, sodium bicarbonate, vegetable tannins, syntans, resins, polyurethane, dyes, fat emulsions, pigments, binders, waxes, lacquers and formaldehyde. Various types of processes and finishing solvents and auxiliaries 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 rest is released as waste (UNIDO, 2005). Tanneries have been found to discharge not only Cr which is an inherent product of the tanning process but also significant amounts of Zn, Mn, Cu and Pb, have been observed at the main waste disposal points exceeding the toxic range in soils (Imamul Huq, 1998). This anthropogenic activities, contribute significantly to the elevated level of Zn in the studied area.

CONCLUSION

The locations of the studied zones in the anthropogenically affected areas are characterized by Zinc enrichment of all the tested soils and in all cases well exceeding even 100% (EF>2) against matrix. The dynamics of humus content, pH, prevailing environmental conditions and anthropogenic impacts, account for zinc accumulation in the studied areas.

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