A LEGACY OF LEADERSHIP: A SPECIAL ISSUE HONOURING THE TENURE OF OUR VICE CHANCELLOR, PROFESSOR ARMAYA'U HAMISU BICHI, *OON, FASN, FFS, FNSAP*

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ASSESSMENT OF TOXIC ELEMENT CONTAMINATION AND RISK IN SEDIMENTS NEAR A FERTILIZER PLANT IN KANKARA, NORTHWESTERN NIGERIA

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ABSTRACT

Potentially toxic elements (PTEs) are metallic chemicals with densities that are higher than that of water, its sediments are mainly from two sources, i.e., natural sources such as rock weathering and anthropogenic activities such as mining and agriculture. The composition and concentrations toxic element in sediments in the local fertilizer blending plant at Kankara Local Government Area, Katsina State. Determination of the concentration and elemental composition levels of sediment samples have been simplified by the use of reliable, multi-elemental techniques such as the instrumental neutron activation analysis (INAA) combined with high-resolution germanium gamma-ray spectrometry. A total of twenty-two (22) elements were determined from the six(6) samples of sediments collected. Five (5) of these elements are As, Co, Cr, V and Zn. The range and average values of the concentration are As (1.43 – 5.03mg/kg, 3.70mg/kg), Co (2.3 – 30.9mg/kg; 14.80 mg/kg), Cr (15.6 – 106 mg/kg, 56.18mg/kg), V (23 – 241mg/kg; 116.63 mg/kg) and Zn (24.5 – 130mg/kg, 78.93mg/kg). This study shows that the potentially toxic elements are not yet at elevated stage, except Co and V which were both above the permissible limit, while others are gradually reaching elevation and may be at a high risk of disease caused from toxic element exposure. Potential health risk is associated with accumulation of potentially toxic metals in tissues including Parkinson disease, arsenicosis, acrodynia, selenoises, Alzheimer's disease, hair loss, mental imbalance and abortion in women around in the areas. Alternative fertilizer blending techniques and sensitization on the potential health risk are highly advocated in these communities.

Keywords: Toxic element, Fertilizer, Concentration, Potential health risk, Sensitization

INTRODUCTION

It has been demonstrated that potentially hazardous metals from human and natural sources provide serious risks to our fragile ecology. Due to these metals' bioaccumulation, acute and chronic toxicity, and persistence, they can be hazardous to human health in a number of ways (Mclaughlin et al, 1999; MacDonald et al, 2000; Salmanighabeshi et al, 2015). As it has been documented, these dangerous substances actually enter the ecosystem through a variety of pathways. The majority of these pathways may be harmful to crops and animals, and humans may come into direct contact with them through ingestion, dermal absorption, or inhalation, or through food chains in particular (Sun et al, 2013). It has been noted that these contaminants are hazardous to human health even at very low concentrations. (Arora et al, 2008; Memon and Schr€oder, 2009), especially to the health of adolescents (Ljung et al, 2006; Poggio et al, 2009; Chabukdhara and Nema, 2013), by producing neurological system abnormalities like tremor and ataxia, as well as gastrointestinal illnesses, diarrhea, and stomatitis (USEPA, 1986; Singh et al, 2010).

Potentially hazardous metals have raised health concerns even in minute quantities because of their bioaccumulative nature (Qiu, 2015).

The Environmental Protection Agency has identified a number of these elements as priority contaminants that need to be controlled because they are non-biodegradable, such as arsenic (As), Cadmium (Cd), Chromium (Cr), Nickel (Ni), Lead (Pb), and Zinc (Zn) (Tóth et al. 2016).

As long as the physiochemical parameters of the sediments or the surrounding water remain constant, the majority of metals in aquatic systems, for instance, are accumulated and sequestered in the particulate phase in sediments (Martínez-Santos et al, 2015; Zhang et al, 2016). Sediments tend to release these metals into the aquatic media when certain conditions change, such as during remedial dredging, flood events, and benthic bioturbation (Wang et al, 2012; Perazacastro et al, 2016).

Nigeria has a vast amount of soil that is used for farming in all of its regions, and the quality of the soil that is cultivated is especially important. Because they are very mobile in the air and water, potentially toxic elements are transported in a variety of ways through the exchange of substances among ecosystems. The soil system provides resources, goods, and services to humanity as well; it should be mentioned (Berendse et al, 2015; Brevik et al, 2015; Decock et al, 2015; Smith et al, 2015). It is vital to study how societies affect soils because soils have been used to detect the deposition, accumulation, and distribution of heavy metals in various locations (Alirzayeva et al, 2006; Onder et al, 2007). Among these harmful human endeavours is pollution, about which more data and analysis are required (Mahmoud and El-Kader, 2015; Riding et al, 2015; Roy and Mcdonald, 2015; Wang et al, 2015).Several of the classes of potentially harmful metals have been the subject of in-depth discussions by academics. According to a number of academics (Nizami & Rehman, 2018 Ali et al., 2019), dangerous metals are the pollutants found in groundwater. Because of the potential health effects, these dangerous substances are categorized into four classes: Essential, Less toxic, Extremely poisonous, Non-essential. Contamination of both land and marine environments by various harmful metals has become one of the most problematic pollutions concerns due to the obvious severity, permanence, and eventual biomagnifications of hazardous metals in the body (Okoro et al, 2017; Emenike et al, 2022).

Studies on heavy metal pollution in some parts of Nigeria have been reported in the literature (Ahaneku and Sadiq, 2014; Opaluwa et al., 2012; Abdullateef et al, 2014; Orisakwe et al, 2012). However, there is a lack of documentation in the literature regarding the levels of potentially toxic elements in the sediments and the risk assessment of these elements in the local fertilizer blending plant in North Western Nigeria, specifically in Katsina State. These studies have evaluated in terms of their potential effects on soil quality and human health.

In the human environment, potentially toxic elements are widely distributed, naturally occurring substances that are usually formed through the weathering of parent materials. However, a range of human activities, such as the extraction and processing of minerals, the smelting and processing of metals, industrial emissions, the use of pesticides and fertilizers, irrigation of sewage, and air transportation, have resulted in a significant build-up of potentially toxic elements in the global environment recently, especially in soil and sediment environments (Lu et al, 2010; Chen et al, 2015). The two main sources of potentially toxic elements in the sediments are anthropogenic activities like mining, agriculture and natural sources like rock weathering. To the best of our knowledge no research of this kind has been conducted in Northwestern Nigeria and particularly in Katsina State which has become a major hub for local fertilizer blending..

The elemental composition of potentially toxic elements and their concentrations in sediments in the local fertilizer blending plant at Kankara Local Government Area, Katsina State North – West Nigeria using instrumental neutron activation analysis (INAA) was studied, to identify and quantify the total amount of each potentially harmful element found in the sediment samples; to look into the distribution and degree of contamination of these elements within the study area; and to calculate the risk to human health and the environment related to the mining of locally blended fertilizer within the study area.

Environmental monitoring and assessment are important in regulatory and advisory policy making for the safety of the public due to radiation exposure. Relevant studies have been carried out to assess the levels of concentration and radiations in Nigeria. Some of these studies are in areas of high background radiation (Umar, *et al.*, 2008) and those of economic interests like cement factories (Avwiri *etal*, 2011) and mining site (Jibiri and Agomuo, 2007). The study will also provide information to mining professionals and policy makers on the level of toxic elements pollution in Kankara. It have also provide useful database on heavy metals and their corresponding concentration in the study area, so that the populace can obtain a proper measures and protection against any form of pollution.

MATERIALS AND METHODS

This research, is limited to the measurement of potentially toxic of soil in Kankara fertilizer blending plants instrumental neutron activation analysis and risk assessment of incurring fatal effects due to exposure from this source. Sampling was limited to Kankara and nearby villages where the activities of fertilizer blending is taking place.

Geology and Geography of the study area

With a total area of roughly 1,462 km^2, Kankara local government is situated between latitudes 11"42'-11"51' N and longitudes 7"30' 0-7"39' E. With a population of roughly 245, 739, it is situated in the southern portion of Katsina, roughly 143 km south of the capital city. Refer to Figures 1 and plate 1. The majority of the people living in the Local Government are Fulani and Hausa people. Farming and animal raising are their primary jobs. Its borders are shared by Zamfara state to the west, Faskari LGA to the south, Danmusa LGA to the north, Musawa LGA to the east, and Malumfashi LGA to the south. The average yearly rainfall in the study area is between 800 and 1000 mm (Olofin, 1989).

There are two distinct seasons in the area. Two seasons: arid (Harmattan) and wet (summer). The harmattan winds, low temperatures, and relative humidity are the defining features of the harmattan season, which runs from November to March of the following year. Every year, there is a wet/summer season that lasts from April to October and is defined by rainfall—more than 90% of the total rainfall falls during this time. The shortest season, known as Hausa: Rani, is dry and warm and lasts from roughly the end of October to mid-November (Olofin, 1989).

During the harmattan, there is a significant drop in relative humidity. The daytime maximum temperature is approximately 33.1ºC, while the daytime minimum is approximately 19.2ºC. Because of the town's latitudinal location and distance from the sea, the climate is generally hot and dry for many months of the year (Mortimore, 1970). The primary economic activity in the study area, crop farming, is impacted by these climate-related factors.

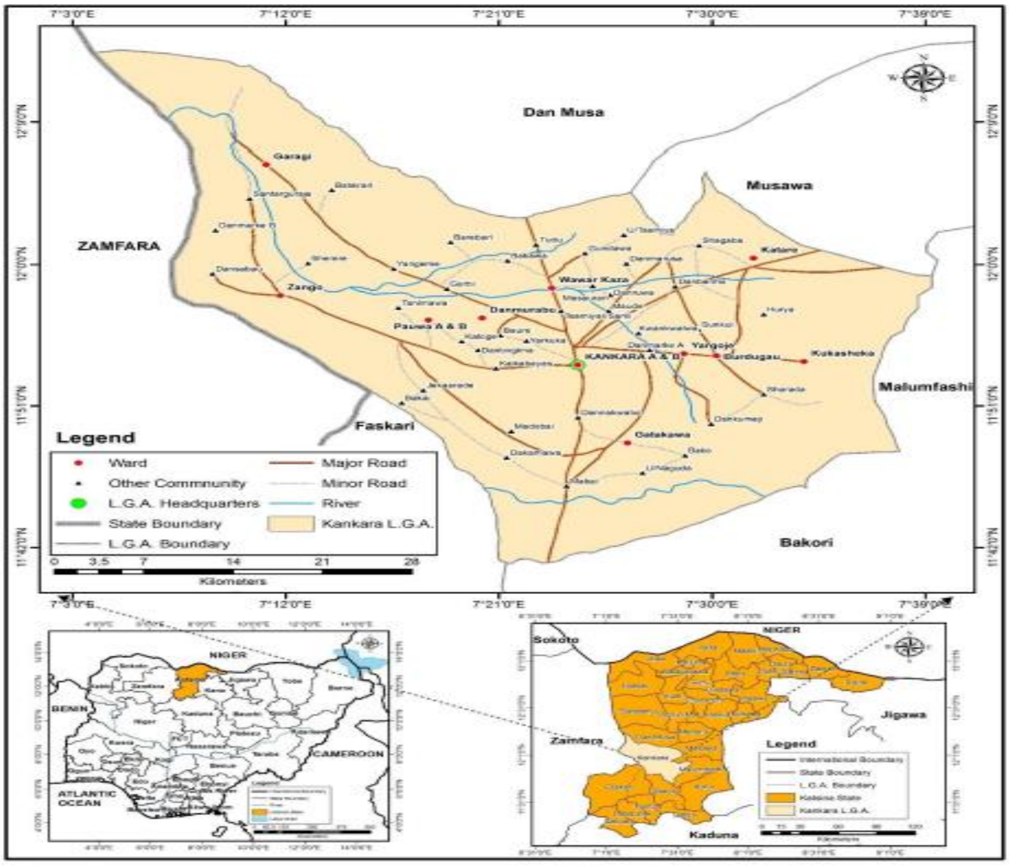

Figure 1: Map of Kankara Local Government
Source: Adapted from the administrative map of Katsina State (2014)

Plate 1: Google Map of the study area

Materials
The following materials are employed at different stages of sample collection: Small Shovel, Global Positioning System (Model: GPSMAP 78s), Ink Marker, Original Bic Biro, Polythene Bag, Exercise Book, Electronic Balance and Rubber container (cylindrical container of 7 by 7 diameter in dimension)

Sample Analysis procedure
For many years, an essential component of ecological and chemical research activities has been the elemental analysis of different samples (Adriano, 1992; Allen, 1974; Fiedler and Riisler, 1992; Iyengar, 1989; Lieth and Markert, 1988). Therefore, the chemical element analysis of these samples can be broken down into the following steps to ensure accurate

results: planning, representative sampling, sample preparation, instrumental measurement of the analytical signal, and data evaluation.

Sample Collection

Six (6) distinct study area locations provided the sediment samples (see figure 1). After that, they were well combined and put into labelled, spotless plastic containers so the laboratory could analyze them. The samples were first allowed to dry naturally at room temperature in a clean room, and then they were oven dried for six hours at 105ºC to constant weight (Inuwa et al, 2007). The representative sample was taken from the oven dried material, which was crushed and sieved through a 20μm plastic mesh (Inuwa et al, 2007; IITA, 1979).

Sample Preparation for INAA

For INAA irradiation, the samples were prepared at the NAA sample preparation laboratory section of Ahmadu Bello University in Zaria's Centre for Energy Research and Training (CERT). One hundred samples were ready for INAA's examination. Using a METTLER TOLEDO balance model AE 240, the samples were weighted and placed in a high-density polythene vial. A modern dryer was used to apply heat to double heat seal small pieces of cleaned polythene sheets containing the measured samples, which ranged in weight from 150.0 mg to 200.0 mg.

Superior Certified Reference Materials (CRMs) of NIST Montana Soil 2710, provided by the International Atomic Energy Agency (IAEA), Vienna, Austria, were prepared using the same methodology for quality control and verification purposes. C

Irradiation facility for INAA

The Nigeria Research Reactor-1 (NIRR-1) at the Centre for Energy Research and Training (CERT), Ahmadu Bello University Zaria, served as the irradiation facility for this study. In February 2004, the Miniature Neutron Source Reactor (MNSR) facility was put into service. Since NIRR-1 was created especially for neutron activation analysis (NAA), it can analyze trace, minor, and major elements in a variety of sample matrices (Jonah et al, 2006). Low enriched uranium (after conversion) is used as fuel in the low-power nuclear reactor NIRR-1 (Jonah et al, 2005, M S Anas et al, 2023).

The device used to measure radioactivity is a gamma-ray data acquisition system that includes a personal computer, related electronic modules manufactured by EG & G ORTEC, a horizontal dip-stick High-Purity Germanium (HPGe) detector with a relative efficiency of 10% at 1332.5keV gamma-ray line, and the MAESTRO emulation software (Jonah et al, 2006).

Procedure for Irradiation

Two processes are used in the irradiation, covering both long-lived and short-lived nuclides as described by Jonah et al. (2005). For the analysis of short-lived nuclides that require shorter irradiation times of one minute, polythene vials are placed in the larger $7cm^3$ rabbit capsules, a larger transport device that travels from the laboratory into the reactor by an air-driven pneumatic transport system into the outer irradiation channel B4, where the neutron spectrum is "soft." This is done to remove corrections due to nuclear interferences caused by threshold reactions, specifically Mg in the presence of Al; Al in the presence of Si; and Na in the presence of P (Jonah et al, 2006). This is so because the proximity of the inner channels of MNS reactors to the core leading to relatively higher ratio of fast-to-thermal neutrons.

For elements requiring longer irradiation times (i.e, long-lived activation products), samples wrapped in polythene films are packed in a stack inside the $7cm^3$ rabbit capsules and sealed for irradiation. The samples were irradiated for 6 hours at an average thermal neutron flux of $5 \times 10^{11} ncm^{-2}s^{-1}$ in the small irradiation channels A1, B2 and B3 of the same facility, taking the advantage of the maximum value of thermal neutron flux in this inner channel.

Upon placement of the samples in close proximity to the reactor core, the reactor's released neutrons interact with the atoms' nuclei, turning them into radioactive substances. This interaction forms elemental radioisotopes, which decay by releasing energy-dense gamma rays (γ-rays) that are distinct in their half-life. Each element has its own unique set of energy-signatures that are used to positively identify the targeted element(s) in the sample. The quantification of the element(s) is based on the ratio of intensity to concentration of the relevant element in the sample. Unlike electrons, which interact with the electron shell, neutrons interact with the atom's nucleus because they are chargeless and can pass through almost any material.

Counting and Analysis Schemes for NIRR-1

A semi-conductor detector, related electronics, and a computer-based multichannel analyzer make up the standard instrumentation used to measure gamma rays from radioactive samples (MCA computer). Hyper pure or intrinsic germanium (HpGe) detectors are high resolution gamma spectrometers used in the majority of NAA laboratories. They function at liquid nitrogen temperature (77 degrees Kelvin) by mounting germanium crystals in vacuum and connecting them to copper rods or "cold fingers" (plate 2). Sand holes in the ionization process are caused by gamma rays striking the detector. Using M.C.A., the detector divides the gamma rays into distinct channels based on their energy. Channel assignment for energy identification requires energy calibration.

Plate 2: HPGe Detector inside a liquid nitrogen Dewar

After returning from the radiation process, the first round of counting was carried out for 600 seconds for the brief radiations, which lasted one minute, and after the cooling period of two to fifteen minutes. The samples were set up on a 5 cm-geometric plexi-glass sample holder (H2). After waiting three to four hours and cooling for an additional 600 seconds, the second round of counting was conducted. The samples were set up this time on a plexi-glass sample holder (H1) that corresponded to a 2 cm source-detector geometry.

Using the holder H1, the first round of counting was carried out for long irradiations lasting six hours, following a decay period of four to five days, for 1800 seconds. Using the holder H1, all of the specimens were counted once more for 3600 seconds following a further decay period of 10–15 days. Jonah et al. (2006) state that the detector's dead time is controlled to be less than 5% by selecting the decay period and sample-detector geometry. A High-Purity Germanium (HPGe) detector with a relative efficiency of 10% at the 13332.5 keV gamma-ray line makes up the detection system utilized for the analysis

Table 1: Routine NIRR-1 irradiation and measuring regimes used for this work

Neutron Flux & Irradiation Channel	Procedure	Time Irradiated (T_{irr})	Decay Time (T_d)	Time measured (T_m)	Activation Products
2.5×10^{11} n/cm^{2}s Outer Irradiation Channel B4	S1	1 min	10 - 15 min	10 min	^{27}Mg, ^{28}Al, ^{49}Ca, ^{51}Ti, ^{52}V, ^{66}Cu
	S2		3 – 4 hrs	10 min	^{42}K, ^{56}Mn, ^{165}Dy
5×10^{11} n/cm^{2}s Inner Irradiation Channels A1, B2 & B3	L1	6 hrs	4 -5 days	30 min	^{24}Na, ^{72}Ga, ^{76}As, ^{82}Br, ^{122}Sb, ^{140}La, ^{153}Sm, ^{198}Au, ^{238}U
	L2		11 - 12 days	60 min	^{46}Sc, ^{51}Cr, ^{59}Fe, ^{60}Co, ^{65}Zn, ^{86}Rb, ^{131}Ba, ^{134}Cs, ^{141}Ce, ^{152}Eu, ^{160}Tb, ^{175}Yb, ^{177}Lu, ^{181}Hf, ^{182}Ta, ^{232}Th

Calculation of the concentrations of measured elements

The INAA (relative) method was employed to compute the elemental concentrations measured in the irradiated samples. The identification of gamma-ray of product radionuclides through their energies and quantitative analysis of their concentration was done using computer software for the INAA (relative) calculations available at the NAA laboratory, CERT, WINSPAN 2004.

Instrumental Neutron Activation Analysis (Relative) Method

The China Institute of Atomic Energy (CIAE) in Beijing, China developed the gamma-ray spectrum analysis software WINSPAN 2004 (Liyu, 2004), which was utilized for the quantitative analysis of concentrations and the identification of gamma-ray product radionuclides based on their energies. It is crucial and mandated that calibration factors for elements of interest be pre-determined by a multi-element standard reference material using adopted irradiation and counting regimes when using WINSPAN 2004 for NAA calculations. In addition to NAA calculations, WINSPAN 2004 can also be used for peak analysis, remote MCA control, and other auxiliary tasks like nuclear data generation and efficiency calibration nuclear data generation and efficiency calibration, for example.

Equation 1 and 2 respectively, provides the INAA (relative) equation that was utilized to determine the concentrations of the elements measured in the samples.

$$W_s = \frac{W_{st} N e^{\lambda td(s)}}{N_{st} e^{\lambda td(st)}} \qquad (1)$$

But $$C = \frac{W_s}{M} = \frac{M_{st} C_{st} e^{\lambda td(s)}}{M N_{st} e^{\lambda td(st)}} \qquad (2)$$

where;

C = concentrations of elements in the samples in $\mu g/g$

C_{st} = certified values of the concentrations of elements in the standard in $\mu g/g$

N= net photo peak area of radionuclide of interest in sample

N_{st}= net photo peak area of radionuclide of interest in standard

W_s= weight of unknown element in samples irradiated

W_{st}= $M_{st} C_{st}$ = known weight of the element in the amount standard irradiated

M = mass of the samples

M_{st} = mass of standards

$td(s)$ = decay time before counting of samples

$td(st)$ = decay time before counting of the standards

λ= decay constant for radionuclide of interest

Potential ecological risk assessment

In many studies on soil and sediment Heavy metals (HM), potential ecological risk assessment (RI) was used. The following are the calculation formulas:

$$Cf_i = {CD_i}/{CR_i} \qquad (3)$$

$$Er_i = Tr_i \times Cf_i \qquad (4)$$

$$RI = \sum_{i=1}^{m} Er_i \qquad (5)$$

The potential ecological risk index is called Eri; the toxic factor for HM is called Tri; the values for Cd, Pb, Cu, Cr, and Zn are 30, 5, 5, 2, and 1. The pollution factor is called Cfi; the measured concentration is called CDi; the reference value is called CRi; and the sum of all the indexes of the five HMs is called RI. Low possible ecological risk (Eri < 40), moderate potential ecological risk (40 Eri < 80), significant potential ecological risk (80 Eri < 160), high potential ecological risk (160 Eri < 320), and very high ecological risk (Eri 320) are the five categories of monomial moderate risk. Low ecological risk (RI < 150), moderate ecological risk (150 RI < 300), significant ecological risk (300 RI < 600), and very high ecological risk (RI < 600) are the four categories of RI values (Hakanson, 1980).

Potential health risk assessment

Hazard quotient (HQ), a ratio of an exposure level (oral soil ingestion/dermal) over a given time period with a reference dose (RfD) for a comparable exposure period, was used to assess the potential long-term effects (USEPA, 2002). A hazard index (HI) approach equal to the sum of all HQs has been introduced to evaluate the total potential chronic effects posed by multiple pollutants (USEPA, 1992, 2003). The following are the formulas for HQ, HI, and the average daily dose (ADD):

$$ADD = \frac{C \times IR \times EF \times ED}{BW \times AT} \qquad (6)$$

$$HQ_i = \frac{ADD}{RfD_i} \qquad (7)$$

$$\mathrm{H}I = \sum_{i=1}^{n} HQ_i \qquad (8)$$

Where, C is the soil's measured heavy metals HM concentration. The recommended soil ingestion rate (IR) for adults is 100 mg d^{-1} and for children is 200 mg d^{-1} (USEPA, 2011). The term "BW" stands for "average body weight," which is defined as 15 kg for children and 70 kg for adults (Lee et al, 1994; Leung et al, 2008). It is advised that the exposure frequencies (EF), exposure durations (ED), and average times (AT) be 365 d, 30 d and 2190 d. For Cd, Cr, Cu, Pb, and Zn, the RfD is 0.001, 0.003, 0.04, 0.0035, and 0.3 mg (d kg1) (Leung et al, 2008; USEPA, 2014).

Adverse health effects should be considered cautiously if HQ or HI >1, whereas HQ or HI<1 suggested that no severe adverse effects to human health (USEPA, 1989; Leung et al, 2008).

The carcinogenic and non-carcinogenic health risks associated with the dermal absorption of the contaminated with toxic heavy metals were assessed using hazard quotient (HQ), Hazard index (HI) and carcinogenic health risk (CR)

Table 2: Health risk assessment standard ranges and risk grade

Risk grades	Ranges of risk value	Acceptability
Grade I (Extremely low risk)	$< 10^{-4}$	Completely acceptable
Grade II Low risk)	$(10^{-6}$ to 10^{-5}	Not willing to care about risk
Grade III (Low-medium risk)	10^{-5} to 5×10^{-5}	Do not mind about the risk
Grade IV (Medium risk)	5×10^{-5} to 10^{-4}	Care about the risk
Grade V (Medium–high)	10^{-4} to 5×10^{-4}	Care about the risk and willing to invest
Grade VI (High risk)	5×10^{-4} to 10^{-3}	Pay attention to the risk and take action to solve it
Grade VII (Extremely high risk)	$> 10^{-3}$	Reject the risk and must solve it

RESULTS AND DISCUSSION

Results

Quality Assurance and Quality Control

Quality assurance is the proactive process of lowering the possibility of errors in an analytical technique. It also entails quality control, which is the process, used to look for issues following the conclusion of the analysis. Every stage of the neutron activation analysis process is thoroughly covered, including test portion preparation, analytical protocol selection, calibration, instrument performance checks, irradiation, decay, measurement, spectrum analysis and interpretation, internal and external quality control, and protocols for guaranteeing the technical competence of the personnel involved. Two CRMs were used in this investigation for quality control in INAA determinations: NIST 1515 for apple leaves and NIST 1547 for peach leaves (Tables 3 and 4).

To evaluate the lab performance, we computed the relative bias (RB), Z-score, and U-score. These measurements were computed using the subsequent formulas:

$$\text{U-score} = \frac{|X_{Lab} - X_{Ref}|}{\sqrt{\mu_{Lab}^2 + \sigma_{Ref}^2}} \qquad (9)$$

$$\text{Z-score} = \frac{|X_{Lab} - X_{Ref}|}{\mu_{Lab}} \qquad 10)$$

$$\text{R-bias} = \frac{X_{Lab} - X_{Ref}}{X_{Ref}} \times 100 \qquad (11)$$

Where XRef stands for recommended uncertainty,
σRef for standard uncertainty,
µLAB for standard deviation, and
XLAB for laboratory results.

The laboratory performance is assessed in the following ways: it is considered satisfactory if the U-score is less than 1, questionable if the Z-score is between two and three, and unsatisfactory if the Z-score is greater than three.

Table 3: Comparison of recorded values with the certified values in the certified reference materials of NIST 1515 (apple leaves)

Elements mg/kg	NIST 1515 Certified Values	NIST 1515 Recorded Values	U-score	Z-score	R-bias
K	1.61±0.02	1.433±1.19	0.15	8.85	10.99
Al	286±9	300.3±17.3	0.73	1.59	5
Ba	49±2	53.9±7.3	0.65	2.45	9.6
Cl	579±23	573.21±23.9	0.18	0.25	-1
Mn	54±3	57.24±7.7	0.39	1.08	6
Br	1.8	1.49±1.2	0.26	-	-17.2
La	20	27.6±5.3	1.43	-	38
Sm	3	4.38±2.09	0.66	-	46

Values represent mean ± standard deviation

Table 4: Comparison of recorded values with the certified values in the certified reference materials of NIST 1547 (peach leaves)

Elements mg/kg	**NIST 1547 Certified Values**	**NIST 1547 This work measured values**	**U-score**	**Z-score**	**R-bias**
K	2.43±0.03	2.6487±1.6	0.14	7.3	9
Al	249±8	257±16.03	0.45	1	3.21
Ba	124±4	136.4±11.8	1	3.1	10
Cl	360±19	284.4±16.9	2.97	3.9	-21
Mn	98±3	104.86±10.24	0.64	2.3	7
Br	11	10.45±3.2	0.17	-	-5
La	9	9.36±3.1	0.12	-	4
Sm	1	1.09±1.04	0.09	-	9

Values represent mean ± standard deviation

Following the use of two CRMs, NIST 1515 and NIST 1547, the illustrated results in tables (3 and 4) demonstrate that all element concentrations are in good agreement with the certified values. This computation revealed an excellent outcome that could be obtained by statistical assessment and evaluation in this practice. The calculated U-score and Relative bias statistics for every element are acceptable; however, the Z-score indicates dissatisfaction with certain element concentrations.

Results of the elemental composition and concentrations in the Samples

The present study examines the elements and their concentrations in six (6) distinct sediment samples that were collected from different locations of Kankara local fertilizer blending plants and the environs of Katsina State, North-West Nigeria, and analyzed using the INAA technique. The twenty-two elements that were determined in total are listed in Table 4.3: Magnesium (Mg), aluminum (Al), calcium (Ca), titanium (Ti), vanadium (V), manganese (Mn), dysprosium (Dy), sodium (Na), potassium (K), arsenic (As), chromium (Cr), bromine (Br), lanthanum (La), samarium (Sm), holmium (Ho), uranium (U), iron (Fe), cobolt (Co), zinc (Zn), rubidium (Rb), barium (Ba), europium (Eu), and thorium (Th). These components can all be categorized as ultra-trace, micro, or macro elements (major, minor, or both).They might also be poisonous or not. If these inorganic elements or minerals are present in a tolerable level, all forms of living matter will require them for their regular life processes, according to Hays and Swenson (1985) and Ozcan (2003)

Table 5: Concentrations of various elements in the sediments investigated by INAA (relative) (in mg/kg, unless otherwise stated)

ELEMENT	**SS 1**	**SS 2**	**SS 3**	**SS 4**	**SS 5**	**SS 6**
Mg	12970 ± 623	11090 ± 521	9583 ± 652	2155 ± 308	5388 ± 507	1243 ± 261
Al	93120 ± 1024	90910 ± 818	86190 ± 690	33850 ± 745	92160 ± 645	12630 ± 240
Ti	11090 ± 543	8987 ± 440	8647 ± 493	3267 ± 330	10270 ± 431	1506 ± 203
V	241 ± 7	118 ± 5	123 ± 5	41.8 ± 3.85	153 ± 5	23.0 ± 1.8
Mn	712 ± 3	575 ± 3	2615 ± 16	221 ± 2	366 ± 3	240 ± 2
Dy	6.53 ± 0.29	7.15 ± 0.26	6.65 ± 0.42	2.44 ± 0.17	5.00 ± 0.3	0.88 ± 0.13
Na	1094 ± 2	899 ± 20	1124 ± 1	314 ± 12	226 ± 10	557 ± 2
K	16720 ± 75	15860 ± 381	20460 ± 243	9742 ± 1159	7609 ± 1034	9249 ± 1627
As	4.93 ± 0.33	5.03 ± 0.40	4.04 ± 0.43	1.87 ± 0.25	1.43 ± 0.23	4.91 ± 0.34
Br	0.75	1.94 ± 0.36	2.46 ± 0.32	BDL	0.45 ± 0.13	BDL
La	37.0 ± 1.9	48.8 ± 3.1	52.0 ± 3.32	14.6 ± 0.3	4.00 ± 0.12	16.8 ± 0.2
Sm	6.07 ± 0.02	7.75 ± 0.04	8.36 ± 0.04	2.14 ± 0.24	0.76 ± 0.02	2.52 ± 0.02
U	1.90 ± 018	2.53 ± 0.28	2.97 ± 0.23	0.78 ± 0.12	0.99 ± 0.12	1.25 ± 0.16
Sc	31.3 ± 0.2	16.1 ± 0.1	17.4 ± 0.1	3.92 ± 0.05	4.40 ± 0.06	5.98 ± 0.07
Cr	106 ± 4	82.7 ± 3.2	86.1 ± 3.3	17.4 ± 1.9	15.6 ± 1.6	29.3 ± 2.3
Fe	80220 ± 642	61500 ± 554	60400 ± 554	17600 ± 281	6420 ± 180	24400 ± 318
Co	23.1 ± 0.4	19.6 ± 0.4	30.9 ± 0.5	5.10 ± 0.21	2.30 ± 0.16	7.78 ± 0.26
Zn	119 ± 14	130 ± 13	102 ± 11	25.8 ± 7.0	24.5 ± 5.6	72.3 ± 7/4
Rb	91.1 ± 8.2	115 ± 7	138 ± 10	40.1 ± 4.3	19.8 ± 3.6	71.5 ± 5.4
Ba	497 ± 41	890 ± 42	828 ± 54	183 ± 24	269 ± 26	300 ± 26
Eu	1.36 ± 0.11	1.65 ± 0.11	1.13 ± 0.21	0.56 ± 0.06	0.42 ± 0.05	0.62 ± 0.08
Hf	11.7 ± 0.4	13.7 ± 0.4	15.6 ± 0.4	2.57 ± 0.19	1.74 ± 0.15	4.44 ± 0.21
Th	9.46 ± 0.25	12.2 ± 0.2	16.0 ± 0.3	2.77 ± 0.13	2.53 ± 0.12	4.52 ± 0.10

BDL – Below Detection Limit

In all the samples, five (5) potentially harmful elements were measured. They consist of Zn, V, As, Co, and Cr. The following are the concentration range and average values for these elements: 1.43 – 5.03 mg/kg, 3.70 mg/kg of As, 2.3 – 30.9 mg/kg, 14.80 mg/kg of Co, 15.6 – 106 mg/kg 56.18 mg/kg of Cr, 23 mg/kg-241mg/kg V and 23 – 241 mg/kg of 116.63 mg/kg of Zn are among the substances. The distribution of As, Co, Cr, V, and Zn concentrations (mg/kg) in the sediment samples from Kankara is depicted in Figure 2, with vanadium having the highest concentration.

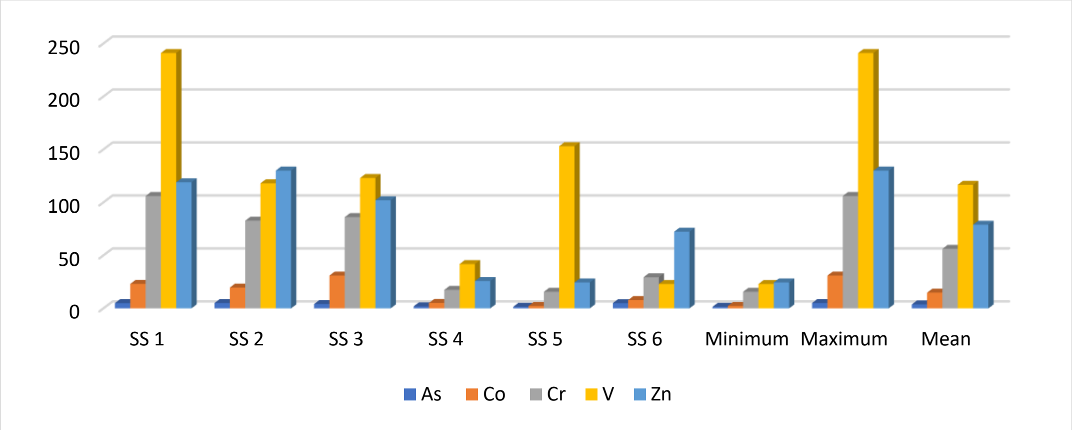

Figure 2: The distribution of the concentrations of As, Co, Cr, V and Zn (mg/kg) in the sediment samples from Kankara

Discussion of Toxic Elements

The table below shows the distribution of potential toxic element in the sediment of fertilizer bleeding plant in Kankara local government.

Table 6: Concentrations of potentially toxic elements in the sediments investigated by INAA (relative) (in mg/kg)

ELEMENT	SS 1	SS 2	SS 3	SS 4	SS 5	SS 6	Average	Permissible limit
As	4.93 ± 0.33	5.03 ± 0.40	4.04 ± 0.43	1.87 ± 0.25	1.43 ± 0.23	4.91 ± 0.34	3.70	20.0
V	241 ± 7	118 ± 5	123 ± 5	41.8 ± 3.85	153 ± 5	23.0 ± 1.8	116.5	100.00
Cr	106 ± 4	82.7 ± 3.2	86.1 ± 3.3	17.4 ± 1.9	15.6 ± 1.6	29.3 ± 2.3	56.1	100.00
Co	23.1 ± 0.4	19.6 ± 0.4	30.9 ± 0.5	5.10 ± 0.21	2.30 ± 0.16	7.78 ± 0.26	14.78	5.0
Zn	119 ± 14	130 ± 13	102 ± 11	25.8 ± 7.0	24.5 ± 5.6	72.3 ± 7/4	78.33	80.00

Arsenic

Group 1 carcinogen arsenic (As) is found naturally in rocks and soils and is regarded as one of the most important environmental toxicants in the world (Müller et al, 2022; Rokonuzzaman et al, 2022). It is extremely rare to find as a pure element, despite the fact that it is commonly found as a component of minerals. Generally speaking, the amounts of arsenic in food reflect natural environmental buildup (Roychowdhury, 2008). Both man-made activities and natural geologic processes have resulted in arsenic contaminations. Arsenic comes from anthropogenic sources, which include human activities like ore processing and mining. The concentration of arsenic (As) (Figure 4.2) is below the allowable limit established by the European Community (EC), according to our current results. The European Community (EC) states that a high concentration of arsenic is toxic to plants and will gradually lower crop yields (FAO, 2006; Kabata-Pendias & Pendias; Rahman et al, 2007). The maximum allowable limit of arsenic for agricultural soils is 20 mg/kg.

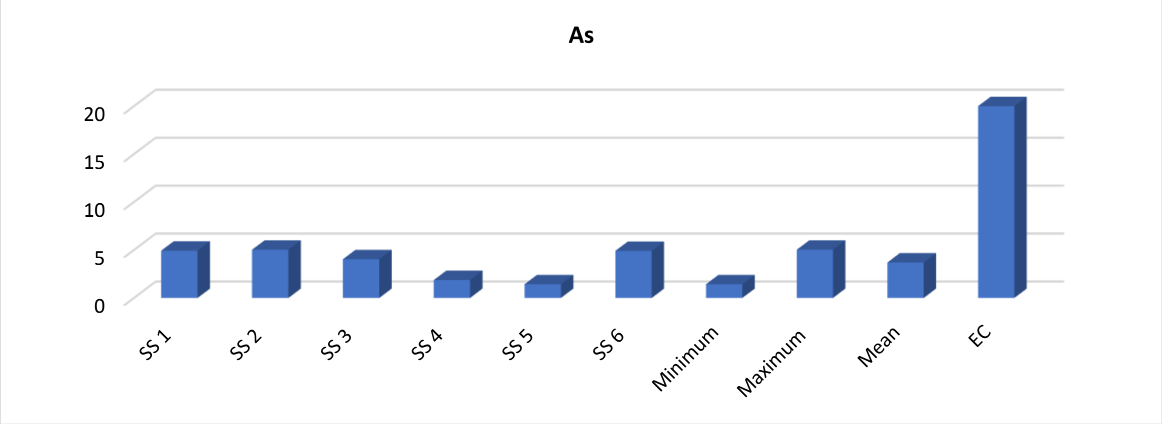

Figure 3: The distribution of the concentrations of As (mg/kg) in the sediment samples from the study area

Arsenic is found in ores that contain metals like copper and lead; it is also found in volcanic eruptions ATSDR (2007). Widespread in the earth's crust, arsenic is frequently found as sulfides, metal arsenides, or arsenates.

Exposure to arsenic has numerous detrimental effects on human health. Exposure to arsenic affects almost every system in the human body, but it most severely affects the cardiovascular, neurological, hepatic, renal, hematological, endocrine, respiratory, and reproductive systems (Rahman et al, 2018; Rahaman et al, 2021; Shaji et al, 2021). Furthermore, a compromised immune system, a lower IQ, neurotoxicity, delayed child growth, spontaneous abortion, stillbirth, preterm birth, low birth weight, and neurodevelopmental impairment are all increased risks associated with As exposure during pregnancy (Vahter, 2008). Amputation due to gangrene and skin conditions like keratosis are +among the symptoms of chronic poisoning.

Lower exposure levels to arsenic can result in blood vessel damage, prickling sensations in the hands and legs, reduced erythrocyte and leukocyte production, nausea, and vomiting. Skin lesions, internal cancers, neurological issues, pulmonary disease, peripheral vascular disease, hypertension, cardiovascular disease, and diabetes mellitus can all result from prolonged exposure. Smith and others (2000). Additional side effects could include a decrease in red and white blood cell production, which could lead to exhaustion, an irregular heartbeat, blood vessel damage that could result in bruises, and a decline in nerve function that could cause your hands and feet to feel "pins and needles." The ATSDR, 2007.The mortality rate is higher and numerous irreversible changes in the vital organs are the outcome of chronic arsenicosis. Despite the severity of this potentially fatal toxicity, there is currently no cure for this illness. Mazumder, 2008. A pattern of skin changes may be the most distinctive consequence of long-term oral exposure to inorganic arsenic. These include darker areas of skin and the development of tiny "corns" or "warts" on the hands, feet, and upper body; they are frequently linked to modifications in the skin's blood vessels. When these skin patches were noticed on two men in Ikenyi, they assumed that they were just signs of aging. Skin cancer can also occur. Absorption of arsenic has also been linked to an increased risk of lung, bladder, and liver cancer. Inorganic arsenic has been identified as a known human carcinogen by the Department of Health and Human Services (DHHS) in 1995. Human carcinogenesis has been linked to inorganic arsenic, according to the International Agency for Research on Cancer (IARC) (1980, 2004). Additionally, inorganic arsenic was listed by the EPA (2005) as a known human carcinogen.

Cobalt

The properties of cobalt, a naturally occurring element, are comparable to those of nickel and iron. The majority of rocks, soil, water, plants, and animals all naturally contain trace amounts of cobalt. Barceloux (1999) found cobalt in meteorites as well. Nonetheless, cobalt is typically found in the environment in combination with elements like sulfur, oxygen, and arsenic. The plot in Figure 4.3 illustrates the cobalt concentrations in the sediment samples, which varied from 2.3 to 30.9 mg/kg with an average of 14.80 mg/kg. With the exception of one site, the concentrations in the majority of the research areas are higher than the 5 mg/kg WHO/FAO limits (FAO/WHO, 2011).High concentrations of cobalt can be extremely hazardous to one's health because it is a highly radioactive metal (ATSDR, 2004). The outcome demonstrates a notable concentration in the study region. This is related to local volcanic rock weathering and mining. Cobalt behaves differently in water depending on the acidity and redox potential. Because rising H+ concentrations compete with metal binding sites, the adsorption of cobalt by particulate matter decreases as pH drops (Andreev and Simenov 1990).

High levels of cobalt have been linked to respiratory issues such as wheezing, asthma, and pneumonia, according to the ATSDR (2004). Long-term exposures can result in bleeding, diarrhea, comas, and even death. Lower exposures can only cause skin rashes, nausea, and vomiting. Radioactive cobalt is carcinogenic and damages cells, resulting in hair loss, burns and blisters on the skin, and temporary sterility.

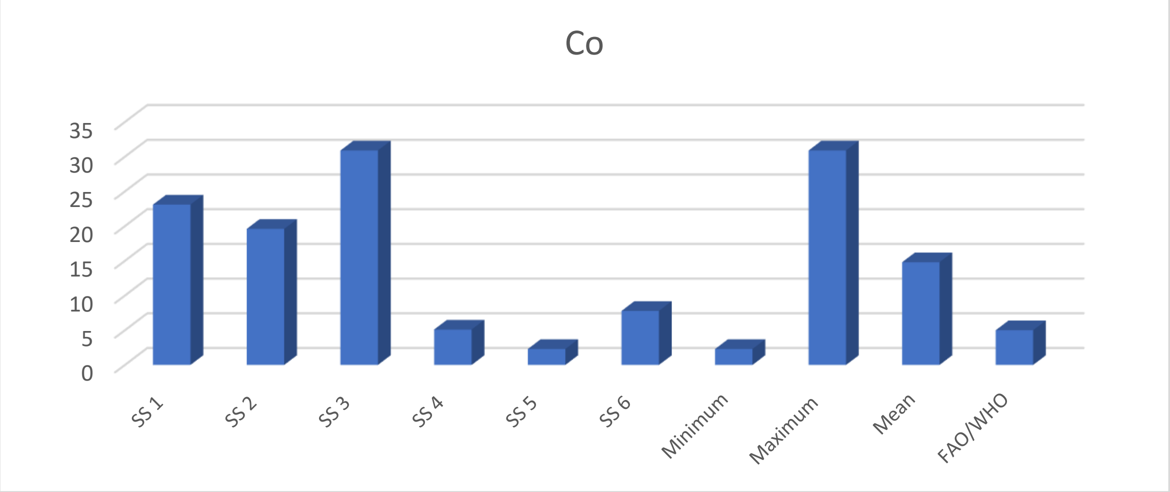

Figure 4: The distribution of the concentrations of Co (mg/kg) in the sediment samples from the study area

Chromium

The crust of the Earth is rich in chromium. It can have valences ranging from +2 to +6. Food seems to be the main source of intake overall, according to Robson (2003) and Jardine et al. (1999). Due to its high carcinogenicity, it has been recommended to consume minimal amounts of chromium (WHO 2011). According to the analysis, the study area's chromium concentrations range from 15.6 to 106 mg/kg, with an average of 56.18 mg/kg. These concentrations are all below the WHO's permissible limit (1996). High grade igneous and baked shales make up the region; these may be the sources of the chromium in the area. Research indicates that, in the right circumstances, chromium (VI) can be reduced to chromium (III) in an aqueous medium. Kimbrough et al. (1999) list organic matter, hydrogen sulfide, sulfur, iron sulfide, ammonium, and nitrate as the most frequent reducing agents found in aqueous systems. The reduction half-life of chromium (VI) in water containing soil and sediment varied from 4 to 140 days, according to Saleh et al. (1989). Anaerobic conditions generally resulted in a faster reaction than aerobic ones. In general, acidic environments promote the reduction of chromium (VI) to chromium (III) Kimbrough et al. (1999).

The most hazardous form of chromium is hexavalent chromium, however other forms, such as compounds containing chromium (III), are considerably less hazardous and rarely cause health issues. In addition to having the potential to be corrosive, chromium (VI) can trigger allergic reactions in the body. As a result, inhaling large amounts of chromium (VI) can irritate the nasal lining and result in ulcers. In addition, it can harm sperm and the male reproductive system, induce anemia, and cause stomach and small intestine irritations and ulcers.Chromium-related allergic reactions include extreme skin redness and swelling. Humans may experience severe cardiovascular, respiratory, hematological, gastrointestinal, renal, hepatic, and neurological effects as well as possibly even pass away if exposed to extremely high doses of chromium (VI) compounds Engwa et al. (2018).

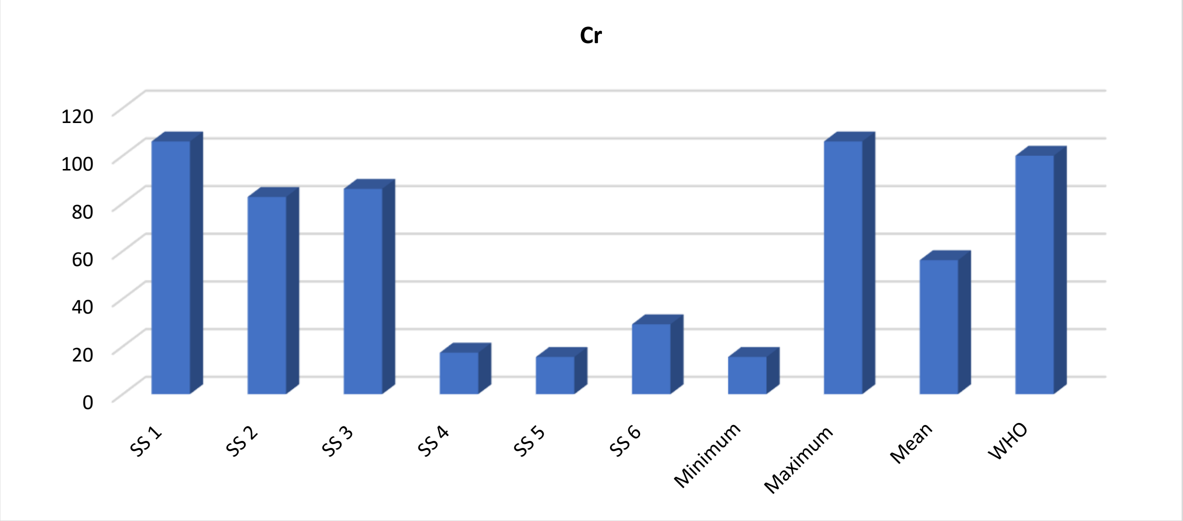

Figure 5: The distribution of the concentrations of Cr (mg/kg) in the sediment samples from the study area

Vanadium

Utilized extensively in the manufacturing of steel alloys and sulfuric acid, vanadium is a strategically significant metal (Zhang et al., 2009; Watt et al., 2018; Mikkonen et al., 2019). Both humans and other animals are toxic to vanadium (Perez-Benito, 2006). However, microbes, animals, and higher plants benefit from low concentrations of vanadium (Tisdale et al., 1993). Vanadium has been linked to increases in plant growth in corn and rice (Hodges, 1995). According to Epstein (1972), the average concentration of vanadium in plant material is approximately 1.0 mg/kg, while the normal concentration needed for plant growth is 2.0 parts per billion (ppb).The concentration of vanadium in this study is above the allowable limit of approximately 100 mg/kg established by the World Health Organization (1996), as shown in Figure 4.5, with a range of 23 to 241 mg/kg and an average of 116.63 mg/kg.

Utilized extensively in the manufacturing of steel alloys and sulfuric acid, vanadium is a strategically significant metal (Zhang et al, 2009; Watt et al, 2018; Mikkonen et al, 2019). Globally, there are mineral and hydrocarbon deposits containing vanadium resources. The top producers of vanadium products are China, South Africa, and Russia (Moskalyk and Alfantazi, 2003; Yu et al, 2019). Vigorous mining and smelting operations have been encouraged by the rising demand for vanadium (Zhang et al, 2018; Li et al, 2020).

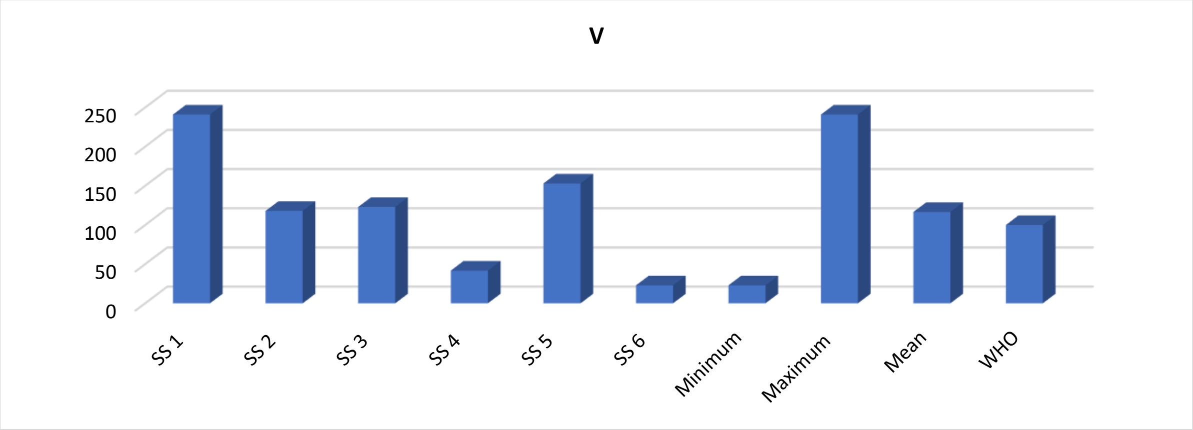

Figure 6: The distribution of the concentrations of V (mg/kg) in the sediment samples from the study area

Zinc

The analysis's findings for the research area varied from 24.5 to 130 mg/kg, with 78.93 mg/kg of availability. (Figure 6). While the WHO (2011) does not specify a permissible limit for zinc, the ATSDR (2007) states that a concentration of 3 to 5 mg/L is beneficial for a healthy lifestyle. The crust of the earth is rich in zinc. It is a chalcophile metallic element that occurs in a variety of minerals, such as zincite (ZnO), smithsonite (ZnCO3), and sphalerite (ZnS), the most common zinc mineral. It is also widely distributed as a trace element in pyroxene, amphibole, mica, garnet, and magnetite. Sutherland and Andrews (2004). Both natural and human-caused sources release it into the environment; however, human-caused releases outweigh those from natural sources Barbera et al.

(1991). Zinc is immobile in water, aside from its dissolution, which increases with acidity Gundersen and Steinnes (2003). Primarily found in the +2 oxidation state in water, zinc also dissolves in strong bases to form zincate anions, which are hydroxo complexes, and in acids to form hydrated Zn cations.e.g., - 2- 2-(Zn[OH]$_3$), (Zn[OH]$_4$), and (Zn[OH]$_4$[H$_2$O]$_2$) Fuhrer (1986).

When zinc concentrations in soil and water approach 400 mg/kg and 3 mg/L, respectively, toxicity in humans may result. Symptoms of irritability, pain and stiffness in the muscles, nausea, and loss of appetite are associated with this. According to Fergusson (1990), zinc seems to have a protective effect against the toxicities of both lead and cadmium. When Zn concentrations surpass 20 mg/kg, it has been demonstrated to have detrimental effects on a range of aquatic organisms' reproductive biochemistry, physiology, and behaviour. However, a variety of factors, including water temperature, hardness, and pH, can affect toxicity (WHO, 2011).

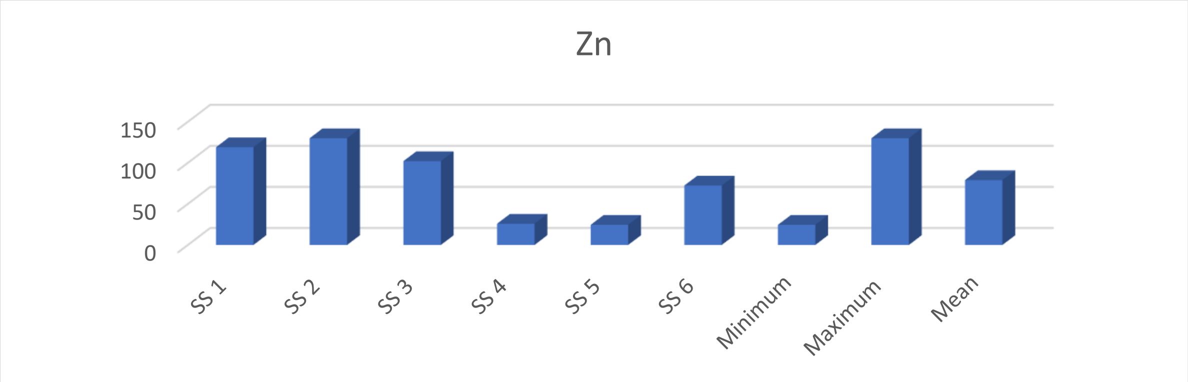

Figure 7: The distribution of the concentrations of Zn (mg/kg) in the sediment samples from the study area

Other element present in the study area

The other elements with high concentration in sediment are Iron (Fe), Magnesium (Mg), Aluminium (Al), Potassium (K) and Sodium (Na).

Iron

The study area is contaminated because Fe, another potentially toxic element, has a range of 6420 – 80220 mg/kg and 41756.67 mg/kg, which is extremely high and above the WHO's (2008) permissible limit of 50000 mg/kg for sediment. The distribution of Fe in the study area is depicted in Figure 8.

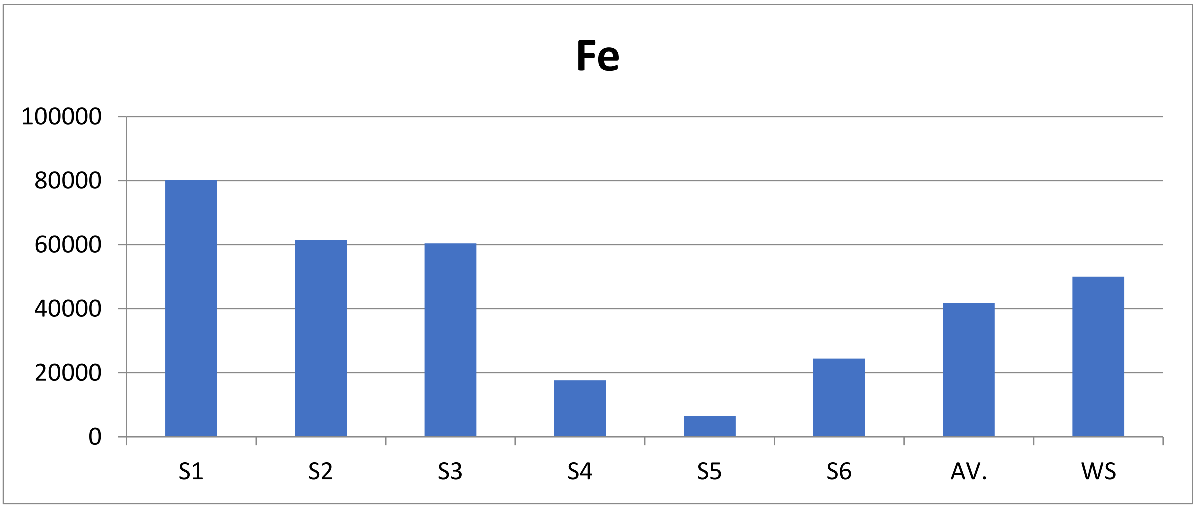

Figure 8: The distribution of the concentrations of Fe (mg/kg) in the sediment samples from the study area

Plants require iron (Fe) as a micronutrient (Krohling et al. 2016). This element can be found in iron-sulfur (Fe-S) clusters and multi-heme cytochromes as cofactors (Ferousi et al. 2017). Numerous essential biological processes in plants, including photosynthesis, respiration in the mitochondria, nitrogen fixation and metabolism, assimilation of sulfur, and the synthesis of hormones and DNA, depend on iron (Balk & Pilon 2011; Ibañez et al. 2021). Fe is extremely abundant in the earth's crust, but in alkaline and oxidative environments, plants have poor availability to it (Lei et al. 2014).Araújo et al. (2014) and Grillet et al. (2014) report that while Fe2+ (the ferrous state) is readily oxidized in aerated soils and can result in plant Fe deficiency, Fe3+ (the ferric state) becomes less soluble as pH rises (Kaya et al. 2020).

Conversely, Fe can upset the cell redox balance and lead to a pro-oxidant state when present in high concentrations in plant tissue (above 500 mg Fe kg-1 leaf dry mass). This can cause changes in the morphological, metabolic, and physiological characteristics of the plants as well as oxidative stress (Siqueira-Silva et al. 2012; Jucoski et al. 2013).

Magnesium

Mg was measured in all samples ranging from 1243±263 to 12970±385mg/kg which is low and this is as a result of the high acidic nature of the investigated soil. Mg plays a major role in the production of chlorophyll, on which photosynthesis depends and also activates many enzymes (Williams, 1992). It has been reported that Mg appears to be associated with protein synthesis via its roles in ribosomal structure and function (Wilkinson et al, 1990)

Aluminium

The concentrations of aluminium in the soil were found in the range of 12630±139 to 93120±463 mg/kg. While aluminum can be toxic at higher levels, it is considerably less toxic than either mercury or lead. In fact, aluminum is found at easily measurable levels in various biological fluids and tissues (NAS/NRC, 1999). However, at high levels aluminum has the potential to cause a number of health problems such as 183 anaemia and other blood disorders, colic, fa-tigue, dental caries, dementia dialactica, kidney and liver dysfunctions, neuromuscular disorders, osteomalacia and Parkinson's disease (NAS/NRC, 1999).

Potassium

Potassium K has many functions in plant growth. It was measured in all our samples in large amount. It is essential for photosynthesis, activates enzymes to metabolize carbohydrates for the manufacture of amino acids and proteins, facilitates cell division and growth by helping to move starches and sugars between plant parts, adds stalk and stem stiffness, increases disease resistance, increases drought tolerance, regulates opening and closing of stomates, gives plumpness to grain and seed, improves firmness, texture, size and color of fruit crops and increases the oil content of oil crops (Tucker, 1999). However, deficiency in plants exhibit chlorosis (loss of green color) along the leaf margins or tips starting with the bottom leaves and progressing up the plant, among others (Tucker, 1999).

Standard for health risk Assessment

By the used of standard parameter in the Table 7 below we calculate the carcinogenic and non-carcinogenic health risks associated with the ingestion/dermal absorption of soil that is contaminated with toxic heavy metals was assessed using hazard quotient (HQ), Hazard index (HI) and carcinogenic health risk

Table 7: Standard for health risk Assessment

Parameter	Adult	Children	Units
Ingestion Rate (IR)	1.5	0.7	L/d
Exposure Frequency (EF)	365	365	D
Exposure Duration (ED)	30	12	R/hr
Average Body Weight (BW)	70	15	Kg
Average Exposure Time (AET)	10,950	4380	D
Constant Duration (t)	0.4	0.4	h/d
Skin Permeability coefcient (Kp)	0.001	0.001	cm/h
Conversion factor (CF)	0.001	0.001	
Average Height (H)	165	153	cm

The non-carcinogenic health risk index The non-carcinogenic hazard index was determined using the formula in equation (8) The hazard quotient (HQ) was used to assess the potential for non-carcinogenic health risk for all the heavy metals that were encountered in the sediment samples. The health quotient of each metal was determined using the formula in Eq.(7) ADD is the average daily dose RfD is the oral reference dose for each of the metals in mg/Kg/day . The average daily dose (ADD) through ingestion and dermal absorption were alculated using the formula in equation (6)

Table 8: Calculate ADD, HQ and HI

	ADULT			CHILDREN		
Element	**ADD**	**RfD**	**HQ**	**ADD**	**RfD**	**HQ**
As	0.0214	0.0003	0.0700	0.3700	0.0003	0.12333
Cr	1.2021	0.005	2.4404	5.6100	0.005	1.1220
V	2.464	0.009	2.7738	11.6500	0.009	1.2944
CO	0.3167	0.003	1.0500	1.4780	0.003	0.4946
Zn	1.6785	0.300	0.0595	7.8350	0.300	0.026
HI			6.3573			3.0493

CONCLUSION

A total of five (5) potentially toxic elements were measured in all the samples. They include As, Co, Cr, V and Zn. The range and average values of the concentration of these elements are given as follows: As (1.43 – 5.03 mg/kg, 3.70 mg/kg), Co (2.3 – 30.9 mg/kg; 14.80 mg/kg), Cr (15.6 – 106 mg/kg, 56.18 mg/kg), V (23 – 241 mg/kg; 116.63 mg/kg), (80220 mg/kg- 6420mg/kg; 41756.67 mg/kg) and Zn (24.5 – 130 mg/kg, 78.93 mg/kg).

This study shows that the potentially toxic elements are not yet at elevated stage, except Co and V which were both above the permissible limit, while others are gradually reaching elevation within the study area.

Moreover, this study provides evidence that gradually the local residents in the study area may be at a high risk of disease caused from toxic element exposure.

And lastly, the Average daily dose, Hazard index and Hazard quotient associated the mining of the locally blending was calculated.

Based on the findings of this work, it is recommended that,

Proper monitoring of the potentially toxic elements in study area should be implemented

The local method adapted for the production of the blended fertilizers be sanctioned and abolished

Relevant authorities should ensure the enforcement of all articles of laws and legislations regarding the protection of the environment.

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