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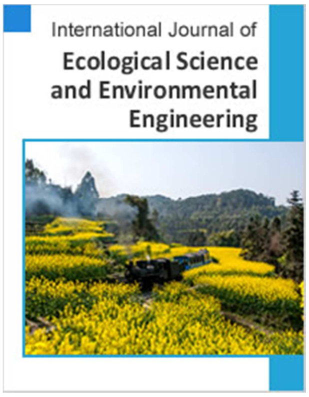

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White Fulani Cattle and Red Sokoto Goats as Biomarkers of Cadmium, Chromium and Nickel Pollution in Zaria Ecological Geochemical Environment

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Abstract
Recent years have seen the development of biological measurements (biomarkers) as tools for use in monitoring and environmental impact assessment, such biomarkers being indicative of contaminant exposure and/or impact. This study was designed to determine the concentration of Cadmium (Cd), Chromium (Cr), and Nickel (Ni) in whole blood of free ranging white Fulani cattle (*Bos primigenius indicus)* and red Sokoto goats (*Capra aegagrus hircus*) as biomarker to provide sensitive indexes, or early warning signals of potential degradation of Zaria ecological geochemical environment as well as possible health risk posed by the consumption of this major source of animal protein from the area. The assessment was carried out by Atomic Absorption Spectrophotometry using Shimadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) after wet digestion. Results indicates that the blood cadmium, chromium and nickel levels ranged from 0.321 mg/l to 1.421 mg/l, 2.171 to 4.856 mg/l and 3.158- 7.135 respectively for *Bos primigenius indicus* and from 0.321 to 1.421 mg/l, 2.171 to 4.856 mg/l and 3.158 to 7.135mg/l respectively for *Capra aegagrus hircus*. Since the observed levels of the metals were significantly ($p < 0.05$) higher than the control and the maximum permissible limits, pollution of the environment where the animals feed could be inferred. Consumption of edible tissues of these animals could pose serious toxicological risk. Implication of findings to public health is fully discussed.

1. Introduction

Ecological systems are dynamic and possess a certain degree of resilience to recover from stress. An ecological stressor is any action or material that imposes changes on an ecological System (NGCERA, 1999). Stressors can be broadly classified as physical, biological or chemical. Physical stressors are actions that directly remove or alter habitats (e.g., soil tilling, wetlands filling, dredging. road construction, logging and agriculture). Biological stressors are living organisms intentionally or unintentionally introduced into an ecosystem that they would not normally inhabit, that cause adverse impacts to existing species. Chemical stressors include hazardous waste, industrial chemicals, pesticides, and fertilizers introduced into the ecosystem (NGCERA, 1999). At contaminated or polluted sites the concern is primarily with chemical stressors, although stress from physical and biological forces may also come into play, especially when evaluating remedial alternatives. Of the chemical stressors, heavy metals constitute the major contaminants/pollutants in the environment (Adedeji *et al*., 2012). Heavy metal contamination has actually become a grave challenge in Nigerian cities. More and more attention has been drawn due to the wide occurrence of its pollution. These chemical substances are persistent in the environment and can cause serious environmental and health hazards. According to Abdulkhaliq *et al*., (2012), they are released into the environment from both natural and man-made activities. Such man-made activities include amongst others- rapid industrial growth, advances in agricultural chemicals, and other urban activities of man. Ecological risk assessments are most commonly used for examining chemical stressors like the heavy metals. Pollution or contamination due to these elements can be estimated effectively by means of biological methods with the help of biological indicator organisms which give information on the quality of their environment (Pokorny, 2000). Biological indicators (bioindicators) are precisely any biological species or population that can be used to monitor the health or determine the environmental integrity of an ecosystem. According to Grodziński and Yorks (1981) and Ten Houten (1983) cited in Zakrzewska *et al*., (2010), bioindicators are classified into three main categories:

i. Species scales: Organisms that have such a narrow range of ecological tolerance that their presence or absence in an ecosystem is a good indication of environmental conditions. Their presence does not provide an indication of ecosystem health but a rough indication that the basic ecosystem components necessary to support the species in question are present. Generally, composition of organisms changes depending on contaminant concentration in the ecosystem.
ii. Real indicators: organisms that show a varied degree of damage depending on the level of contamination.
iii. Accumulators: organisms accumulating contaminants in their tissues which can be quantified.

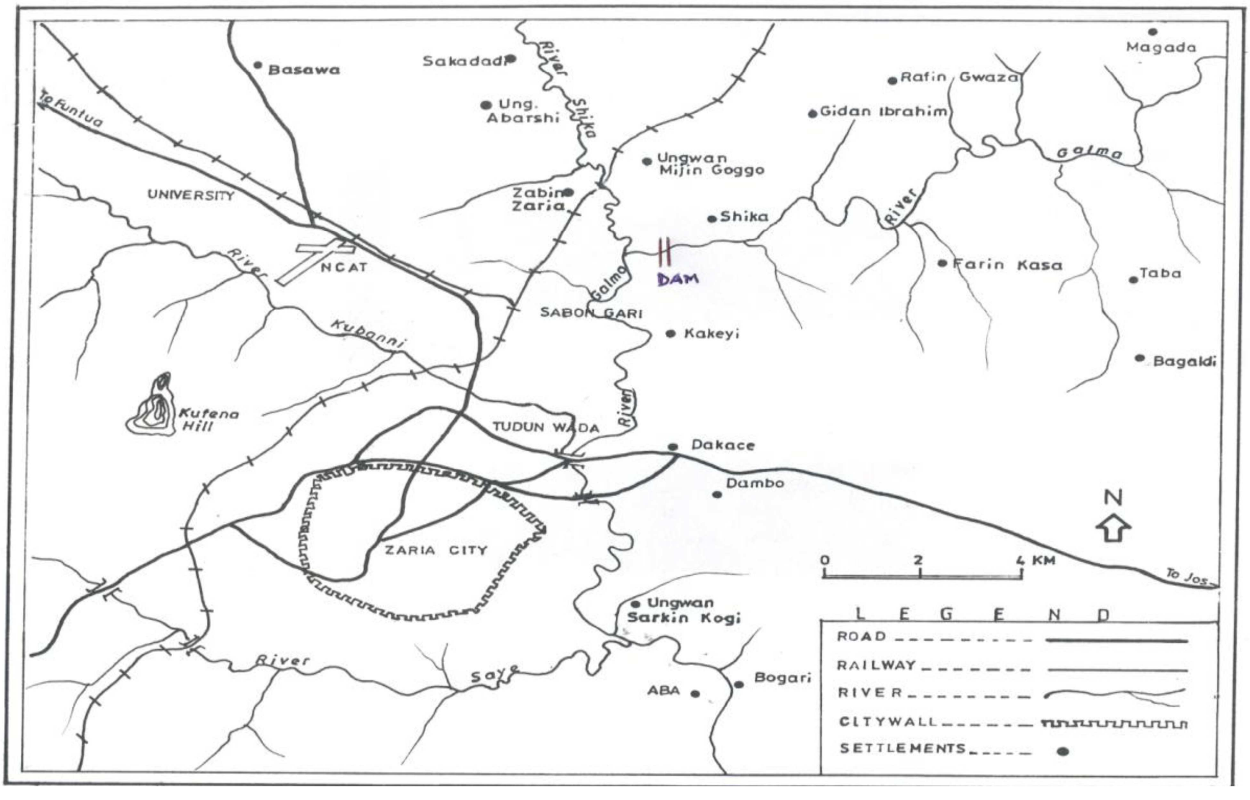
Plant species are most often used for bioindicative purposes. Nevertheless, many wildlife species can also be used as bioindicators of environmental conditions (Arndt et al. 1987; Pokorny, 2000). The most significant advantage of animals over plants in environmental pollution monitoring is its comparability to man (Wittig 1993).

Plants grown on contaminated soil or irrigated with contaminated water accumulate metal contents and other extraneous substances (Ward and Savage, 1994). Both internal and external metals from plants are available for grazers. Livestock reared in such contaminated environment accumulates the contaminants in their tissues and are a continuous source of these extraneous substances to other animals higher up in the food chain. Residues of these substances eventually gets to man found at the peak of the food chain (Udiba *et al*., 2015). Farm animals reared freely on open pasture are good indicators of environmental pollution. Respiration of polluted air, ingestion of contaminated feed/water and skin contacts are the major exposure routes through which metals gain entrance into and bioaccumulates increasingly in organs and tissues of these animals. Blood is a good indicator of current metal exposure and is the most frequently used sample for monitoring metal status in livestock (Rumbeiha *et al*., 2001). While some heavy metals are essential to maintain proper metabolic activity in living organisms, others have no biological importance. At concentrations above certain thresholds both beneficial and non beneficial metals can pose serious risk of toxicity especially when the rate of intake exceeds the rate of elimination. Monitoring of these substances in food animals is therefore of absolute importance not only as an indication of the environmental integrity but also as a matter of great concern for food safety and human health (Aslam, 2011; Abdulkhaliq *et al*., 2012). Milk, dairy products and meat constitute a major source of animal protein world over. Monitoring heavy metal levels in livestock is also of great importance as biomarkers which represent changes from the molecular to the organism level that can be related to toxic effects of and/or exposure to the chemical contaminants. In addition biomarkers act as early warning signals of ecosystem-level damage. It's worthy to note also that biochemical and cellular biomarkers may indicate exposure to specific contaminants (Adedeji *et al.,* 2012). The objective of this research was to determine the concentration of Cd, Cr, and Ni in blood of white Fulani cattle and red Sokoto goats grazed freely on natural pastures around Zaria, Nigeria as a biomarker to provide sensitive indexes, or early warning signals of potential degradation of Zaria ecological geochemical environment as well as possible health risk posed by the consumption of these major source of animal protein from the area using similar species of cattle and goats reared intensively, grazed on cultivated pastures and concentrates at National Animal Production Research Institute (NAPRI), Zaria as control. Bearing in mind however that much more information is needed about the exact relation between the biomarker responses and the health of animals and even more so between the biomarker responses and risks for the ecosystem. Early detection of hazardous exposures of humans or the ecosystem will aid policy-makers and other stakeholders to design programs and policies that may significantly reduce adverse effects through appropriate reductions of the presence of these chemicals in the general environment. Monitoring and systematic gathering of information on heavy metal levels in the environment are therefore essential components of heavy metal pollution-control system (Zielhuis 1991). White Fulani cattle and Red Sokoto goats are grazing animals which are constantly in contact with the environment in Zaria and other parts of northern Nigeria where grazing by privately owned livestock is the most extensive use of public lands. In addition these animals are the most common source of milk, dairy products and meat in Nigeria, hence the use as biomarkers of Cadmium, Chromium and Nickel in the study.

2. Methodology

2.1. Study Location

Zaria is located within latitude 11^{0}3N and 11^{0}15`N of the Equator and longitude 07$^0$33`E and 07^{0}45`E of the Greenwich Meridian, 128kn Southeast of Kano and 64km Northeast of Kaduna City. River Galma is the main drainage channel in Zaria since other rivers and streams discharge into it. It is located at the South-eastern part of Zaria and originates from Jos Plateau in the South-western area of the Shetu Hills, which is some 350 km away from Zaria. Galma Dam is located on the Galma River, at a distance of about 10 km Northeast of Zaria town. (Abdulrafiu, 1997). The other river that drains the ancient city of Zaria is the Kubanni River which originates from the precincts of the Ahmad Bello University (ABU) Main Campus, Zaria, as a trench in an undulating agricultural land and is fed by a number of tributaries (Uzairu *et al.,* 2009). Kubanni River drains the northwest zone of the city of Zaria and receives effluents mainly from domestic activity and runoff from intense cropping located in the adjoining land. The ABU dam is on the river (Uzairu *et al.,* 2009). The geology of the study area is basement of complex rock composed mainly of fine grain gneisses and migmatite with some coarse-grained granite outcrop in few places. The gneisses are moderately to weakly floated, primarily made up of quartz and oligoclase, depth of weathering is regular but thorough, the depth ranges from 10 meters to deep pocket, occasionally extending to about 60 meter. Due to poor conservation and land use practice like extensive vegetation clearance for agricultural and urban development purposes intensive grazing, livestock tracks and human foot paths criss-crossing the area overland flow, rilling and gullying have become the dominant mode of rain water disposal from the landscape. (Ologe, 1971; Bello, 1973; and Iguisi, 1996). The catchment area lies in the natural vegetation zone known as the Northern Guinea Savannah. Unfortunately, this characteristic vegetation cover is hardly preserved due to urbanization, other anthropogenic activities and poor management practices, like cultivation, intensive grazing, fuel wood harvesting and annual bush burning (Ologe, 1971). Rainfed agriculture and irrigation are the two major forms of agricultural activities practiced in the Galma catchment. The rainfed agriculture is a rainy season activity which takes place in the upland fields.



Source: Nnaji *et al.,* 2007

Figure 1. *Zaria showing Rivers and Settlement.*

2.2. Sample Collection

Measurement of Cadmium, Chromium and Nickel levels in animal blood was carried out following methods described by Ogabiela *et al.,* (2011). Whole blood samples were collected from twenty (20) randomly sampled white Fulani cattle (*Bos primigenius indicus*) and twenty (20) randomly sampled red Sokoto goats (*Capra aegagrus hircus*) grazed extensively on natural pastures and fed with water around Zaria. Blood samples were also collected from white Fulani cattle (*Bos primigenius indicus*) and red Sokoto goats (*Capra aegagrus hircus*) fed on cultivated pastures/concentrates at National Animal Production Research Institute, Zaria. The latter was used as control. Blood collection was carried out by venipuncture using sterilized disposable syringe and needles. About 3 ml of blood was taken into sterilized polypropylene tubes containing ethylenediaminetetraacetic acid (EDTA) as anticoagulant.

2.3. Preservation and Preparation of Animal Blood Samples

The polypropylene tubes containing blood samples were preserved in ice-chest and transported to the Environmental Laboratory, National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria at temperature of < 4^{o}C for preparation and analysis.

1ml of the blood sample was pipetted into a clean test tube using 1ml micro pipette and digested with 10 ml concentrated nitric acid and concentrated perchloric acids in the ratio of 3:1 on a hot plate at 60°C. The digest was filtered warm using Whatman filter paper No. 1 into 50 ml volumetric flask and the filtrate made upto the mark with distilled deionized water.

2.4. Sample Analysis

Cadmium, chromium and nickel concentrations in the digests were determined by Atomic Absorption Spectrophotometry, using Shimadzu Atomic Absorption Spectrophotometer (model AA-6800, Japan) equipped with Zeeman background correction and graphite furnace at National Research Institute for Chemical Technology (NARICT), Zaria, Nigeria. The calibration curve was prepared by running different concentrations of the standard solutions. The instrument was then set to zero by running the respective reagent blanks and metal concentration determined at the respective wavelengths. Average values of three replicates were taken for each determination. Data obtained were subjected to statistical analysis.

2.5. Analytical Quality Assurance

In order to check the reliability of the analytical method employed for metal determination, one blank and combine standards were run with every batch of 20 samples to detect background contamination and monitor consistency between batches. The result of the analysis was validated by digesting and analyzing Standard Reference Materials, animal blood coded IAEA-A-13 following the same procedure. The standard reference material was obtained from Internal Atomic Energy Agency, analytical quality control unit, Vienna international center, 1400 Vienna, Australia. The analyzed values and the certified reference values of the elements determined were compared to ascertain the reliability of the analytical method employed. The reagents used- HNO_3 (Riedel-deHaen, Germany), and $HClO_4$ (British Drug House Chemicals Limited, England) were all of analytical grade.

2.6. Statistical Analysis

Independent t-test was used to compare blood metal concentrations of white Fulani cattle (*Bos primigenius indicus)* grazed freely on open fields in Zaria and the blood metal levels of *Bos primigenius indicus* from NAPRI (control). The blood metals concentrations of red Sokoto goats (*Capra aegagrus hircus*) grazed freely on open pastures around Zaria and blood metal levels of *Capra aegagrus hircus* from NAPRI (control) were also compared using independent t-test. Probabilities less than 0.05 ($p < 0.05$) were considered statistically significant. Pearson product moment correlation coefficient was used to determine the association between metals. SPSS software 17.00 for windows was used for all statistical analysis.

2.7. Results

To evaluate the accuracy and precision of the analytical procedure employed standard reference materials of animal blood coded IAEA-A-13 was analyzed in like manner as our samples. The analyzed values and the certified reference values of the elements determined were very close suggesting the reliability of the method employed (Table 1).

Table 1. *Results of analysis of reference material (animal blood IAEA-A-13) compared to the certified reference value (mg/kg).*

Element (mg/kg)	Pb	Ni	Cu	Fe	Zn
A Value	0.20	1.20	4.45	2399	14.2
R value	0.18	1.00	4.30	2400	13.0

A value = Analyzed value R value = Reference value

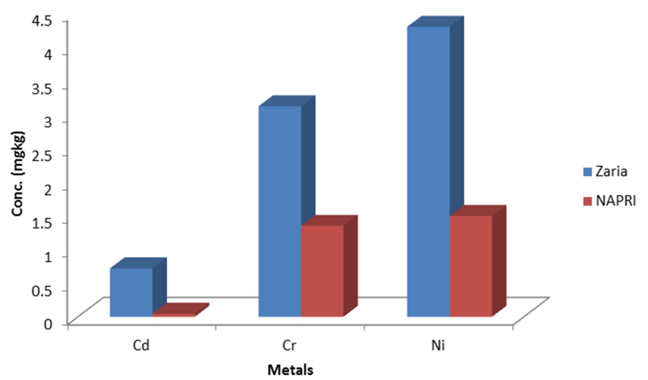


Figure 2. *Spatial distribution of the blood metal levels of White Fulani cattle (Bos primigenius indicus) grazed freely on natural pastures around Zaria and those fed on cultivated pastures and concentrates at NAPRI.*

Results obtained from the determination of blood cadmium, chromium and nickel levels of cattle and goats grazed freely around Zaria and National Animal Production Research Institute are presented in Table 2 and Table 3 respectively. Spatial distribution of the metal levels in blood of these animals is presented in Figure 2 and Figure 3.

Table 2. *Blood cadmium, chromium and nickel levels of White Fulani cattle (Bos primigenius indicus) grazed freely on natural pastures around Zaria and those fed on cultivated pastures and concentrates at NAPRI.*

Metals	Cadmium		Chromium		Nickel	
S/N	Zaria	NAPRI	Zaria	NAPRI	Zaria	NAPRI
1	0.551	0.031	2.171	1.395	3.237	0.925
2	0.415	0.034	3.187	0.439	7.135	0.175
3	0.321	0.051	3.224	1.025	4.431	1.725
4	0.556	0.017	2.295	1.145	3.841	0.925
5	1.295	0.025	4.555	1.145	4.984	2.621
6	0.601	0.034	2.701	1.285	3.951	1.265
7	0.503	0.025	2.323	1.385	3.411	2.705
8	0.431	0.145	2.256	2.952	5.572	1.597
9	0.769	-	3.902	-	4.331	-
10	0.801	-	3.785	-	3.158	-
11	0.831	-	3.367	-	4.622	-
12	0.429	-	2.578	-	3.901	-
13	0.622	-	3.807	-	3.558	-
14	1.101	-	2.867	-	3.281	-
15	1.421	-	2.904	-	4.251	-
16	0.532	-	2.445	-	4.601	-
17	0.467	-	2.989	-	3.162	-
18	0.596	-	2.405	--	5.921	-
19	1.205	-	3.695	-	3.693	-
20	0.801	-9	4.856	-	4.693	-
Mean	0.7124	0.04525	3.1156	1.346375	4.2867	1.49225
Std Dev.	0.315442	0.041503	0.779072	0.716476	1.028156	0.865227

Table 3. *Blood cadmium, chromium and nickel levels of Red sokoto goats (Capra aegagrus hircus) grazed freely on natural pastures around Zaria and those fed on cultivated pastures and concentrates at NAPRI.*

Metals	Cadmium		Chromium		Nickel	
S/N	Zaria	NAPRI	Zaria	NAPRI	Zaria	NAPRI
1	0.425	0.045	1.564	1.895	3.628	1.209
2	0.515	0.025	1.838	1.365	0.415	0.885
3	0.425	0.033	2.264	0.679	0.763	0.645
4	0.486	0.014	2.915	1.253	4.895	1.485
5	0.338	0.045	2.931	0.639	0.542	1.728
6	0.342	0.014	2.054	0.515	3.161	0.393
7	0.421	0.048	1.615	0.395	3.361	0.262
8	0.323	-	2.191	-	2.939	-
9	0.341	-	1.265	-	2.542	-
10	0.387	-	1.469	-	2.223	-
11	0.332	-	1.803	-	2.252	-
12	0.467	-	2.045	-	2.382	-
13	0.472	-	2.231	-	0.544	-
14	0.471	-	2.912	-	0.643	-
15	0.367	-	2.762	-	2.839	-
16	0.571	-	1.594	-	4.978	-
17	0.227	-	2.623	-	4.022	-
18	0.224	-	1.443	-	0.523	-
19	0.412	-	1.276	-	0.458	-
20	0.224	-6.4	1.519	-	0.468	-
Mean	0.3885	0.032	2.0157	0.963	2.1789	0.943857
Std Dev.	0.096831	0.014674	0.567554	0.551254	1.55128	0.55365

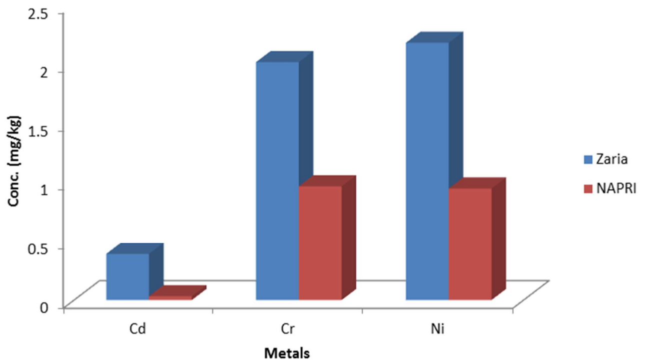


Figure 3. *Spatial distribution of the blood metal levels of Red sokoto goats (Capra aegagrus hircus) grazed freely on natural pastures around Zaria and those fed on cultivated pastures and concentrates at NAPRI.*

Table 2 and Figure 2 show that the blood cadmium levels of white Fulani cattle (*Bos primigenius indicus)* grazed freely on open fields in Zaria ranged from a minimum of 0.321 mg/l to a maximum of 1.421 mg/l with a mean value of 0.712±0.315 mg/l and the blood cadmium levels of *Bos primigenius indicus* from NAPRI (control) ranged from 0.017mg/l to 0.145mg/l with a mean value of 0.045±0.041mg/l. Statistical analysis revealed that the difference in blood cadmium levels of *Bos primigenius indicus* from the different sampling locations in the study was found to be statistically significant ($p < 0.05$), with the blood cadmium levels of *Bos primigenius indicus* grazed freely around Zaria being significantly ($p < 0.05$) higher than the blood cadmium level of *Bos primigenius indicus* from NAPRI. The blood chromium and nickel levels of white Fulani cattle grazed freely on open pastures in Zaria ranged from 2.171- 4.856 mg/l and 3.158- 7.135 respectively. The mean values were found to be 3.116±0.779 mg/l for chromium and 4.287±1.028 mg/l for nickel. The blood chromium and nickel levels of the cattle from NAPRI ranged from 0.243-2.952 mg/l with a mean value of 1.346±0.716 mg/l and 0.925-2.705mg/l with a mean value of 1.492±0.865mg/l respectively. Statistically significant ($p < 0.05$) difference in chromium and nickel levels between cattle grazed freely on natural pasture around Zaria and those fed on cultivated pasture/ concentrates from NAPRI were also observed, chromium and nickel levels in blood of cattle grazed freely in Zaria being significantly ($p < 0.05$) higher than those from NAPRI. Pearson product moment correlation coefficient revealed a positive correlation between cadmium and chromium ($r = 0.177$), and between chromium and nickel ($r = 0.351$). A negative correlation was observed between cadmium and nickel ($r = 0.267$). The correlations were not statistically significant.

On the other hand, Table 3 and Figure 3 revealed that the blood cadmium, chromium and nickel levels of red Sokoto goats (*Capra aegagrus hircus*) grazed freely on open pastures around Zaria ranged between 0.224 and 0.571mg/l with a mean value of 0.389 ±0.097 mg/l, 1.265 and 2.931 mg/l with a mean value of 2.016±0.568 mg/l and 0.415 and 4.978 mg/l with a mean value of 2.179±1.551 mg/l respectively. The blood cadmium, chromium and nickel levels of *Capra aegagrus hircus* from NAPRI ranged from 0.014 to 0.048 mg/l with a mean value of 0.032±0.014 mg/l, 0.385 to 1.895 mg/l with a mean value of 0.963±0.551 mg/l and 0.262 and 1.728 mg/l with a mean value of 0.944±0.554 mg/l respectively. The difference in blood concentration of each of the metal (cadmium, chromium and nickel) in *Capra aegagrus hircus* from the two sampling locations was found to be statistically significant ($p < 0.05$) with the blood cadmium, chromium and nickel levels of *Capra aegagrus hircus* grazed freely around Zaria being significantly higher than the blood cadmium, chromium and nickel levels of *Capra aegagrus hircus* grazed on cultivated pastures and concentrates from NAPRI. Pearson product moment correlation coefficient revealed a positive correlation between cadmium and chromium ($r = 0.208$), Cadmium and nickel ($r = 0.116$), and between chromium and nickel ($r = 0.016$). The correlations were not statistically significant.

3. Discussion

The traditional system of management of livestock has remained the most practiced in the country. Reports by the Federal Ministry of Agriculture and Water Resources show that 99.97% of goats, 99.50% of cattle are traditionally managed (Okoye and Ugwu 2010). Free ranging animals as is the case in the traditional management of livestock in Nigeria can be good indicators of the general environmental pollution status. White Fulani cattle and Red Sokoto goats are free ranging animals which are constantly in contact with Zaria ecologicalgeochemical environment. Cadmium, chromium and nickel levels in blood of these animals could reflect current exposure hence a good biomarker of the environmental integrity and food safety. Present study indicated that the mean cadmium concentration in blood of both cattle (0.712±0.315 mg/l) and goats (0.389 ±0.097) grazed on open pastures (free ranging) in Zaria were higher than the World Health Organization (WHO) tolerable limits of 0.005 ppm for cadmium (WHO, 2001 cited in Nwude *et al*., 2011). The mean blood cadmium level of free ranging cattle in the study was over 142 times the allowable limit and that of goats was about 78 times the limit. Cadmium accumulated in environment by pollution could be responsible for soil and pasture contamination. Plants can accumulate this mineral, so this toxic element is ingested by animals grazing such plants. Ingested and inhaled cadmium together with that obtained through body contact could therefore be responsible for the elevated level of the metal in the test animals. When compared to the mean blood cadmium level of cattle and goats from NAPRI, the mean blood cadmium level of free ranging cattle and goats in Zaria was found to be about 16 times and 12 times higher in spite of the fact the blood cadmium level of the animals from NAPRI also exceeded the WHO acceptable limits. The significantly higher concentration of cadmium recorded in cattle and goats grazed freely in open pasture compared to cattle and goats from National Animal Production Research Institute (control) could be regarded as an indication of level of the metal in the environment in which they live and with which they interact, though the effectiveness and reliability of using the levels of metals in living organisms as biomarker of pollution are functions of several factors such as level of pollution, chemistry of the metal, metal uptake potential of the animals, feeding habit and animal part/tissues considered (Okoye and Ugwu 2010). In addition to being constantly in contacts with the environment, cattle and goats are the most common source of meat and dairy products in Nigeria. The finding of this study also indicates that consumption of free ranging white Fulani cattle and red Sokoto goats from Zaria could pose serious risk of cadmium intoxication. Cadmium concentration recorded in this study was found to be higher than those recorded in literatures. A mean value of 0.12±0.04 mg/l was recorded for cows reared and fed predominantly on grasses grown around challawa industrial area kano – Kano and 0.17±0.14 kg/l for cow around Zngo area, Zaria Nigeria (Ogabela *et al.,* 2011) a range of 0.523-0.834 was reported for cattle at Ota abattoir, Nigeria (Nwude *et al.,* 2011)

Cadmium is one of the most abundant, naturally occurring elements; it is a soft, malleable, ductile, bluish-white bivalent metal and is highly carcinogenic for living beings. Cadmium is an extremely toxic metal and number 7 on ATSDR's "Top 20 list". It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It can be found in soils because insecticides, fungicides, sludge, and commercial fertilizers that use cadmium are used in agriculture. Cigarettes also contain cadmium. Other known sources of exposure are electroplating, motor oil, and exhaust. Literature indicates that excessive intake of cadmium in cattle can lead to loss of appetite, anemia, poor growth, abortions and teratogenic effects. Excessive intake of cadmium alters the metabolism of zinc and copper in animals (Aslam *et al.,* 2011). It has been found that cadmium has not a single physiological function within the human body. Even low concentration of cadmium can adversely affect the number of metabolic processes in the human body. Once absorbed, it accumulates in the body even throughout the life. Cadmium intoxication can lead to kidney, bone and pulmonary damages. 2-7% of ingested cadmium is absorbed in the gastrointestinal system. Target organs are the liver, placenta, kidneys, lungs, brain, and bones (ATSDR, 2008).

There are no set standards for chromium and nickel concentrations in meat by international bodies such as Codex Alimentarium and/or the WHO/FAO (Ihedioha *et al*., 2014). However, Brazil has set a standard of 0.1 μg/g fw for chromium in meat and fish, and Russia has a permissible limit of 0.5 mg/kg fw for nickel in meat and meat products (Ihedioha *et al*., 2014) The mean chromium concentrations in blood of cattle and goats grazed on open pastures (3.116±0.779 mg/l and 2.016±0.568 respectively) recorded in this study exceeded the Brazilian standard. When compared to the mean chromium concentration of cattle (1.346±0.716) and goats (0.963±0.551) from NAPRI, the mean blood chromium level of the free ranging cattle and goats were both found to be over two times higher. Chromium concentration ranging from 3 to 5 μg/l was reported for dairy cows during the postpartum period (Pechova *et al.,* 2002). Apart from this study, high values of chromium have been reported in Nigerian cattle, suggesting considerable levels of chromium in the environment. A mean value of 2.12±1.54 mg/l was recorded for cows reared and fed predominantly on grasses grown around challawa industrial area Kano and 2.81±0.90 kg/l for cow around Zango area, Zaria Nigeria (Ogabela *et al.,* 2011). A range of 0.942-1.357 was reported for cattle at Ota abattoir, Nigeria (Nwude *et al.,* 2011). According to McDowel (2003) cited in Ogabiela *et al*., (2011), Chromium concentration for livestock requirement ranges from 0.3 to 1.6 mg/kg, levels higher than these values are toxic to livestock and it badly affects the reproductive potential of ruminants. The mean chromium concentration recorded in this study was found to be above the livestock requirement suggesting that the livestock are at risk of chromium intoxication.

Chromium is the 21^{st} most abundant mineral in the earth crust. Although chromium may theoretically occur in all oxidation states from –2 to +6, it is most often found in 0, +3 and +6 and its harmful effects on humans, animals and plant health are partially related to the valence state. Toxicity and carcinogenicity of the metal are associated mainly with hexavalent chromium. Whole trivalent Chromium is believed to be a highly safe mineral. Elemental chromium (0) is not naturally present in the earth crust and is biologically inert. Almost all naturally found Cr is trivalent while hexavalent Cr is mostly of industrial origin (Pechova and Pavlata, 2007). Chromium may be considered as an essential metal for both human and as well as for animals but intake exceeding the permissible limit can cause its poisoning in both animals and humans and can also lead to the carcinogenic effects. Absorbed Cr circulates in blood, transported mostly to tissues bound to transferrin. Chromium from blood is relatively quickly absorbed by bones, accumulating also in the spleen, liver and kidneys. Low level Cr can irritate skin and can produce ulcer. Its chronic exposure can produce kidney and liver damage. It can also cause damage to circulatory and nerve tissues. National Academy of Science has established a safe and ample daily intake for chromium in adults to be 50 μg/day. Current exposure of white Fulani cattle and red Sokoto goats in Zaria to elevated level of chromium as indicated by the blood chromium level in the study suggest that consumption of these animals could pose serious risk of intoxication.

In the same vein, the mean nickel concentrations in blood of cattle and goats grazed on open pastures (4.287±1.028 mg/l and 2.179±1.551 mg/l respectively) recorded in this research exceeded the Brazilian standard. When compared to the mean nickel concentration of cattle (1.492±0.716 mg/l) and goats (0.943±0.553) from NAPRI, the mean blood nickel level of the free ranging cattle and goats were both found to be over two times higher. These findings suggest the presence of elevated level of nickel in the environment and that consumption of these animals could pose toxicological risk of nickel intoxication. A mean value of 2.49±1.28 mg/l was recorded for cows reared and fed predominantly on grasses grown around Challawa Industrial area Kano – Kano and 20±0.55 kg/l for cow around Zango area, Zaria Nigeria (Ogabela *et al.,* 2011) a range of 0.106-0.414 kg/l was reported for cattle at Ota abattoir, Nigeria (Nwude *et al.,* 2011)

Nickel is a naturally occurring element that may exist in various mineral forms. It is used in a wide variety of applications including metallurgical processes and electrical components, such as batteries (ATSDR, 1988). Most nickel enters the body via food and water consumption, although inhalation exposure is the primary route for nickel-induced toxicity in occupational settings. The absorption of nickel is dependent on its physicochemical form, with water soluble forms being more readily absorbed. Animals and humans absorb approximately 1-10% of dietary nickel (EPA 1986). Nickel metal is poorly absorbed by the skin but some nickel compounds such as nickel chloride or nickel sulfate can penetrate occluded skin resulting in up to 77% absorption within 24 hours (ATSDR 1988). Some evidence suggests that nickel may be an essential element for animals as well as for humans and plays physiological role in the body. But there is contrast to this study that no specific function of nickel in higher animals including man have not yet been identified (Nicklin and Nielsen, 1994). This fact, according to the authors explains why National Research Council has not set the recommendation limits for the metal. Much of the toxicity of nickel may be associated with its interference with the physiological processes of manganese, zinc, calcium, and magnesium in plants, animals and humans (Coogan et al., 1989). The primary target organs for nickel-induced systemic toxicity are the lungs and upper respiratory tract for inhalation exposure and the kidneys for oral exposure (ATSDR 1988; Goyer 1991). Other target organs include the cardiovascular system, immune system, and the blood. Excessive intake of nickel is also associated with many complications such as dermatitis, itching of fingers, hands and forearms (EPA, 1986).

The positive correlation observed between cadmium and chromium, and between chromium and nickel in both cattle and goats indicates that as the concentration of cadmium in blood of these animals' increases, the concentration of chromium also increases suggesting that same source is responsible for the presence of these metals at the concentration determined. The negative correlation observed between cadmium and nickel (r = -0.267) in cattle indicates that as the concentration of cadmium increases, the concentration of nickel decreases suggesting that different sources are responsible for their presence at the concentration determined. The correlations were however not statistically significant.

4. Conclusion

Monitoring and systematic gathering of information on heavy metal levels in the environment are essential components of heavy metal pollution-control system. Whole blood of free ranging white Fulani cattle and red Sokoto goats which are constantly in contact with Zaria environment was used as biomarkers of Cadmium, Chromium, and Nickel to provide sensitive indexes, or early warning signals of potential degradation of Zaria ecological geochemical environment as well as possible health risk posed by the consumption of this major source of animal protein from the area. Results obtained showed high levels of the metals in the test animals. Since the observed levels of the metals in the study were significantly higher than the control and the maximum permissible limits, pollution of the environment where the animals feed could be inferred. Consumption of these animals could pose serious toxicological risk. Quantification of metals in popular edible tissue of white Fulani cattle and red Sokoto goats grazed freely in Zaria is strongly recommended.

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