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INVESTIGATION OF HEAVY METAL CONTENTS AND ITS HEALTH RISK IN COW MILK SAMPLES FROM OWUKPA COAL MINE AREA OF BENUE STATE, NIGERIA

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ABSTRACT

This study investigated heavy metal contents in cow milk samples from Owukpa coal mine area of Benue State, Nigeria. The milk samples were randomly collected from different cows, treated with nitric acid and hydrogen peroxide and then heated. The samples were later cooled and distilled water was added. The samples were then analyzed using atomic absorption spectrometry to determine their heavy metals contents. The Estimated Daily Intakes (EDI) of heavy metals, Health Risk Assessment, Health Risk Index (HRI) and Carcinogenic Risk (CR) were all determined using standard procedures. The results of average heavy metal concentration (mg/L) showed: 0.64±0.01 (Cd), 1.63±0.02 (Cr), 4.78±0.02 (Fe), 2.09±0.01 (Mn), 2.11±0.02 (Ni) and 0.42±0.00 (Pb) with a variation pattern in the increasing order of: Fe>Ni>Mn>Cr>Cd>Pb. The trend of EDIs (mg/day/kg) for heavy metals analyzed in the cow milk samples were observed to increase in the order: Fe (26.500, 8.833, 1.893) > Mn (3.256, 1.085, 0.233) > Ni (0.127, 0.042, 0.009) > Cr (0.095, 0.032, 0.008) > Cd (0.023, 0.008, 0.002) > Pb (0.018, 0.006, 0.001) for infant, children and adult respectively. The HRIs of Ni, Mn, Cr and Fe were below 1 (HRI<1). With Carcinogenic Risk values of 0.0025 (Cd), 0.0010 (Cr), 0.0054 (Fe), 0.0017 (Mn), 0.0015 (Ni) and 0.00 below detection limit (Pb). The study indicates that regular consumption of cow milks in the study area will have disastrous long time health effects due to high concentrations of Cd, Cr, Fe, and Pb and as a result recommends further research on soils and water sources which cows feed on around the vicinity.

Keywords: Atomic absorption spectroscopy, health risk index, carcinogenic risk, heavy metals.

INTRODUCTION

Milk is a readily available, low-cost product that is nutrient-dense and boosts the diet's overall nutritional quality. Consuming cow's milk is linked to several health advantages such as reducing the risk of Type 2 diabetes and improving the management of weight as well as decreasing the risk of hypertension, osteoporosis, cardiovascular disease, certain malignancies, stroke and kidney stones [1]. Cow milk is very beneficial to human health as an excellent supplier of proteins, lipids and important minerals. It is regarded as a complete diet [2]. According to Dolganyuk et al [3], raw milk from different parts of the world contains about 38 micro and trace components. The concentrations of these minerals in raw cow milk can change based on a number of variables, such as seasonal fluctuations, cows' lactation cycles, health issues, climatic circumstances, the composition of the yearly feed and environmental pollution [4].

The minerals in milk provide a variety of health benefits for the body [5]. Some of which include:

i. Bone health: Due to its high calcium and vitamin D content, this helps to prevent osteoporosis.
ii. Brain health: The quantity of glutathione, a potent antioxidant, in adults' brains is higher when they consume more dairy products.
iii. Blood pressure and heart health: The risk of cardiovascular disease decrease by consuming more potassium and less sodium. However, the saturated fat included in full-fat dairy products raises the chance of developing heart disease and atherosclerosis. Therefore, skim or low-fat milk should be chosen by those who are at risk for stroke or cardiovascular disease.
iv. Depression: Serotonin, a hormone linked to hunger, sleep, and mood, is produced when vitamin D levels are adequate. Vitamin D supplements can assist persons with significant depression control their symptoms.

There are numerous substances that may be found in milk and its derivatives, many of which are crucial, including pollutants such as heavy metals. These metals function as cofactors in enzymes and other enzymatic processes. Although the proportion of metals in uncontaminated milk is precise, it can change significantly during the manufacturing and packaging stages. Additionally, metals including nickel, lead, chromium, cadmium and cobalt are capable of polluting can negatively affect human health [6].

Studies have shown that anthropogenic activities have been a leading factor to high concentration of some these metals in milk. Cow milk having heavy metal concentrations within the safe limit can also pose a long term health risk when consumed on regular basis. In order to quantify the levels of certain metals in cow milk and the hazards they pose to human health in Nigeria, Iwegbue et al [7] randomly sampled milk from several states from the six (6) geopolitical zone in Nigeria, including those with and without mining operations, for heavy metals assessment. They came to the conclusion that areas with high concentrations were particularly those with mining activity.

As many food items are now produced in big numbers on an industrial scale, milk and its derivatives stand out as one of the most prominent and widely recognized commodities. The industrialization of countries has led to the acknowledgment of heavy metals as the primary pollutants, which in turn affects their occurrence in milk and dairy products [8]. Heavy metal analysis was conducted on cow milk samples in Dhaka a non-industrial area. It was found that Bangladeshi milk samples had heavy metal concentrations that were below the allowable limit [9]. On the other hand, this showed difference to findings of Muhib et al [10] from the assessment of heavy metal concentration in milk samples from Dhaka, Bangladesh, where mining activities were conducted, as the results showed high concentration of the analyzed metals [10].

Areas around coal mines often face environmental pollution due to the release of heavy metals and other pollutants into the soil, water, and air [7]. These contaminants can enter the food chain, leading to their presence in dairy products like cow milk. They could have detrimental effects on the health of the cattle and the economic well-being of the local communities relying on dairy production [9].

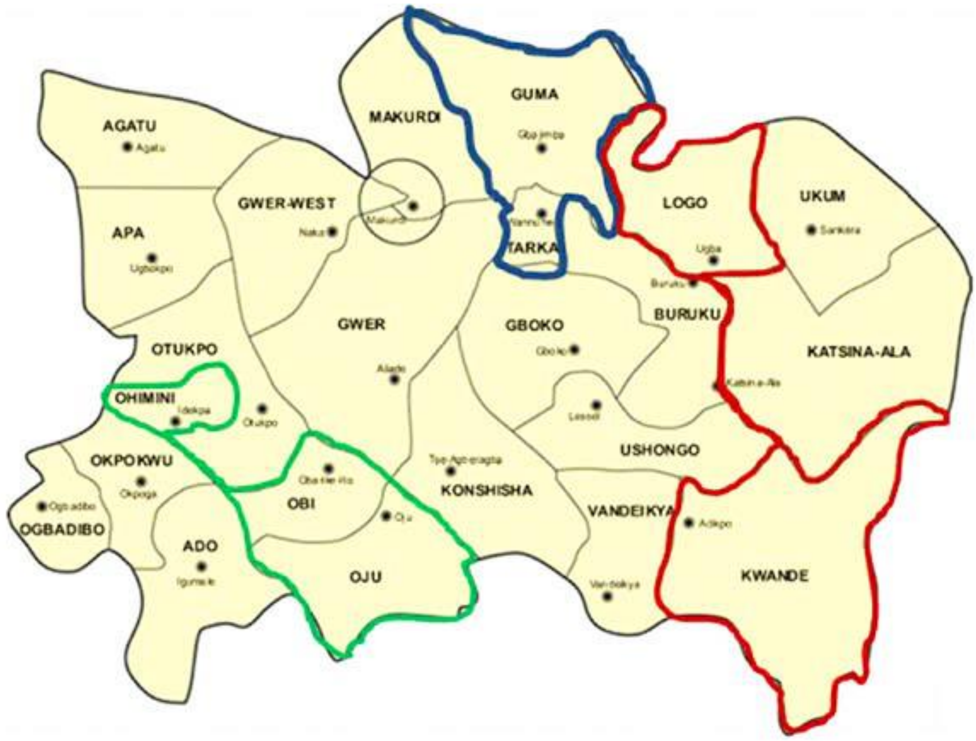
There is limited research on heavy metal contamination in cow milk from this specific region despite the presence of coal mining. The findings from this study can lead to changes in agricultural practices, food safety regulations, and community health interventions.

In this work, milks were obtained from cows grazing around Owukpa coal mine in Benue state, Nigeria. The milks were then assessed for their heavy metal concentrations. The obtained values were compared with established safety standards or regulatory limits set by World Health Organization. The potential health risks associated with the consumption of the milks were also investigated.

MATERIALS AND METHODS

Study Area

This study was conducted in Owukpa. The research region is situated between latitudes 6°30' and 7°26'N and longitudes 7°10' and 7°30'E. It is located in Ogbadibo Local Government Area of Benue State, Nigeria. It has an abundant coal resource with 80 million tons of total reserves, which Owukpa Consolidated Mines Limited is actively mining. Orokam borders Owukpa in the west and has a border with Obollo Eke in Udenu Local Government Area, Enugu State. Its total size is approximately 1286 km^2. The study area is characterized by both rainy and dry seasons. From April through October, there is a seven-month rainy season. Between 1,200 and 1500 mm of rain fall are recorded annually. In March and April, daytime temperatures are often fairly high. In the summer, the region's daily maximum and lowest average temperatures are 35°C and 21°C, respectively, and in the winter, they are 37°C and 16°C. Cows are usually grazed on lands and drink from water sources around the study area.



Key	
Studied zones	Local Governments Areas selected
Zone A	
Zone B	OGBADIBO LGA
Zone C	

Collection and preparation of cow milk samples for analysis

Total number of 10 cow milk samples were randomly obtained from 10 different cows grazing around the mining area into sterilized sampling bottles for preservation and stored at low temperature 10 ^{o}C using ice-bags prior to analysis [11]. The samples were labeled MS1, MS2, MS3, MS4, MS5, MS6, MS7, MS8, MS9 and MS10.

About 5 mL (65%) nitric acid and 2 mL (30%) hydrogen peroxide was mixed and used to treat 5 g of raw cow milk. The mixture was then heated on an electric hot plate, reaching a temperature of 90 °C and gradually increasing it to 120 °C. This temperature rise continued until the appearance of brown fumes, indicating the complete oxidation of organic substances. In doing so, it was ensured that the biological matrix is eliminated and the components were left in their natural state. After the cooling process, the transparent liquid was strained into a 25 ml volumetric flask, and about 100 mL of distilled water was introduced. This procedure was repeated for each sample. After creating a control digestion solution for comparison, samples were collected for atomic absorption spectroscopic analysis [12].

Elemental Analysis

The solutions of each of the metals tested for were made using deionized water. Each 1.0 g metal sample was measured into 10 mL of a 1:1 nitric acid solution and then transferred to a 1000 mL volumetric flask. Stock solution was then prepared by addition of 1L of distilled water. Each metal's 1000 mg/L stock solution was used to create standard solutions. Through multiple dilutions of the stock solution, a calibration curve was created. For comparison, working standard solutions of lead (Pb), cadmium (Cd), nickel (Ni), chromium (Cr), manganese (Mn), and iron (Fe) were utilized. pH 2.5 was achieved by adding 1 M nitric acid to a 100 mL sample of each metal's solution.

Each standard solution and sample was then aspirated directly into the flame and absorbance was recorded using Ice 3000 AA02134104 v1.30 Thermo Scientific Atomic Absorption Spectrophotometer equipped with each hollow cathode lamp at 228.8 nm, 357.9 nm, 232.0 nm, 283.2 nm, 279.5 nm and 248.3 nm wavelengths for Cd, Cr, Fe, Ni, Mn and Pb respectively. Every time a sample was taken, deionized water was used to flush the nebulizer, atomizer, and burner. With the highest operating standard solution and a blank, the equipment's stability was periodically tested. In order to get the highest absorbency and linear response while aspirating established standards, the settings were tuned prior to sample analysis.

Health Risk Assessment

The method of Sajjad et al [13] was adopted for the determination of health risk assessment of metals.

Estimated Daily Intakes (EDI) of heavy metals

The EDIs for heavy metals were derived by dividing the average weight of people ($B_{Average\ weight}$ = 65 kg) in the environment by the weight of the food item consumed (D_{Intake}), multiplied by the corresponding average concentration in food samples (C_{Metal}). Daily intakes of metals were determined for average weight of infant (5 kg, children (15 kg) and adult (60 kg) using the following equation [14]:

$$EDIs = \frac{C_{Metal} \times D_{Intake}}{B_{Average\ weight}} \quad (1)$$

Health Risk Index (HRI)

Health risk index (HRI) was calculated by dividing the Daily Intake (DIM) of Metals in food by the Reference Oral Dose (RfD). The formula is:

$$HRI = \frac{DIM}{RfD} \quad (2)$$

Carcinogenic Risk (CR)

Carcinogenic risk (CR) refers to a person's lifetime chance of acquiring cancer as a result of exposure to a suspected carcinogen. The cancer slope factor (CSF) provided by USEPA was multiplied by estimated daily consumption and used to calculate the cancer risk [16]. The formula is given as:

$$CR = CSF \times EDI \quad (3)$$

Where, CSF is the carcinogenic slope factor of 0.91 $(mg/kg/day)^{-1}$ for Ni, Zero slope factor for Fe, 6.3 $(mg/kg/day)^{-1}$ for Cd, 0.5 $(mg/kg/day)^{-1}$ for Cr, 0.0085 $(mg/kg/day)^{-1}$ for Pb, and 0.000 $(mg/kg/day)^{-1}$ for Mn set by USPEA [15]. The acceptable risk values vary from 10^{-4} to 10^{-6} [16].

RESULTS AND DISCUSSION

Average concentrations (mg/L) of heavy metal in milk around Owukpa mine fields are shown in Table 1.

Table 1: Heavy metal concentrations (mg/l) in Cow milk samples

SAMPLE	Cd	Cr	Fe	Mn	Ni	Pb
MS1	0.75±0.02[b]	1.59±0.01[c]	4.74±0.02[f]	2.25±0.01[d]	2.41±0.02[e]	ND
MS2	0.70±0.01[b]	1.58±0.02[d]	6.08±0.03[f]	2.17±0.01[e]	1.03±0.01[c]	0.66±0.01[a]
MS3	0.57±0.04[a]	2.76±0.01[e]	5.85±0.03[f]	1.70±0.01[c]	2.33±0.01[d]	0.95±0.03[b]
MS4	0.65±0.01[b]	2.64±0.02[f]	2.28±0.02[d]	2.11±0.02[c]	2.56±0.04[e]	ND
MS5	0.54±0.02[b]	0.79±0.02[c]	5.42±0.01[e]	2.00±0.02[d]	2.00±0.03[d]	ND
MS6	0.69±0.01[a]	2.89±0.01[e]	6.16±0.01[f]	2.22±0.01[c]	2.01±0.04[b]	2.62±0.01[d]
MS7	0.75±0.00[b]	0.73±0.01[b]	4.68±0.01[d]	2.45±0.01[c]	2.46±0.01[c]	ND
MS8	0.65±0.01[b]	1.76±0.02[c]	5.00±0.01[f]	2.13±0.01[e]	2.08±0.01[d]	ND
MS9	0.56±0.02[c]	0.48±0.04[b]	2.52±0.00[f]	1.71±0.00[e]	1.54±0.02[d]	ND
MS10	0.57±0.00[b]	1.06±0.02[c]	5.07±0.01[f]	2.11±0.01[d]	2.66±0.01[e]	ND
Mean±SD	0.64±0.01	1.63±0.02	4.78±0.02	2.09±0.01	2.11±0.02	0.42±0.00
Range	0.54 - 0.75	0.48 - 2.89	2.28 - 6.16	1.70 - 2.45	1.03 - 2.66	0.66 - 2.62

Results are expressed in mean ± standard deviation of triplicate determination. Results with same alphabet superscript show no significant difference while results with different alphabet superscript within the row show significant difference at $p < 0.05$. Where MS1 to MS10 represent Milk sample 1 to 10; ND = not detected.

The results of heavy metal analysis of cow milk samples from farms around Owukpa mine field revealed the following mean concentrations and range values of heavy metals: Cd: 0.64±0.01 mg/l (0.54 – 0.75 mg/l), Cr: 1.63±0.02 mg/l (0.48 – 2.89 mg/l), Fe: 4.78±0.02 mg/l

(2.28 – 6.16 mg/l), Mn: 2.09±0.01 mg/l (1.70 – 2.45 mg/l), Ni: 2.11±0.02 mg/l (1.03 – 2.66 mg/l), Pb: 0.42±0.00 mg/l (0.66 – 2.62 mg/l).

Table 2: Estimated Daily Intake (mg/day/kg.bw) of Heavy Metals in Cow Milk Samples

Age	Cd	Cr	Fe	Mn	Ni	Pb
Infant	0.023	0.095	26.500	3.256	0.127	0.018
Children	0.008	0.032	8.833	1.085	0.042	0.006
Adult	0.002	0.008	1.893	0.233	0.009	0.001

Table 3: Health Risk index (HRI)/ Carcinogenic risk of Heavy Metals in Cow Milk

	Cd	Cr	Fe	Mn	Ni	Pb
Health Risk index	0.4000	0.6330	0.0080	0.0120	0.8800	0.0860
Carcinogenic Risk	0.0025	0.0010	0.0054	0.0017	0.0015	0.0000

Cd, Cr, Fe, Mn, Ni and Pb were detected at varying concentrations in milks obtained from cows grazing around the coal mine with the exception of Pb which was not detected in sample MS1, MS4, MS5, MS7, MS8, MS9 and MS10 as presented in Table 1. This phenomenon may be attributed to the typically minimal presence of lead and cadmium in milk and dairy products, except in instances where animals have ingested contaminated feed [17]. Among all the milk samples, Fe exhibited the highest concentration, except for sample MS4, which showed an exception. Cd on the other hand, demonstrated the lowest concentration in all the samples.

Cadmium concentration was highest in sample MS1 and MS7 (0.75 mg/l) and lowest in sample MS5 (0.54 mg/l) as shown in Table 1 with mean concentration of 0.64±0.01. The value (0.002 - 0.11 mg/l) obtained from a similar investigation in milk and milk products in Nigeria by Iwegbue et al [7] were slightly lower compared to Cd concentration observed in this study. The values observed in this study were higher than the WHO permissible limit of 0.003 mg/l [18]. This suggests a red flag of the possible adverse effect that may arise from consumption of milk obtained from cow grazing around the coal mine as the coal mine is suspected to influence the high concentration recorded [12]. Cadmium is a non-essential element, plays no significant role during metabolism and is very toxic [19].

Highest chromium concentration was observed in sample MS6 (2.89 mg/l) and lowest in sample MS9 (0.48 mg/l) with mean concentration of 1.63±0.02 mg/l as shown in Table. 1. Mean Cr concentration observed in this study was slightly higher than 1.21 mg/l reported in milk and milk products in Nigeria [7]. However, the above mean concentrations are lower when compared to Cr concentration range of 4.54 - 9.86 mg/l in the work of Muhib et al [10]. The mean concentrations of Cr reported in this work are above Cr safe limit of 0.05 mg/l [18] Coal mining activities is suspected to have influenced the high concentration through food chain. Cr is essential for the metabolism of glucose, fat, and cholesterol. While it is harmful and carcinogenic at high concentrations, its lack results in hyperglycemia, increased body fat, and a drop in sperm count [20].

Iron concentration was highest in sample MS6 (6.16 mg/l) and lowest in sample MS4 (2.28 mg/l) with mean concentration of Fe of 4.78±0.02 mg/l as shown in Table 1. The concentrations of Fe in all milk samples were above the permissible limit of 0.37mg/l for cow milk [18]. This may arise from grazing cows on grass and water around the mining area. Other possible sources can be through feed, and farm packaging material. Despite the fact that milk has the least amount of Fe, it is nevertheless vital to the body's functioning. According to research, having low iron levels causes the body to absorb more cadmium. Therefore, it is important to pay special attention to getting enough iron [21]. Infant milk formula and certain powdered milk samples were discovered to have additional ingredients since an iron deficiency has been shown to reduce immunological activities and produce browning chemicals and the oxidized form of sulfur containing amino acids [22].

The concentration of Mn is presented highest in sample MS7 (2.45 mg/l) and lowest in sample MS3 (1.70 mg/l) with mean Mn concentration of 2.09±0.01 mg/l as presented in Table 1. The mean concentration of Mn was within the WHO permissible limit of 2-5 mg/l [18]. A similar investigation by Ogabiela et al [23] recorded a lower Mn concentration of 1.79 mg/l in milk obtained from cows grazed around Challawa Industrial Estate in Kano, Nigeria, where many tanneries are located. Results obtained were also found to be within the safe and adequate daily dietary intake limit. This suggests that mining and other industrial activities have the tendency of influencing Mn contamination in milk, Mn content in milk from cow around Owukpa coal mine is safe for consumption. Manganese just like other nutrients such as calcium, potassium is naturally found in cow milk. However high concentration may be ascribed to activities such as coal mining in the study area. Manganese plays an essential role in the development of both flora and fauna. Insufficient levels of manganese in mammals can lead to severe issues in their skeletal structure and reproductive health.

Elevated concentrations of manganese in the human body can have detrimental effects on the lungs and brain [24]. Compared to other micronutrient toxicity, poisoning is a very prevalent issue.

Nickel concentration was highest in sample MS10 (2.66 mg/l) and lowest in sample MS2 (1.03 mg/l) with the mean concentration of 2.11±0.02 mg/l as presented in Table 1. The mean concentrations for Ni obtained in this study were above the WHO limit of 0.02 mg/l in milk [18]. In a similar investigation by Iwegbue et al [7] in milk and milk products randomly sampled across Nigeria for both industrialized and non-industrialized area, presented Ni mean concentration was 0.03 mg/l which was slightly higher than the 0.02 mg/l limit in non-industrialized area and 1.94 for industrialized area [18]. The cause of contamination and higher Ni concentration in study area can be due to mining activities, as cows grazed on plants and drank from water bodies around the mine field. Nickel is an essential mineral element but when it exceeds its permissible limit, it is considered a toxin [9]. Excess intake can lead to enzyme alteration, cell damage and alteration of hormonal activities which can affect bioavailability of other mineral elements [25].

Lead was not detected in sample MS1, MS4, MS5, MS7, MS8, MS9 and MS10 milk samples. The highest Pb concentration was seen in sample MS6 (2.62 mg/l) and lowest in sample MS2 (0.66 mg/l) with mean concentration of 0.42± 0.01 mg/l as shown in Table 1. Various authors reported low Pb concentrations in milks obtained from cows in Nigeria. Ali and Abdelgadir [26] reported 0.63 mg/l for fresh cow milk samples obtained from different sites in Niger State, Nigeria. Iwegbue et al [7] observed that the concentration of Pb in milk and milk products in Nigeria varied from 0.002 - 0.40 mg/l. In similar report by Ogabiela et al [23], Pb concentration of 1.264 mg/l was observed in milk obtained from cows grazed around Challawa Industrial Estate, Kano. The values obtained from this study are above the WHO permissible limit of 0.02 mg/l by WHO [18] and that of Khan et al [27], which suggest mining activities is capable of influencing high concentration of metals in milk around the area. Other sources of Pb contamination may be related to feed and environmental composition of the study area. High levels of Pb have been linked to learning disabilities in youngsters [28]. Due to its high toxicity, it is crucial to monitor its presence in food. Lead buildup affects the activities of several enzymes and structural proteins in the human body [29].

Estimated Daily Intake

The Estimated Daily Intake of heavy metals was estimated based on the mean concentration of individual heavy metals and considering the average weight of infants (5 kg), Children (15 kg) and adult to be 70 kg person as shown in Table 2. The result of EDI of heavy metals (Ni, Fe, Cd, Cr, Pb and Mn,) was observed to be highest for infants. The trend of EDIs (mg/day/kg) for heavy metals analyzed in cow milk samples were observed to increase in the order: Fe (26.500, 8.833, 1.893) > Mn(3.256, 1.085, 0.233) > Ni(0.127, 0.042, 0.009) > Cr(0.095, 0.032, 0.008) > Cd (0.023, 0.008, 0.002) > Pb (0.018, 0.006, 0.001) for infant, children and adult respectively. Studying the contaminant's path from source to human system is key to estimating the degree of exposure. Oral consumption is thought to be the main route for exposure via the food chain [30]. WHO [18] set tolerable intakes for Cd, Cr, Fe, Mn, Ni and Pb to be 0.0600, 0.0160, 0.8, 0.66, 1.4 and 0.214 respectively [8]. This shows that estimated daily intake for Cd, Ni, and Pb were below the tolerable limit for the three categories considered. However, Cr, Fe and Mn daily intake were higher in the analyzed samples for infant, children and adult, except for Mn with lower EDI for adult.

The Health Risk Index

The Health Risk Index is a good indicator for assessing the danger of consuming metals through food chain [31]. The health risk assessment was evaluated for some metals (Cr, Cd, Fe, Mn, Ni, and Pb) as shown in Table 3 shows value less than 1. However, the figures are less than one [32]. Khan et al [27] stated that the population's health risk is acceptable if the HRI value is less than 1 (HRI < 1). The population is exposed to unacceptable health risk, if the HRI is equal to or greater than 1 (HRI ≥ 1) [32].

Carcinogenic Risk

The average daily consumption (mg/kg day) over a lifetime was multiplied by a cancer slope factor (SF) shown in Table 3 to get the cancer risk (CR) [33]. According to the USEPA [16], acceptable risk limits for carcinogens vary from 10^{-4} (risk of having cancer over the course of a human lifetime is 1 in 10,000) to 10^{-6} (risk of developing cancer over the course of a human lifetime is 1 in 1000000). For instance, a CR of 10^{-4} means that 1 in 10,000 people will acquire cancer. Table 3 shows Carcinogenic Risk values of 0.0015 (Ni), 0.0054 (Fe), 0.0025 (Cd), 0.0010 (Cr), BDL (Pb) and 0.0017 (Mn), all greater than 10^{-4}, except for Pb with zero CR. This suggests that consumption of cow milk in the area pose a significant risk of cancer. These call for concern due to their carcinogenicity except for Fe [34]. Mn however is known to be non-carcinogenic.

CONCLUSION

This study reveals that the concentrations of the analyzed metal Cd, Cr, Fe, and Pb except for Mn in the milk samples were above the WHO recommended permissible limit, which shows a strong correlation with results obtained for analysis carried out on soil, water and vegetable in the same area [35]. Also it is in agreement with high results observed in physicochemical parameters of water bodies in Owukpa [36]. The study further showed that while health risk index, carcinogenic risk and estimated daily intake investigation pose no serious immediate traits, it has disastrous long time effect on the environment and human health of inhabitants in the study area

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