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Seasonal Variation of Selected Mineral Elements in Raw Cow Milk obtained from Benin City, Nigeria

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ABSTRACT

Inter dependence exists between food quality indices and their supporting environment. Therefore, in this work, raw cow milk samples collected during the wet and dry seasons in Benin City, Nigeria, were investigated for some mineral elements. Specifically, zinc (Zn), copper (Cu), calcium (Ca), iron (Fe), chromium (Cr), cobalt (Co), cadmium (Cd) and lead (Pb) in the raw cow milk samples were investigated. It is discernible from results, that Ca with mean total of 121.680±19.386mg/kg for samples collected during the wet season and mean total of 120.822±13.762mg/kg for samples collected during the dry season, occurred most among the examined mineral elements. On the other hand, Pb with mean total of 0.027±0.009mg/kg for samples collected during the wet season and mean total of 0.017±0.004mg/kg for samples collected during the dry season was the lowest occurring. Results further indicated that variations occurred in the levels of occurrence of the examined mineral elements with respect to the season of sampling. The remarked variations were statistically significant ($P<0.05$). It is hoped that findings from this work would be beneficial to milk handlers.

Keywords: Digestion, Milk, Mineral elements, Nutrition, Toxicology

INTRODUCTION

Nigeria experiences two distinct weather conditions, viz: The dry and wet seasons. Varying inherent effects of these two weather conditions on humans and the environment are well known. Significantly, the dry season is associated with little or no rainfall, dusty environment and hotness. The drought associated with the dry season adversely affects the Nigerian vegetation. The severity however varies, depending on the duration of occurrence. The wet season on the other hand is associated with plenty rainfall, cold conditions and flourishing vegetation. Presently in Nigeria cattle ranching is not standardized as such and the dietary intake of the animals is poorly regulated. It is imperative to say that when cows are not confined to ranches wherein standardized diets could be fed to them, the chances exists that the various effects of the different weather conditions on their foliages and water would manifest in the compositional chemistry of milk obtained from the openly grazed lactating cows.

Investigations involving the use of milk as study material have been of continuous interest among researchers, considering the relevance of milk in the feeding habits of many persons worldwide. Notably, Choodamani *et al.* (2018) posited that infants and the elderly which constitute the vulnerable age group, consumes more milk and dairy products. Ensuring that milk and its products that reach consumers are safe, is therefore a matter of primary concern to researchers and milk handlers.

Literature report presented by Rezaei *et al.* (2014) noted that the safety of dairy products decreases with increasing concentration of toxic compounds and environmental pollutants, especially heavy metals. Apparently, the aforementioned factors that have been implicated as having adverse consequences on the safety of dairy products are promoted by increases in urbanization and industrialization; which most parts of the world are currently witnessing. The magnitude of environmental pollution associated with increases in urbanization and industrialization, could vary from country to country, depending on regional environment protection measures practiced.

In Nigeria and perhaps in some developing countries of the world, rising environmental pollution appeared to be poorly controlled, as the emphasis is on promotion of industrialization and other economic activities. Among the adverse consequences of poorly checked environmental pollution, is the contamination of the foliages and water fed to reared animals. The need for continuous monitoring of the compositional chemistry of the foliages and water fed to reared animals is important, both from nutritional and economic point of view. Also important, is the need to monitor the carcass and products from reared animals, as consumption of these materials if contaminated, could present significant challenges. According to Dibie and Ukhun (2018) dietary sources are significant means of human exposure to various mineral elements. If some of the ingested mineral elements are toxicologically relevant, then consumers could be at risk of suffering their toxic effects.

The interests of this study entailed investigations of raw cow milk samples collected during the wet and dry seasons in Benin City, Nigeria; for their levels of Cu, Zn, Ca, Fe, Cr, Co, Cd and Pb. It is imperative to mention that the levels of some mineral elements in milk samples collected elsewhere in the world, have been reported by Fatima *et al.* (2011); Ogabiela *et al.* (2011); Abdelkhalek *et al.* (2015); Ahamad *et al.* (2017) and Ziarati *et al.* (2018). However, the concern of this study has remained undressed by previous workers. Significantly, literature reports on the aspects of studies relating to effects of weather conditions on the mineral elements in raw cow milk as examined in this work are scarce. It is therefore hoped that findings from this work will be relevant in expanding the frontier of knowledge with respect to studied area.

The quantifications of Cu, Zn, Ca, Fe, Cr, Co, Cd and Pb levels in the studied raw cow milk samples will be spectrophotometrically carried out, using atomic absorption spectrophotometry. Additionally, data which the study will generate would be statistically analyzed. With respect to statistical evaluation of data that would be generated in this work, aspects of descriptive statistical evaluation of data and statistical determination of the relation between variables (ANOVA) would be carried out. Use would be made of International Business Machine (IBM) Statistical Package for Social Sciences.

MATERIALS AND METHODS

Samples Collection

Raw cow milk samples were obtained from lactating cows in Benin City, Nigeria. Samples collection was carried out on weekly basis in May, June and July which represented the wet season of the year, and also, on weekly basis in November, December and January, for the dry season of the year.

During each sampling operation, 200ml of raw cow milk samples were collected from five lactating cows and pooled together. The collections of the raw cow milk samples were carried out, using sterile plastic containers. The collected and pooled raw cow milk samples were placed in tightly corked sterile plastic containers and kept in cooler containing ice blocks. Subsequently, the cooler and its contents were taken to the laboratory. On arrival in the laboratory, prior to the actual sample pre-treatment and subsequent determinations of the examined mineral elements, the sterile plastic containers containing the milk samples were kept in a refrigerator, maintained at a temperature of 4ºC.

The digestion of the raw cow milk samples and subsequent investigations of the various digests for their levels of the examined mineral elements were done within twenty-four (24) hours of samples arrival in the laboratory.

Sample Digestion

The collected and cooled raw cow milk samples before digestion, were allowed to equilibrate to room temperature and subsequently homogenized. Thereafter, three of 10ml portions were separately measured into each of three digestion flasks that were subsequently pre-treated, after which they were subjected to wet digestion process, to produce triplicate digests.

The digestion of the raw cow milk samples entailed in part, the use of concentrated tri-acid (HNO_3-H_2SO_4-$HClO_4$) as digestion mixture. The preparation of the tri-acid mixture (HNO_3-H_2SO_4-$HClO_4$) used in this study, was in accordance with the method described by Esterfan *et al.* (2013), which entailed thorough mixing of concentrated HNO_3, H_2SO_4 and $HClO_4$ in the ratio of 10:1:4 and the mixture allowed to cool before use.

The actual digestion process involved the following procedures: 20ml concentrated H_2SO_4 was added to each of the 10ml raw cow milk samples contained in various digestion flasks. The flasks and their contents were subsequently swirled thoroughly. Thereafter the separate digestion flasks with a glass funnel placed in their respective neck, were placed on the surface of a thermostatically controlled hot plate. This was followed by gradual increase of the temperature of the hot plate to 145ºC and the heat maintained at this temperature for 30 minutes. Subsequently, the digestion flasks were removed from the hot plate and left to cool to room temperature. Thereafter, 10ml tri-acid mixture (HNO_3-H_2SO_4-$HClO_4$) was separately added to the cooled digestion flasks. They were subsequently swirled properly. This was followed by another process of heat treatment of the digestion flasks with their contents. With respect to the latter heat treatment, the temperature setting of the hot plate was gradually increased to 200ºC. Heating was maintained at this temperature for one hour, during which the colour of the individual digest mixture became clear.

At the completion of the digestion operation, each of the digestion flasks and its content were left to cool to room temperature. Thereafter, the content of each flask was transferred to separate 100ml volumetric flasks. Subsequently, deionized distilled water was added to each of the 100ml volumetric flasks, intermittent shaking was carried out, until the volume of the contents of each of the flasks reached the 100ml mark. Besides the raw cow milk samples, reagents blank that was subjected to similar digestion processes as were done with the samples and the subsequent volume make-up, was prepared for each batch of digests produced.

Measurements

The examined mineral elements in this work viz: Cu, Zn, Ca, Fe, Cr, Co, Cd and Pb contents in the studied raw cow milk samples, were quantified using atomic absorption spectrophotometer (Buck Scientific Model 210VGP), after the various raw cow milk samples were subjected to wet digestion. Operation of the buck scientific model 210VGP atomic absorption spectrophotometer was in accordance with the procedures provided by its manufacturer. Investigations of the levels of the examined mineral elements in the different diluted samples digests had been carried out, after similar investigations were carried out in series of corresponding suitable separate standards. The same atomic absorption spectrophotometer was used in all investigations. Calibration curves were produced using values obtained from the respective standards measured for the individual mineral element investigated.

Quality Control

Chemicals used in this work were all of analytical grade. Replicate measurements of at least three determinations were carried out. The method described by Ismail *et al.* (2017) was used to determine the limit of detection (LOD). Significantly, replicate blanks were digested in a manner similar to the method used for the digestion of the various milk samples. Subsequently, the levels of the examined mineral elements in the blank digests were measured. Buck scientific model 210VGP atomic absorption spectrophotometer that was used for the investigations of the examined mineral elements in the samples digests was also used for the determination of the corresponding mineral elements in the various blank digests. Similar equipment operating conditions were maintained in all cases. The values of the limit of detection for the various examined mineral elements in this work, were recorded.

The percentage recovery for each of the examined mineral elements was obtained in accordance with the method described by Ismail *et al.* (2017). The method entailed spiking known concentrations of standard solutions of the various examined mineral elements in the investigated milk samples. Thereafter, both the spiked and the non-spiked milk samples were analyzed in accordance with the procedures described earlier in this work, for the determinations of the various examined mineral elements. The aim was to calculate the percentage recovery for the examined mineral elements in the studied milk samples. Triplicate determinations were done and the average of the replicate measurements carried out, was used as the final concentration and subsequently, used for calculation.

The calculation of percentage recovery in the spiked milk samples was carried out using the equation described by Ismail *et al.* (2017), as presented in equation 1:

$$\% \text{ Recovery} = \frac{\text{Conc. in spiked milk} - \text{Conc. in non spiked milk}}{\text{spiked amount}} \times 100 \quad (1)$$

Data Analysis

Statistical analysis of data generated in this study was carried out. Aspects of descriptive statistical evaluation of data used were arithmetic means and standard deviation. Furthermore, one-way analysis of variance (ANOVA) was carried out to statistically evaluate the relation between the examined variables in this study. Confidence interval was set at $P<0.05$. Statistical evaluation of data was carried out using International Business Machine (IBM) Statistical Package for Social Sciences (SPSS).

RESULTS AND DISCUSSION

The results obtained in this study with respect to the investigations of raw cow milk samples collected during the wet and dry seasons in Benin City, for Cu, Zn, Ca, Fe, Cr, Co, Cd and Pb are presented in the Tables below. Specifically, the obtained levels of the examined mineral elements in raw cow milk sampled during the dry season are presented in Table 1. On the other hand, the levels of similar examined mineral elements in raw cow milk samples collected during the wet season, are presented in Table 2.

It is discernible from the results presented in Tables 1 and 2, that all the examined mineral elements in this study, were present in the investigated raw cow milk samples, though in varying amounts. At $P<0.05$, statistical significant difference occurred with respect to the levels of occurrence of the examined mineral elements. Additionally, at $P<0.05$, there were statistical significant differences in the levels of occurrence of the separately examined mineral elements with respect to the studied seasons of the year. However, at $P<0.05$, variations in the weekly obtained values for specific examined mineral elements within the same season of the year were not statistically significant

The safety of dairy products decreases with increasing concentration of toxic compounds and environmental pollutants, especially heavy metals (Rezaei *et al.*, 2014). Significantly, Swarup *et al.* (2005) remarked that lead is one of the most toxic heavy metals. Furthermore, Zaidan *et al.* (2013) posited that Cd toxicity in humans may lead to kidney failure, as well as liver and skeletal disorders. The relevance of the examinations of the levels of Pb and Cd in the studied cow milk samples, as well as the particular concern with respect to the occurrance of these two highly toxic mineral elements in the studied milk samples, could be viewed from these perspectives.

In this work, the results presented in Tables 1 and 2, showed that of all the examined mineral elements Ca with a mean total of 120.822mg/kg for raw cow milk samples collected during the dry season and a mean total of 121.680mg/kg for raw cow milk samples collected during the wet season occurred most. Milk has particularly been recognized by Lean (2006) as a rich source of Ca. Additionally, from the results presented in Table 1, it can be deduced that with respect to levels of occurrence of the examined mineral elements, Zn with a mean total of 2.980mg/kg for raw cow milk samples collected during the wet season and a corresponding mean total of 2.849mg/kg for raw cow milk samples collected during the dry season, was next to Ca. For the other examined mineral elements as findings also indicate, arrangement of their levels of occurrence in decreasing order is thus:

Fe (wet season = 0.667mg/kg; dry season = 0.682mg/kg); Cu (wet season = 0.107mg/kg; dry season = 0.086mg/kg); Co (wet season = 0.090mg/kg; dry season =0.067 mg/kg); Cr (wet season = 0.071mg/kg; dry season = 0.050mg/kg); Cd (wet season = 0.071mg/kg; dry season = 0.055mg/kg); Pb (wet season = 0.027mg/kg; dry season = 0.017mg/kg);

It would appear from the results presented in Tables 1 and 2, that higher mean total values were obtained for Ca, Zn, Cu, Cr, Co, Cd and Pb, in the studied raw cow milk samples collected during the wet season, compared to their corresponding mean total values in the investigated raw cow milk samples collected during the dry season. This observation could be ascribed in part, to the deposition of these mineral elements and perhaps their compounds from the atmosphere during wet season. Significantly, if the deposited compounds of these mineral elements are water soluble, or react with other constituents to give the soluble form, then they should enrich with respect to their levels, the water they come in contact with. The consequence appeared to be that the water enriched with contaminants among which are the examined mineral elements, probably came in contact with the plants the animals fed on; as well as the water they drank. Clearly, through the processes of absorption and simple physical mixing, the foliages the animals fed on and the water they drank, subsequently got enriched with the examined mineral elements and perhaps, other environmental pollutants. If chelating agents exist in the recipient water and plants, then the availability of soluble mineral elements to the consuming animals would be adversely affected. Otherwise, high levels of the soluble forms of the examined minerals will be found in the recipient environment where the cos from which the studied milk samples were obtained, were reared. It is therefore suggested, that these perspectives should be considered, in judging the levels of the examined mineral elements as presented in this work, especially, the environmental pollutant mineral elements.

In Nigeria, farming activities with respect to crops cultivations and maintenance, are carried out mainly during the wet season of the year. It is pertinent to mention that some of the farming activities, involved the use of Plant-Protective Agents (PPA) such as insecticides, fungicides, herbicides and fertilizers. These are chemical substances, and significantly, some of them are rich in certain mineral elements. Hence, the applications of such plant-protective agents on farms, are positive routes of transfer of concerned mineral elements to the plants cultivated on such farmlands. Apparently, grazed animals consumption of produce from the plants treated with PPAs and the plant wastes arising from farms wherein the PPAs were used, should increase their in-take of mineral elements contained therein. Definitely, if the animals that fed on such foliages or drank the water contaminated by the PPAs are lactating, some of the ingested mineral elements would be found in the milk obtained from them. This, therefore, appeared to account even if in parts, the levels of the examined mineral elements in the studied raw cow milk samples, particularly those bearing relationship with environmental pollution.

In the period covering the wet season of the year, there is increased run-offs from various locations. The run-offs would apparently, dissolve soluble components of the materials they come in contact with. The dissolved substances, if they contained mineral elements, would release these mineral elements into the run-off water. Worthy of note is that some of the run-off water could be consumed by the openly grazed cows. The consumption of water enriched with mineral elements apparently, would mean greater in-take of mineral elements; some of which eventually, found their way into the milk of the lactating cows. Also, the run-off water enriched with mineral elements, would most likely increase the mineral elements of the foliages they come in contact with. Again, the openly grazed cows feed on these foliages. These considerations adduced further explanations for the reported higher mean total of Ca, Zn, Cu, Cr, Co, Cd and Pb in the investigated raw cow milk samples collected during the wet season, compared to the results obtained in this work, for the investigated raw cow milk samples collected during the dry season.

The mean total of 0.682mg/kg obtained for Fe in the studied raw cow milk samples collected during the dry season, was higher than the mean total of 0.667mg/kg obtained for Fe, in the raw cow milk samples collected during the wet season. It is therefore difficult to explain this observation, based on the explanations adduced for the results obtained for the other mineral elements examined in the work. It would appear however, that chemical transformations which adversely affected the release of Fe occurred more during the wet season than the dry season. Significantly, what predominates between the supply of the examined mineral elements and the various chemical transformations that could hinder their release, are factors of relevance in the overall availability of the examined mineral elements.

According to the report of Malhat *et al.* (2012), in Egypt, Cu level in milk samples was 1.451µg/g. In Croatia, Bilandžič *et al.* (2011) reported Cu level in milk samples to be 0.914µg/g. The results we obtained in this study, indicated mean total of Cu in raw cow milk samples collected in wet season to be 0.107mg/kg (0.107µg/g) and 0.086mg/kg (0.086µg/g) as the mean total of Cu in raw cow milk samples collected during the dry season. Comparatively, the mean total of Cu in raw cow milk samples collected during the wet and dry seasons in Benin City, Nigeria, were lower than the various reported values for Cu by Malhat *et al.* (2012) and Bilandžič *et al.* (2011) in milk samples obtained in Egypt and Croatia. Varying authorities have proposed different maximum limit for Cu in milk. In particular, IDF (1979) proposed maximum limit of Cu in milk is 0.01µg/g. On the other hand, Puls (1994) proposed a range of 0.1-0.9µg/g for Cu in milk. What is discernible here, is that the levels of Cu in raw cow milk samples collected in both the wet and dry seasons which we investigated, were higher than the maximum limit stipulated by IDF (1979), but within the range proposed by Puls (1994). Differences in the levels of urbanization, industrialization and control measures put in place to check the exposure of cows to contaminated foliages and the water they drank, are responsible for the reported variations in the amount of Cu in milk samples collected from the regions of Egypt, Croatia and Benin City (Nigeria).

Findings from this study further revealed that the mean total of Co in the investigated raw cow milk samples collected during the wet season was 0.090mg/kg (0.090µg/g), while the mean total of Co in raw cow milk samples collected during the dry season was 0.067mg/kg (0.067µg/g). Compared to the reports of some other researchers, Co levels in the milk samples we investigated are discerned to be lower than the 0.19µg/g Co level in cow milk samples from India, as was reported by Patra *et al.* (2008). On the other hand, they were higher than the 0.006µg/g which according to Khan *et al.* (2014) was Co level in milk samples collected from Korea. Rey-Crespo *et al.* (2013) reported that in milk samples obtained from Spain, the levels of Co was 0.005µg/g. This value is much lower than the levels of Co in the milk samples we investigated. Even if partly, the variations in the levels of Co in milk samples reported by the different researchers, could be ascribed to differences in the compositional chemistry of what the lactating cows, from which the milk samples were collected consumed, in addition to the health of the cows from which the various milk samples were obtained. Additionally, the type and amount of drugs administered to the lactating cows, the breed of cows and pollution levels in the different studied regions, could have influenced the results obtained for Co in milk samples collected from the different regions.

Cobalt has both nutritional and toxicological relevance, depending on its level of occurrance. Significantly, it is one of the constituents of Vitamin B12, which makes it nutritionally desirable. However, exceeding the threshold of Co could result in serious health challenges especially as according to IARC (1991) classification, Co is listed as a possible carcinogenic substance. Furthermore, Nordiberg *et al.* (2007) posted that when Co is present in excess, it could disturb the reproductive system and the thyroid glands. The health challenges associated with excess in-take of Co suggest obviously, that the ingestion of foods rich in Co should be done with caution, to avoid exceeding the threshold limit.

Portion of findings in this work indicated that in the studied raw cow milk samples collected during the wet season, mean total value for Cd was 0.071mg/kg (0.071µg/g), while for the raw cow milk samples collected during the dry season, mean total value for Cd was 0.055mg/kg (0.055ug/g). Some researchers have also investigated the levels of Cd in milk samples. Significantly, Erib *et al.* (2009) reported that in bovine milk samples obtained from Egypt, mean value for Cd was 0.086µg/g. Also, Ogabiela *et al.* (2011) posited that in milk samples collected from cows grazed around Challawa industrial estate of Kano (northern Nigeria), mean Cd value was 0.131µg/g. Furthermore, in milk samples obtained from Poland, Pilarezyk *et al.* (2013) noted that the value of Cd was 0.004µg/g. Also, according to Bilanžič *et al.* (2011), Cd level of occurrance in milk samples obtained from Croatia was 0.003µg/g. The apparent variations in the levels of Cd in milk samples studied by the different workers are attributed to the levels of industrialization and urbanization, with respect to the various regions the studied milk samples were collected; as well as season of sample collection as revealed in this study, prevailing pollution level in samples collection area, health status of the cows from which the investigated milk samples were collected, and the compositional chemistry of diets the cows were fed with. It is further perceived that the constituents of the water the cows drank could be factors of importance in explaining the variations in Cd levels in milk, as reported by different researchers.

Table 1: Concentration of Mineral Elements (mg/Kg) In Raw Cow Milk Samples Obtained During Wet Season

MINERAL ELEMENTS	**PERIOD OF SAMPLING**														
	MAY					**JUNE**					**JULY**				**MEAN TOTAL**
	WK 1	WK 2	WK 3	WK 4	MEAN	WK 1	WK 2	WK 3	WK 4	MEAN	WK 1	WK 2	WK 3	WK 4	MEAN	
Cu	0.104 ± 0.046	0.110 ± 0.031	0.098 ± 0.025	0.092 ± 0.011	0.101	0.110 ± 0.052	0.106 ± 0.021	0.108 ± 0.016	0.111 ± 0.074	0.109	0.112 ± 0.038	0.103 ± 0.041	0.110 ± 0.024	0.113 ± 0.055	0.110	0.107 ± 0.047
Zn	2.943 ± 0.286	2.985 ± 0.141	2.994 ± 0.403	2.960 ± 0.093	2.971	2.885 ± 0.064	2.994 ± 0.182	2.988 ± 0.366	2.997 ± 0.256	2.966	3.001 ± 0.682	2.995 ± 0.311	3.006 ± 0.084	3.011 ± 0.296	3.003	2.980 ± 0.091
Ca	120.884 ± 19.786	121.093 ± 11.472	121.114 ± 6.337	121.646 ± 15.702	121.184	120.558 ± 10.329	121.743 ± 4.228	121.896 ± 16.517	122.085 ± 8.669	121.571	122.108 ± 20.773	121.934 ± 11.626	122.538 ± 7.394	122.659 ± 15.081	122.285	121.680 ± 19.386
Fe	0.619 ± 0.224	0.625 ± 0.108	0.638 ± 0.091	0.651 ± 0.117	0.633	0.661 ± 0.112	0.653 ± 0.208	0.671 ± 0.054	0.684 ± 0.225	0.667	0.689 ± 0.121	0.695 ± 0.248	0.701 ± 0.033	0.715 ± 0.192	0.700	0.667 ± 0.108
Cr	0.058 ± 0.016	0.065 ± 0.009	0.069 ± 0.025	0.068 ± 0.031	0.065	0.066 ± 0.011	0.064 ± 0.023	0.071 ± 0.031	0.073 ± 0.014	0.069	0.076 ± 0.008	0.073 ± 0.014	0.081 ± 0.031	0.084 ± 0.022	0.079	0.071 ± 0.012
Co	0.084 ± 0.036	0.081 ± 0.022	0.089 ± 0.006	0.092 ± 0.014	0.087	0.086 ± 0.043	0.088 ± 0.015	0.091 ± 0.036	0.094 ± 0.021	0.090	0.085 ± 0.017	0.090 ± 0.031	0.095 ± 0.024	0.098 ± 0.032	0.092	0.090
Cd	0.062 ± 0.014	0.062 ± 0.021	0.064 ± 0.009	0.065 ± 0.028	0.063	0.068 ± 0.031	0.069 ± 0.018	0.072 ± 0.013	0.074 ± 0.025	0.071	0.073 ± 0.011	0.078 ± 0.029	0.082 ± 0.033	0.085 ± 0.016	0.080	0.071
Pb	0.019 ± 0.002	0.023 ± 0.008	0.023 ± 0.004	0.025 ± 0.009	0.023	0.025 ± 0.011	0.023 ± 0.006	0.026 ± 0.003	0.028 ± 0.005	0.026	0.029 ± 0.002	0.031 ± 0.014	0.034 ± 0.009	0.037 ± 0.012	0.033	0.027 ± 0.009

WK 1 = Week 1; WK 2 = Week 2; WK 3 = Week 3; WK 4 = Week 4

Table 2: Concentration of Mineral Elements (mg/Kg) in Raw Cow Milk Samples Obtained During Dry Season

MINERAL ELEMENTS	PERIOD OF SAMPLING															
	NOVEMBER					DECEMBER					JANUARY					MEAN
	WK 1	WK 2	WK 3	WK 4	MEAN	WK 1	WK 2	WK 3	WK 4	MEAN	WK 1	WK 2	WK 3	WK 4	MEAN	TOTAL
Cu	0.106 ± 0028	0.095 ± 0.041	0.109 ± 0.008	0.088 ± 0.022	0.100	0.092 ± 0.014	0.085 ± 0.036	0.076 ± 0.025	0.079 ± 0.048	0.083	0.068 ± 0.031	0.074 ± 0.018	0.077 ± 0.029	0.084 ± 0.046	0.076	0.086 ± 0.016
Zn	2.997 ± 0.441	2.916 ± 0.283	2.904 ± 0.096	2.883 ± 0.117	2.925	2.936 ± 0.085	2.810 ± 0.152	2.759 ± 0.356	2.608 ± 0.109	2.778	2.695 ± 0.311	2.852 ± 0.213	2.911 ± 0.468	2.918 ± 0.152	2.844	2.849 ± 0.128
Ca	120.564 ± 8.391	121.622 ± 5.778	122.851 ± 12.644	119.893 ± 3.672	121.233	121.204 ± 11.048	118.942 ± 6.102	122.623 ± 8.014	120.318 ± 15.594	120.772	118.269 ± 3.565	122.077 ± 12.614	120.387 ± 7.115	121.109 ± 17.011	120.461	120.822 ± 13.762
Fe	0.593 ± 0.114	0.741 ± 0.268	0.713 ± 0.094	0.648 ± 0.172	0.674	0.706 ± 0.245	0.691 ± 0.168	0.712 ± 0.114	0.694 ± 0.085	0.701	0.683 ± 0.211	0.724 ± 0.098	0.652 ± 0.264	0.618 ± 0.125	0.670	0.682 ± 0.094
Cr	0.068 ± 0.021	0.063 ± 0.015	0.059 ± 0.008	0.061 ± 0.019	0.063	0.053 ± 0.011	0.049 ± 0.018	0.043 ± 0.009	0.038 ± 0.013	0.046	0.033 ± 0.014	0.037 ± 0.008	0.041 ± 0.005	0.047 ± 0.012	0.040	0.050 ± 0.008
Co	0.094 ± 0.018	0.091 ± 0.025	0.086 ± 0.009	0.078 ± 0.026	0.087	0.073 ± 0.013	0.065 ± 0.019	0.054 ± 0.008	0.050 ± 0.021	0.061	0.046 ± 0.014	0.051 ± 0.018	0.053 ± 0.009	0.058 ± 0.011	0.052	0.067 ± 0.014
Cd	0.061 ± 0.012	0.061 ± 0.019	0.058 ± 0.021	0.056 ± 0.007	0.059	0.056 ± 0.017	0.054 ± 0.008	0.052 ± 0.011	0.050 ± 0.020	0.053	0.048 ± 0.009	0.050 ± 0.013	0.053 ± 0.018	0.055 ± 0.022	0.052	0.055 ± 0.006
Pb	0.022 ± 0.006	0.021 ± 0.009	0.018 ± 0.003	0.017 ± 0.005	0.020	0.017 ± 0.008	0.015 ± 0.002	0.014 ± 0.005	0.014 ± 0.003	0.015	0.013 ± 0.001	0.015 ± 0.006	0.019 ± 0.004	0.020 ± 0.007	0.017	0.017 ± 0.004

WK 1 = Week 1; WK 2 = Week 2; WK 3 = Week 3; WK 4 = Week 4

It is discernible from our findings and the report of Ogabiela *et al.* (2011) that even within the same country, the levels of Cd in milk samples varied. This observation clearly emphasize the relevance of sampling points to Cd level in milk samples. Worthy of note is that the milk samples used in the present study were obtained from cows grazed around residential areas in Benin City, Nigeria. Significantly, Benin City is located in the southern part of Nigeria. On the other hand, as reported in their work, Ogabiela *et al.* (2011) studied milk samples collected from cows grazed around Challawa industrial estate of Kano (northern Nigeria). The influence of pollution arising from industrial activities especially around the immediate environment appeared significant here. It is imperative therefore, that in reporting sampling areas, researchers should emphasize on the specificity of sampling points. Of significance also, is that in choosing grazing areas for cows meant for human consumption, proximity to industrial area should be considered.

Literature reports with respect to the levels of Pb in milk samples obtained from the different regions of the world are well documented. Significantly, Farid and Baloch (2012) noted that heavy metals (cadmium, chromium, lead and nickel) concentrations in milk obtained from Pakistan were higher than the concentrations considered suitable for human consumption. Furthermore, Malhat *et al.* (2012) reported that in milk samples obtained in Egypt, lead value was 4.404µg/g. Interestingly also, in milk samples obtained from Egypt, Sayed *et al.* (2011) reported mean level of Pb in the milk samples they investigated to be 0.327µg/g. In this study, mean total value for Pb in milk samples collected during the wet season was 0.027mg/kg (0.027µg/g) and the corresponding mean total for Pb in milk samples collected during the dry season was 0.017mg/kg (0.017µg/g). Apparently, the values reported for Pb in the raw cow milk samples studied in the work, are lower than the values reported by both Malhat *et al.* (2012) and Sayed *et al.* (2011) in milk samples obtained from Egypt which they investigated. Significantly, differences in regional practices with respect to contamination monitoring and control, urbanization, industrialization, pollution levels at the sites where the cows from which milk samples were collected were grazed; as well as the health status of the lactating cows from which the milk samples were obtained and the medications administered to them, could have been responsible for the observed differences in the results reported by the various researchers.

In Iran as reported by Najarnezhad and Akbarabadi (2013), Pb level in cow milk they investigated was 0.012µg/g. Remarkably, Khan *et al.* (2014) had also reported that Pb level in milk samples obtained from Korea was 0.004µg/g. These values are lower than the various mean total values of Pb in cow milk samples investigated in this work. In addition to the earlier adduced reasons for the variations in Pb levels in milk samples investigated in this work and the milk samples from Egypt that were investigated by Malhat *et al.* (2012) and Sayed *et al.* (2011), the year of sampling and characterization could also be relevant in explaining the various results. Significantly, Swarup *et al.* (2005) posited that the level of Pb in milk and milk products is increasing day by day. This should be of concern to both milk handlers and policy makers, if milk and milk products are to be made available to consumers devoid of Pb toxicity.

The maximum permissible limit for Pb in milk according to Codex Alimentarius Commission (2011) report is 0.02µg/g. Thus, the mean total value of 0.027mg/kg (0.027µg/g) obtained for Pb in the milk samples collected during the wet season and characterized in this work, was higher than the aforementioned permissible limit. On the other hand, the mean total value of 0.017mg/kg (0.017µg/g) obtained as Pb level in the investigated milk samples collected during the dry season in this work, is lower than the stipulated permissible limit for Pb in milk, as stated by Codex Alimentarius Commission (2011). Clearly, Pb is a highly toxic mineral element. In particular, Swarup *et al.* (2005) remarked that Pb is one of the most toxic heavy metals. Expectedly, the safety of food made available to consumers should be a matter of paramount importance to both food handlers and policy makers. Therefore, it is imperative that with respect to the studied area in this work, measures should be put in place to avoid the escalation Pb contents of milk and perhaps, its derived products made available to consumers.

CONCLUSION

The mean total for each of Cu, Zn, Ca, Fe, Cr, Co, Cd and Pb in raw cow milk samples obtained in Benin City, Nigeria, during the wet and dry seasons of the year were determined and reported in the study. Findings showed that Ca, Zn, Cu, Cr, Co, Cd and Pb occurred more in milk samples collected during the wet season, compared to their various occurrance levels in milk samples collected during the dry season. Iron was however found to occur more in milk samples collected during the dry season, compared to the result obtained in milk samples collected during the wet season. It is hoped that findings from this study will be relevant to milk handlers, especially those involved in raw milk collection, storage and processing. It is further believed, that policy makers would find the outcome of this research work useful in policies formulations, especially as it relates to raw cow milk handling.

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