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Seasonal Evaluation of Mineral Elements, Heavy Metals, Essential Amino Acids, Proximate Compositions and Pesticides in Goat Milk

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Abstract Samples of goat milk were collected from different locations of Kano state in wet and dry seasons. The samples were analysed for mineral elements, heavy metals, essential amino acids, proximate compositions and persistent organic pollutants using standard methods of chemical analysis. The flame atomic absorption spectrometry (FAAS) results indicated that the mean concentrations of calcium and magnesium in the samples are 329±15.66 mg/kg and 118±8.75 mg/kg respectively. These values are above the National Environmental Standards Regulations Enforcement Agency (NESREA) set values for food, drug and beverages. The mean concentrations of zinc, copper and nickel in the samples were 2.01±0.29, 0.69±0.02 and 0.89±0.12 mg/kg respectively. These values were slightly above the standard. The mean levels of lead, cadmium and chromium in the samples were 0.02±0.003, 0.02±0.004 and 0.01±0.003 mg/kg respectively. This implies that the samples were rich in mineral elements and essential metals and safe from toxic metals contaminations. The chromatographic analysis for essential amino acids in the samples revealed high concentrations of lysine, histidine, threonine, valine, methionine, leucine, isoleucine and phenylalanine of 7.58, 2.78, 4.22, 5.23, 3.31, 6.99, 9.04 and 4.00 in g/100 g protein respectively compared to Food and Agriculture Organization (FAO) and World Health Organization (WHO) standards values. The Pearson correlation coefficient analysis was performed using MATLAB student version IV software, the results indicated strong and moderate positive correlations between mineral elements and essential amino acids while weak and low correlations were observed between essential metals and toxic metals, this showed the strong metal binding property between the amino acids, mineral elements and essential heavy metals, all the values were determined at significant level of $P \geq 0.05$. The gas chromatography-mass spectrometry analysis of the organochlorine pesticides in the samples indicated that the level of pesticides were below the detection limit (BDL) for both seasons. This indicated that the samples of this study were free from the pesticides contamination; this could be attributed to restriction and compliance for the usage or the economy because most of these pesticides are very expensive.

Keywords: *goat, milk, mineral elements, heavy metals, amino acids, persistent organic pollutant*

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1. Introduction

Food safety, and in particular safety of products of animal origin, is an increasingly important issue concerning human health. With increase in the consumption of products of animal origin the risk of food borne diseases of humans also increases. The raw food movement, characterized by eating raw rather than cooked food has increased the awareness of consumption of raw food. One product that is commonly distributed in raw form is milk. Milk can become contaminated in many ways. For example, if the dairy animal has mammary gland infection (mastitis) or systemic infection, the pathogen can be passed to the milk. Milk can become contaminated by the faeces of the animals and the hand of the milker usually during hand milking procedure, by using pesticides or by equipment used for milk collection and storage.

Milk has been known as nature’s most complete food. However, the traditional and contemporary view of the role of milk has been remarkably expanded beyond the horizon of nutritional subsistence of infants. Milk is more of a source of nutrients for any neonate of mammalian species, as well as for growth of children and nourishment of adult humans. Aside from nutritional values, milk borne biologically active compounds such as casein and whey proteins have been found to be increasingly important for physiological and biochemical functions that have crucial impacts on human metabolism and health ([1,2,3]). Cattle milk has been the major source of milk and dairy products in developed countries, especially in the Western world, although more people drink the milk of goats than that of any other single species worldwide ([4,5,6]).

Goats (*Capra aegagrus hircus)* were the first species to be domesticated as livestock about 8000 BC in Mesopotamia, part of today's Middle East. For centuries, humans have used goats for many purposes in all continents. However, the goat sector has not been well supported worldwide compared with other animal production sectors, especially the cattle's milk sector, despite the fact that in the last few decades the goat has emerged as one of the major livestock species, rising in numbers compared with others [7].

The present total world population of 921 million goats is found mainly in areas with temperate pasture-growing conditions [8]. It is estimated that Asia and Africa together account for as much as 91.5 % of the world's total goat population, while the corresponding figure for Oceania and Europe together is 2.4 %. Goat milk production represents about 2.2 % of total world milk production [7], while in 2009 sheep milk comprised 1.3 % and camel milk 1.3 % [9]. However, on world basis, more people drink goat milk than milk from any other single species, despite the fact that dairy cattles produce the greatest amount of the world's milk, mostly in developed countries [10]. According to Food and Agriculture Organization data for 2009, 59 % of world goat milk production was produced in Asia, 21 % in Africa, and 16 % in Europe [9]. Goat milk production has been increasing during recent years: in 2010 globally by 0.2 %, with the greatest increases in France (6.4 %) and Turkey (3.5 %), but decreases in the Netherlands (–8.6 %), Spain (–2.9 %), and Mexico (–1.0 %). According to current US Department of Agriculture data, the USA has 2.86 million head of goats with 360 000 milk goats [11]. Dairy goat farming is vital sector of agricultural business in developed countries of the Mediterranean region, where 16 % of the world's goat milk is produced [12].

Milk composition varies according to genotype, individuality, stage of lactation, parity, season, feeding, management, reproduction, and sanitary characteristics of animals, locality, and socioeconomic environment [13]. These are the reasons for deviations in compositional data for goat milk presented by different authors. In addition, [14] determined high level of variability in biochemical composition, bacteriological quality, and technological properties of goat milk collected during 1 year from different European countries (Greece, Portugal and France). In local breeds, not bred for high milk production, milk composition is often similar to that of sheep, having very high dry matter (DM) content (135–175 g/kg), fat (45–65 g/kg), and crude protein (40–55 g/kg). Dairy breeds like Saanen, Alpine, and Toggenburg with high milk yields give milk that is low in DM (110–135 g/kg), often due to low levels of fat (30–40 g/kg) and crude protein (27–35 g/kg) [15].

Minerals are inorganic substances, present in all body tissues and fluids and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life. Minerals are chemical constituents used by the body in many ways. Although they yield no energy, they have important roles to play in many activities in the body ([16,17]). Every form of living matter requires these inorganic elements or minerals for their normal life processes [18,19]. Minerals may be broadly classified as macro (major) or micro (trace) elements. The third category is the ultra trace elements.

The term "heavy metals" has been used in environmental legislation publications related to chemical hazards and the safe use of chemicals [20]. This term is universally used by scientists ([21,22,23,24,25]). Ref [26] defined heavy metals as elements with density exceeding 6 g cm^{-3}. Recently, ref [27] defined the term "heavy metal" as any metallic chemical element that has specific density of more than 5 g cm^{-3} and is toxic or poisonous at low concentrations. Heavy metals were defined as collective term for metals of high atomic mass, particularly those transition metals that are toxic and cannot be processed by living organisms, such as Pb, Hg, and Cd. However, there are some definitions based on the atomic number such as any metal with an atomic number beyond calcium [28]. Ref [29] defined them as metals with atomic number between 21 (scandium) and 92 (uranium).

Proteins have many functions in the organism and constitute key compounds for survival of animals and humans. Proteins are naturally constituted by 20 amino acids, which act as basic components of the polymeric structure. Once proteins are ingested, amino acids are released by enzymatic digestion and absorbed into the body. Protein quality strongly depends on its amino acid content and digestibility [30]. Amino acids participate in many biochemical pathways for growth, maintenance, and metabolic activity of cells and organs and their requirements vary, depending on the stage of life [31]. However, the quality of proteins may be affected by processing and storage [32,33].

The term ''pesticide'' covers wide range of substances that belong to many completely different chemical groups. The Food and Agriculture Organization [34] of the United Nations has defined pesticide as substance or mixture of substances intended to prevent, destroy or control any pest. Also included in the FAO definition are chemicals intended for use as plant growth regulators, defoliants or desiccants, even though they are neither normally employed as pest control agents nor usually effective as such. Pesticides include great variety of chemicals used widely in agriculture since significant economic damage can occur when insects, nematodes, fungi and other macro and microorganisms affect food and commodity crops [35]. Large scale use of pesticides began after World War II, when the agriculture production of food accelerated. Ref [36] observed that more than 800 active substances are currently formulated in pesticide products.

2. Materials and Methods

2.1. Study Location, Samples Collections and Preservation

This study was conducted in Kano and its environs; Kano is located within the Sudan Savannah Zone of Nigeria in West African sub-Saharan region. The area is situated between longitude 9° 30'and 12° 30'North, and latitude 9°30' and 8°42' East. The climate is characterized by dry and wet seasons. The dry season stretches from October to April, while the wet season is from May to September. The annual rainfall and temperature is between (787 and 1293 mm) and (14 and 41°C) respectively [37]. Samples were collected from goats at different locations of Kano state in an interval of two (2) weeks in wet and dry seasons. Six (6) sampling locations were used for the collection of milk which comprises of farms, markets and free ranches. In all the sampling locations, six lactating goats (0 - 6 months of lactation) were selected for the collection of milk. The milking was done by hand in the morning between 08:00 - 09:00 hr and directly into polyethylene bottles; this was combined to form the bulk composite sample. This procedure was repeated at an interval of two (2) weeks for six (6) consecutive times in wet and dry seasons in all the sampling locations. The samples collected (in a label plastic sample bottles) were kept in a cooler containing ice, transported to the laboratory and stored in a deep-freezer (below 4 °C) to await analysis [38].

2.2. Samples Preparation for Metal Analysis

About 10 cm^3 of milk sample was weighed into porcelain crucible and evaporated to dryness on a hot plate. The dried milk samples were ashed in muffle furnace at 550 °C for 8 hours. The ash was dissolved in 10 cm^3 of 1mol dm^{-3} HNO_3 and filtered. The dissolved residue was made up to the mark with distilled water [39].

2.3. Preparation of Standard Stock Solutions

The 1000 mg L^{-1} Mg stock standard solution was prepared by dissolving 5.0695 g $MgSO_4.7H_2O$ in about 400 ml of a 0.1 mol L^{-1} H_2SO_4 solution and filling the volume up to 500 cm^3 with distilled water. The 1000 mg L^{-1} Ca stock standard solution was prepared by dissolving 1.1488 g $CaCO_3$ in 5 cm^3 of a 1:1 (v/v) hydrochloric acid solution; after gas evolution, the volume was filled up to 500 cm^3 with distilled water. Similar procedure was conducted for all the heavy metals standard solutions which were prepared by diluting the stock solutions (1000 mg L^{-1}) in 10 % hydrochloric acid. All working standard solutions were stored in polypropylene bottles.

2.4. Analysis

Flame atomic absorption spectrometer (FAAS) machine (Perkin – Elmer 1110B) was used to measure the concentrations of metals and heavy metals present in the samples, as this is commonly used technique for determining metals in environmental samples. Ash, protein, fat, moisture and total solids content were determined according to the method described by Association of official Analytical Chemists [40]. The amino acids profile of milk samples were determined using method described by [41]. The samples were dried to constant weight, defatted, hydrolysed, evaporated in rotary evaporator and loaded into the Technicon Sequential Multi-Sample Amino Acid Analyser (TSM). The model of the machine used is DNA O2O9. The quick, effective, cheap, easy, rugged and safe (QuEChERS) method was chosen to be the method to determine the persistent organic pollutants (POPs) in the milk samples of the animals [42]. The extract was centrifuged to remove the fatty matrix, the resulting solution was analysed for pesticides using Gas chromatography/mass spectroscopy (GC/MS). GC/MS is used world-wide as an analytical method for screening, identification, and quantification of various chemicals. GC/MS analysis is particularly suitable for identification and quantification of chemicals used for food materials. Quantification of the residual or migration levels of such chemicals is important for safety assurance and specification testing for national regulatory purposes in many countries.

3. Results and Discussion

Figure 1 and Figure 2 showed the concentrations of mineral elements and heavy metals in the milk samples for wet season. The results indicated higher values of calcium concentrations in the milk which ranged from (162 - 702 mg/kg) and magnesium ranged between (89 - 172 mg/kg) in the milk samples. The concentrations of calcium and magnesium in the samples compared to NESREA value; this could be due to good provision of feed, quality fodder and water in the farm. The value of calcium and magnesium in goat milk in this research were slightly lower than the reported value by [43]. Milk and other dairy foods are the major source of calcium in Nigeria. It helps nerves to conduct messages; muscle contractions; blood clotting and signaling the heart muscle [44]. On the other hand, magnesium activates 100 enzymes and play role in over 300 enzyme reactions in the body, many of which is directly related to cardiovascular health and help nerves and muscles function. The values of heavy metals were in two folds; the Zn, Cu and Ni were slightly above the NESREA values. The highest values of zinc were obtained from K/Mazugal (2.30 mg/kg) while the low levels were found in the milk collected from U/Uku (1.67 mg/kg), the high value of Zn in K/Mazugal may be attributed to the discharges in Jakara river which is very close to the location where the animals are drinking water from the river. The concentration of Zn can be compared with those reported by [45]. A possible source of contamination of zinc in milk is used metal cans and milk processing equipment [46]. The values of Cu obtained were greater than the reported values by [43] in goat milk. Possible contamination of milk with copper can occur from animal feed, high copper content in animals drinking water and also from copper bearing and copper alloys equipment [47]. The mean concentration of lead in the samples was 0.016 mg/kg, the highest value was found in samples collected from U/Uku (0.021 mg/kg) and the lowest was observed in samples collected from Danmaraya farm (0.010 mg/kg). This can be attributed to the high level of vehicle exhaust causes by heavy traffic at U/Uku. The mean concentration of cadmium in the sample was 0.02 mg/kg, the highest value of Cd was obtained at K/Mazugal (0.018 mg/kg) and the lowest was found in the samples collected from FCE, Kano farm (0.010 mg/kg). The Pb and Cd concentration in the milk samples were below the tolerable limits as reported by [48], these indicated that the milk samples were not contaminated with this metal although no amount of contamination is ignored, especially with lead in order to avoid the effect of accumulation.

Figure 3 and Figure 4 showed the results of mineral elements and heavy metals in dry season. The results showed that the highest concentration of calcium in the milk samples was from FCE, Kano farm (682 mg/kg) and the lowest concentration was obtained at U/Uku (160 mg/kg). The highest magnesium concentrations were obtained in milk samples collected from FCE, Kano farm (171 mg/kg) while the lowest value was obtained at U/Uku (85 mg/kg). The difference in the concentrations may be attributed to the managerial condition and feed intake, because FCE, Kano farm have better feeds and managerial services compared to U/Uku which is just an animal's market where the animals are kept for sales only. The results indicated that the calcium and magnesium have occurred in the samples in high concentrations while the level of heavy metals is almost the same as that of wet season. In comparison with the National Environmental Standards and Regulations Enforcement Agency (NESREA), the calcium and magnesium concentrations were found to be much higher in the milk than the values set by the standard organisation; this indicated that the milk collected is rich in mineral elements. Other heavy metals, Zn, Cu, Cd and Ni means concentrations in the milk relatively equaled the standard values of NESREA. The Pb and Cr concentrations were lower than the standard values; this indicated that the goat milk is safe for consumption as per the heavy metals contamination concerned.

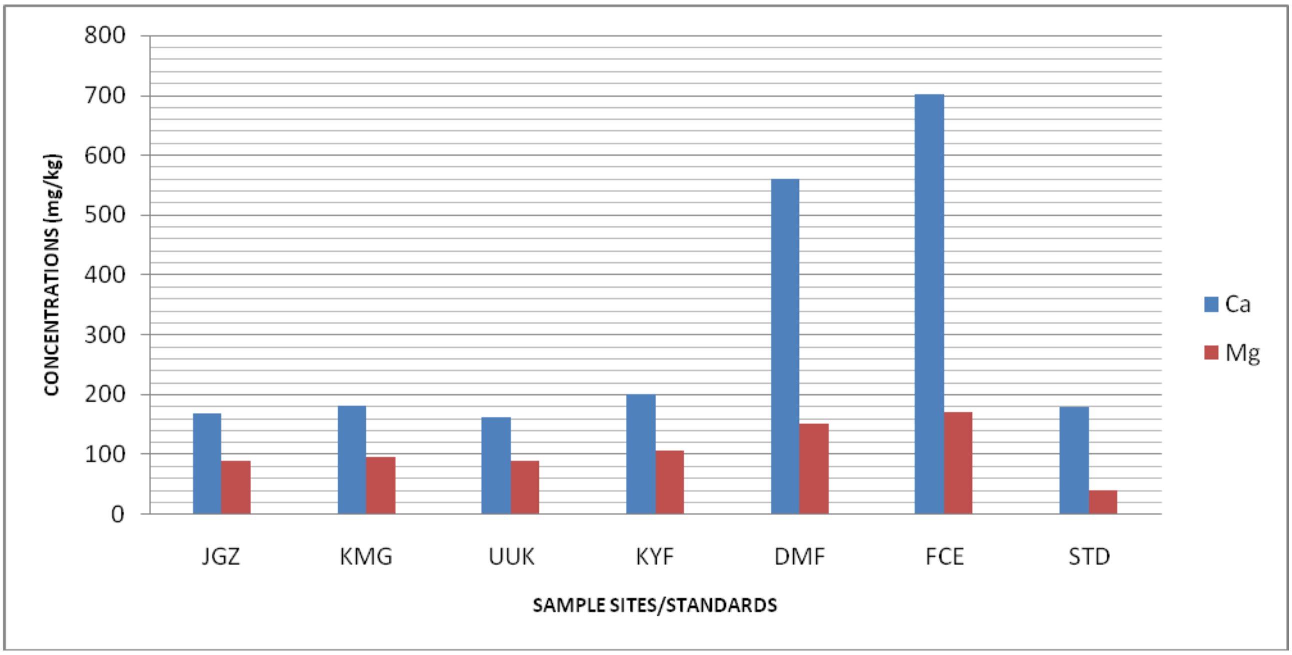


Figure 1. Mineral elements concentrations (mg/kg) in goat milk during wet season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF** = Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm

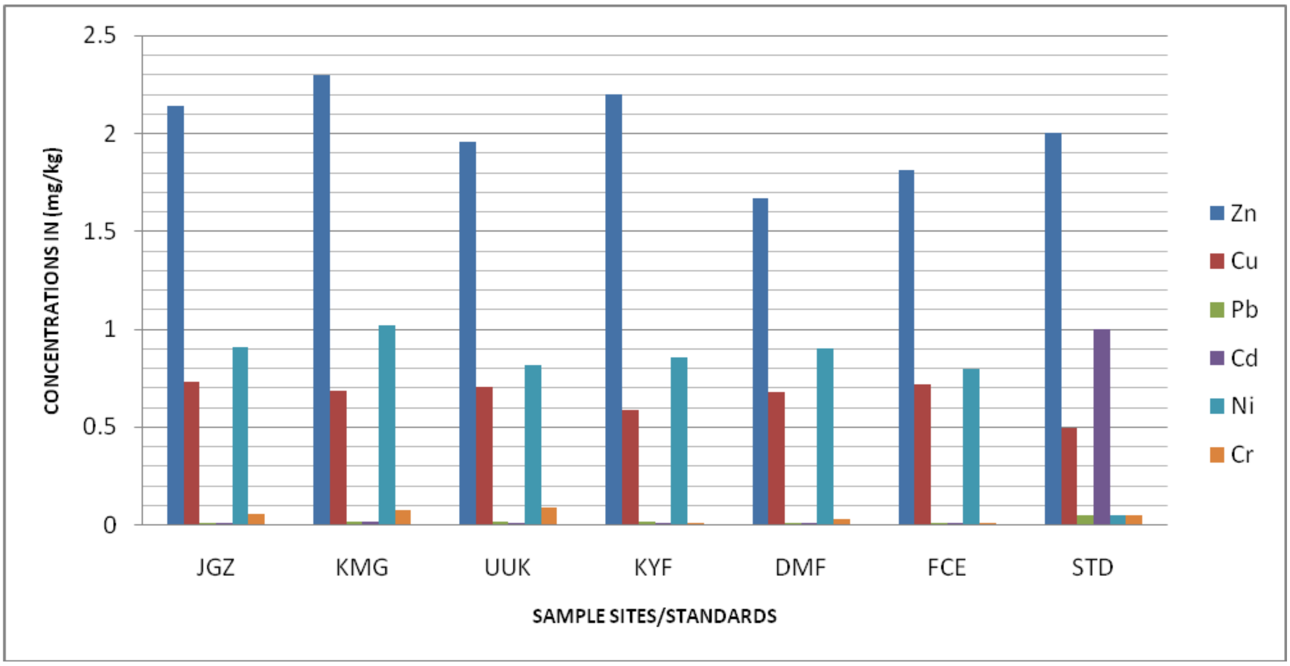


Figure 2. Heavy metals concentrations (mg/kg) in goat milk during wet season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF** = Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm

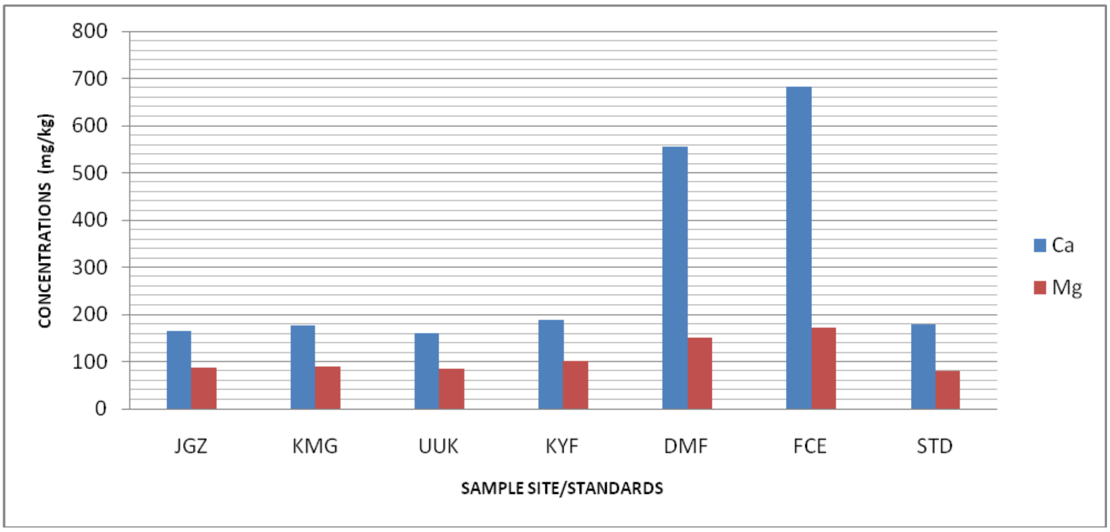


Figure 3. Mineral elements concentrations (mg/kg) in goat milk during dry season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF** = Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm

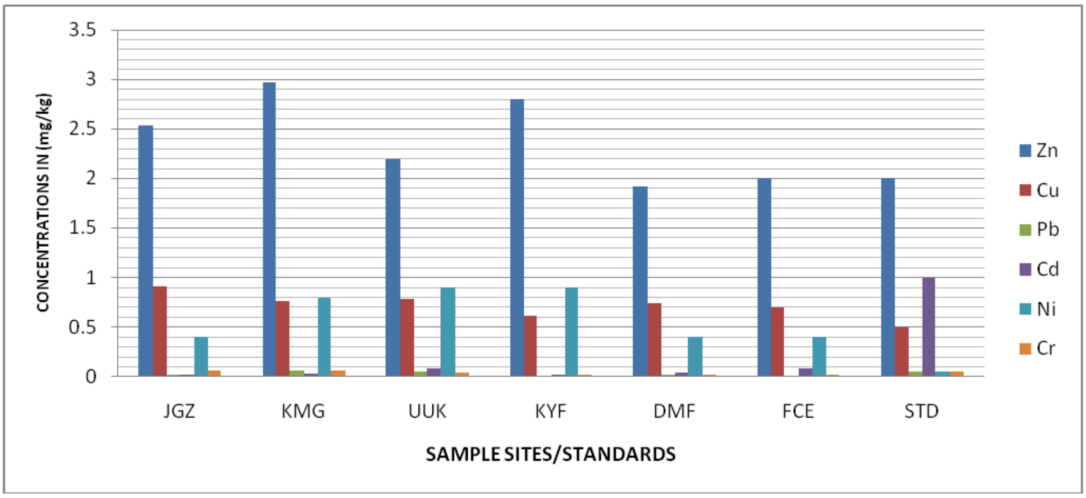


Figure 4. Heavy metals concentrations (mg/kg) in goat milk during dry season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF** = Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm.

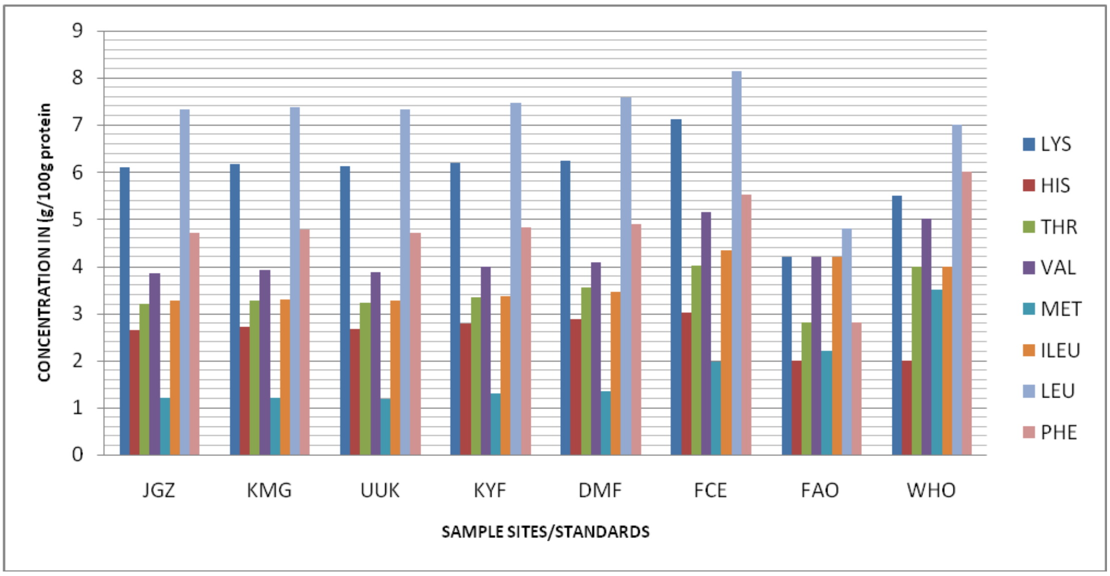


Figure 5. Essential amino acids concentration (g/100g protein) in goat milk during wet season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF**= Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm, **CP=** Crude protein, **TS=** Total solid.

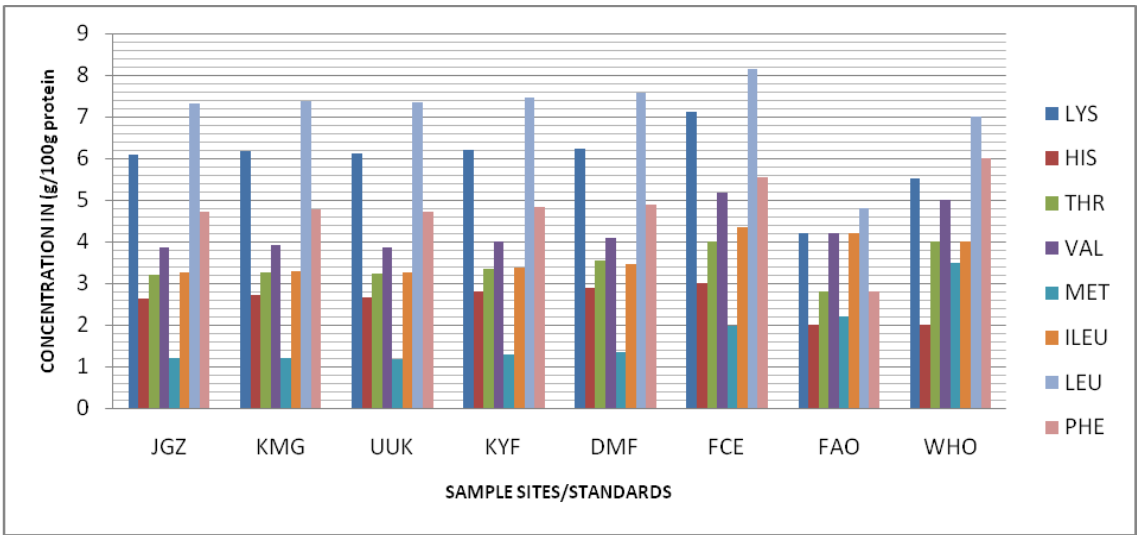


Figure 6. Essential amino acids concentration (g/100g protein) in goat milk during dry season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF**= Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm, **CP=** Crude protein, **TS=** Total solid.

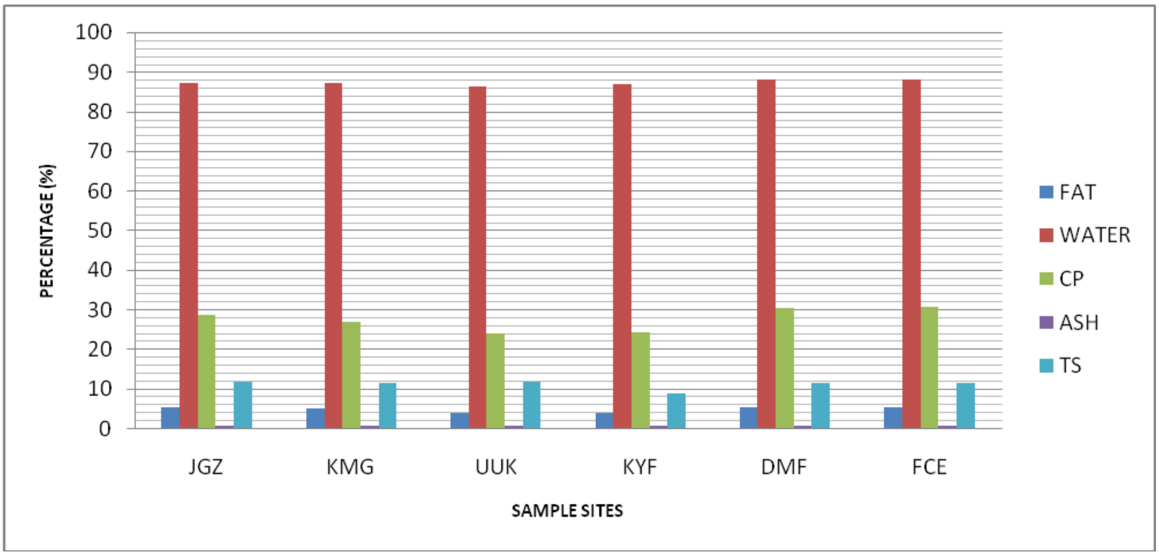


Figure 7. Percentage (%) composition of goat milk in wet season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF**= Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm, **CP=** Crude protein, **TS=** Total solid.

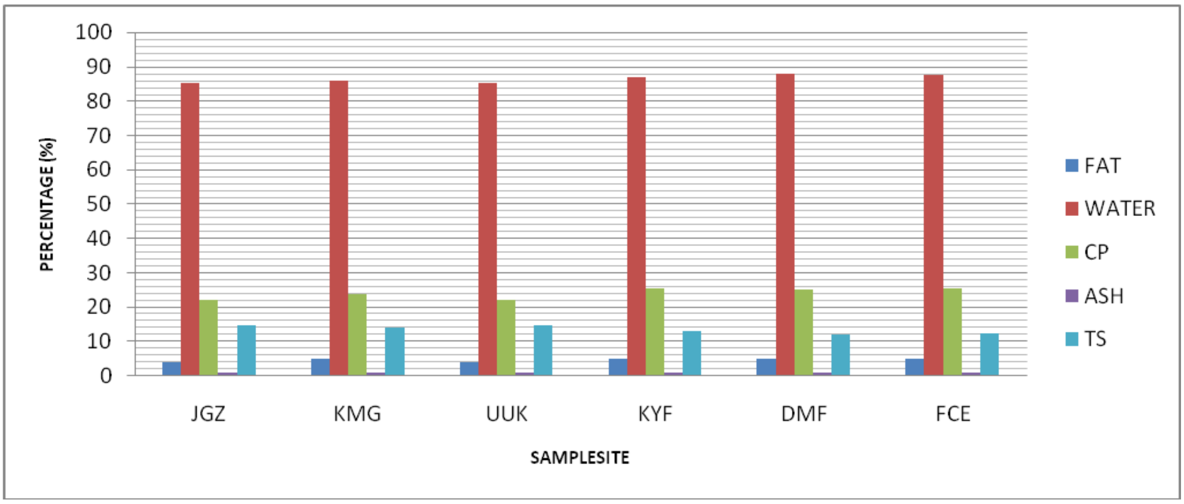


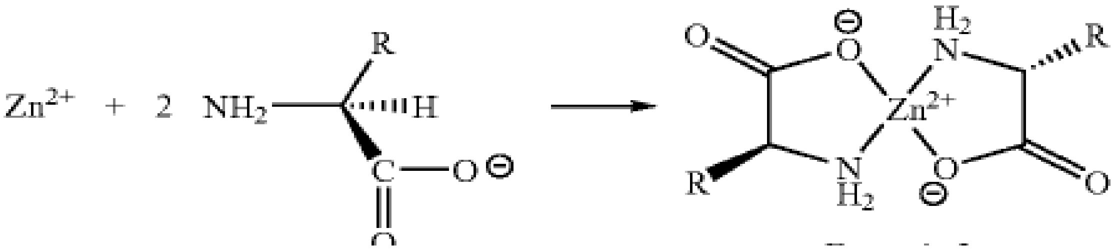
Figure 8. Percentage (%) composition of goat milk in dry season

Where: **JGZ** = Janguza, **KMG** = Kofar Mazugal, **UUK** = Unguwa Uku, **KYF**= Kuyan farm, **DMF** = Danmaraya farm and **FCE** = Federal College of Education, Kano farm, **CP=** Crude protein, **TS=** Total solid.

Figure 5 and Figure 6 showed the quantitative chromatographic analysis of goats' milk from six sampling locations. The results indicated concentrations of essential amino acids in the sample during the wet and dry seasons. The samples showed high concentration of glutamic acid, aspartic acid, leucine, lysine, isoleucine and glycine (13.38, 8.71, 9.04, 6.99 and 5.41 g/100g protein) in the wet season and the values of essential amino acids; histdine, isoceucine, leucine, lysine, methionine, threonine, valine and phenylalanine were 2.79, 3.73, 7.54, 6.32, 1.37, 3.43, 4.15 and 4.91 g/100 g protein respectively in dry season. In comparison with FAO/WHO standard values, it was discovered that the samples equal or exceeding the standard values in the concentration of essential amino acids; lysine, histidine, threonine, valine, leucine and phenylalanine while methionine and isoleucine are lower than the standard values in the sample. These concentrations of amino acids in the samples showed that the goat milk can support the nutrition of both neonate and adult in human and animals.

The Pearson correlation (r) analysis between mineral elements, heavy metals and essential amino acids in goat milk samples was performed using MATLAB student version IV software in wet and dry season indicated strong positive correlation between calcium and magnesium in the sample of $r = 0.993$ and coefficient of determination $r^2 = 0.986$ at significant value of $P \geq 0.05$, this revealed that as the concentration of calcium increases the concentration of magnesium also increases, this could be attributed to the sources of the element as it comes from the diet and water for the animals. The correlation analysis between mineral elements and heavy metals indicated strong and moderate positive correlation at significant level of $P \geq 0.05$. the overall result indicated that the bioavailability of mineral elements reduces the level of heavy metals concentration in the milk samples. Mineral - binding phosphopeptides or caseinophosphopeptides (CPPs) function as carriers for different minerals by forming soluble organophosphate salts, especially Ca^{2+} [49].

For instance the formation of zinc complex from zinc ion and an amino acid molecule which is prepared by the following reaction:



Other heavy metals: Pb, Cd, Ni and Cr had low correlation with the essential amino acids. The coordination sphere of the inert chromium (III) was partly or completely saturated by coordinating amino acids when Cr (Met)-$(NO_3)_3.2H_2O$, Cr $(Met)_2(NO_3)_3.2H_2O$, Cr $(AA)_2$ $(NO_3)_3$. $2H_2O$ (AA = Val, Leu, Thr, Phe and Tyr), or Cr $(AA)_3$ complexes were synthesized. Cadmium (+2) readily complexes to anionic groups, especially sulfhydryl groups, in proteins and other molecules.

Figure 7 and Figure 8 showed the mean percentage of chemical compositions of goats milk samples in wet and dry season respectively. The values of fat and other compositions obtained in this research were similar to those values reported by ([50-55]) for the red sokoto goats and higher than those reported by ([4,56-60]). In comparison with the values of West African Dwarf (WAD) breed and Sahel goats, the Sokoto red goats milk samples in this study have high fat content in their milk than the WAD goat, while the values obtained in this study are comparable to the values obtained for Sahel goat in the previous studies.

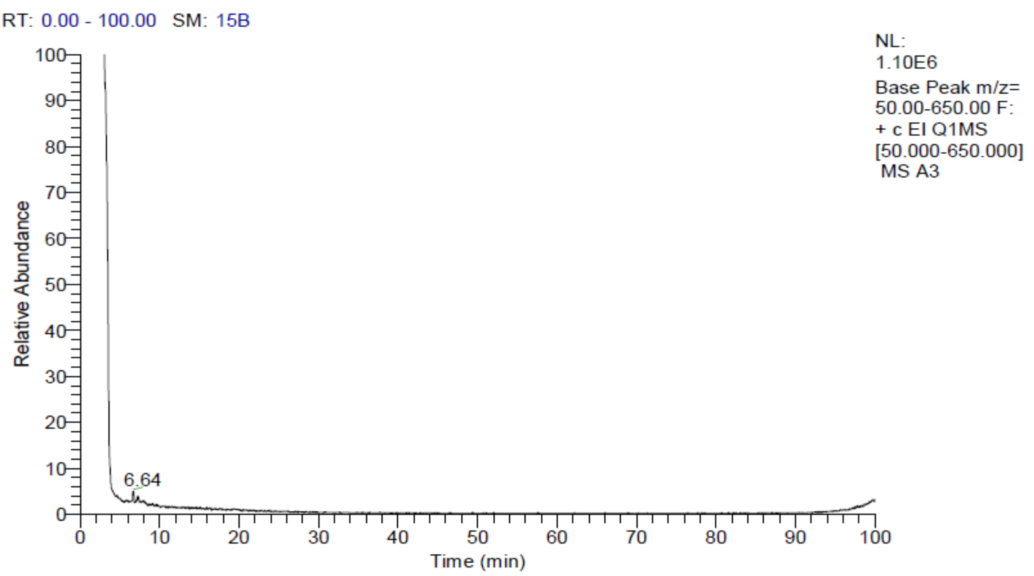


Figure 9. Gas chromatographic mass spectrometry analysis of pesticides in goat milk during wet season

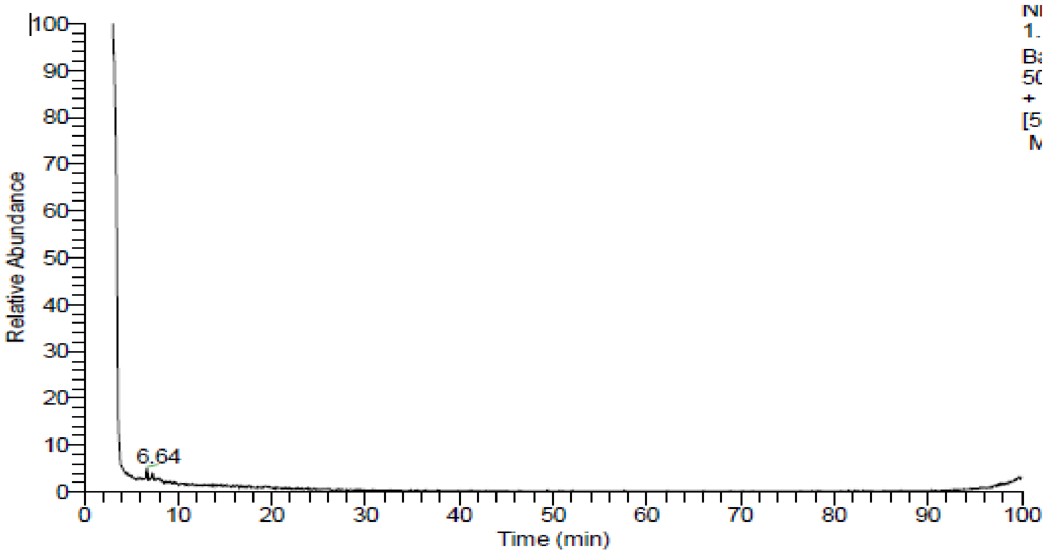


Figure 10. Gas chromatography – mass spectrometry analysis of pesticides in goat milk during dry season

3.1. Results of Persistent Organic Pollutants (POPs) Analysis by Gas Chromatography–Mass Spectrometry (GC/MS)

The results of gas chromatography – mass spectrometry (GC/MS) analysis of persistent organochlorine pesticides (POP) in the sample for wet and dry seasons revealed that none of the target pesticides (α-HCH, β-HCH, γ-HCH, δ-HCH, aldrin, dieldrin, endosulfan, p,p-DDE, o,p-DDT, p,p-DDD and p,p-DDT) was found in the samples. It shows that the pesticides in the milk samples were below the detection limit (BDL). These indicated that there was limited usage of the pesticides either for regulation compliance or economics reasons because most of these pesticides are very expensive (Figure 9 and Figure 10).

4. Conclusion

It has been concluded that goat milk from different locations of Kano state contains the concentrations of mineral elements (Ca and Mg) in sufficient amount to support nutrition in wet and dry seasons. The concentrations of essential metals (Zn, Cu and Cr) were not at toxicological alarming level (TAL) while the level of toxic metals (Pb and Cd) are below tolerable level for food, drugs and beverages. The nickel levels were high in wet season and below the threshold toxic level in dry season. This generally indicated that the milk is nutritionally rich in mineral elements and essential metals. The samples were also considered safe from the toxic metals contaminations. The amino acids content of the milk showed high value of essential amino acids (EAA) in the sample. The Pearson correlation coefficient (r) analysis between the metals and amino acids indicated strong and positive correlation between mineral elements and amino acids while moderate and low correlation was observed between the heavy metals and essential amino acids, this indicated that there is metal-amino acids binding property existing between them by forming useful metal-amino acids complexes that is metallothionein (MT) for human and animals metabolism. The moderate and low correlation between heavy metals and EAA may be as a result of the bioavailability of the calcium and magnesium in the milk which may reduces the level of the heavy metals in the samples. The correlation coefficients (r) are determined at significant value of $P \geq 0.05$. The gas-chromatography and mass spectrometry analysis (GC/MS) of organochlorine pesticides (OCPs) indicated that the pesticides were below the detection limit (BDL) in both seasons. This indicated that the milk is safe and free from pesticides contamination this could be attributed to the regulatory bodies restriction compliance or due to the economy as most of these pesticides are very expensive.

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