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Original Research Article

Effect of the environmental factors on some element contents in camel and sheep milks: A comparative study between Qassim and Riyadh regions, KSA

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To know the effect of environmental factors on the contents of some elements in milks of sheep and camel, samples of animal milks, wild plants and their soils were collected from Qassim and Riyadh regions at Kingdom of Saudi Arabia during March -April , 2016. The digested samples were analyzed for element contents(Fe, Mn, Zn, Cu, Co, Ni, Pb and Cd) using atomic absorption spectrophotometry. The results exhibited high concentrations of Ni and Pb in milk samples (Mean concentrations (ppm) for Pb in camel milk samples of Riyadh and Qassim were 0.54 and 0.59, while for sheep milk samples were 0.68 and 0.88, respectively. In respect of Ni, the mean concentrations in camel milk samples of Riyadh and Qassim were 1.51 and 2.1, while for sheep milk samples were 0.80 and 2.21, respectively). Most concentrations of elements in milk samples are correlated with their concentrations in the soil and their plants, this demonstrate the effect of environmental factors on the milk contents. The bioaccumulation factor of the elements in plants were calculated as well as the percentage of extraction of elements in the milk, which contributed to the interpretation of the results. The study recommends the need to take samples periodically for analysis of milk and components in order to preserve the public health of the citizens.

Key words: Metals, milk, camel, sheep, KSA

INTRODUCTION

Milk is considered as a nearly complete food since it is a good source for protein, fat and major minerals (Enb et al., 2009). On average, mineral elements account for 4 % of total body mass and part of every tissue, liquid, cell and organ in human body. There is a sufficient evidence that minerals, both independently or in proper balance with other minerals, have structural, biochemical and nutritional functions that are very important for overall human health, both mental and physical (Vahcic et al. 2010). Furthermore, they act as catalysts for many biological reactions in the body, including muscle contraction, transmission of nerve impulses and utilization of nutrients from food (Anonymous 2010;Vahcic et al., 2010).

Milk from various mammals such as cow, buffalo, goat, sheep is used for different nutritional purposes, e.g. feeding to young ones and preparation of some nutritional products such as milk cream, butter, yogurt, sour milk, etc.(Hassan 2005). Milk and milk products are the most diversified of the natural foodstuffs in terms of composition, contains more than twenty different trace elements (Stawarz et al., 2007). Most of them are essential and very important such as copper, zinc, manganese and iron. These metals are cofactors in many enzymes and play an important role in many physiological functions of man and animals (Koh and Judson 1986). Some of them, such as copper, nickel, manganese, chromium and iron are essential in very low concentration for the survival of all forms of life (Watson 2001).Only when they are presented in higher quantities, can these, like the heavy metals lead, cadmium be toxic also in very low concentrations and cause metabolic anomalies

(Hernandez-Avila et al. 2003). both toxicity and necessity vary from element to element and from species to species(Mendil, 2006) .Increasing environmental pollution has given rise to concern on the intake of heavy metals in humans. Environmental pollution with heavy metals is a major concernon a global scale and the risk associated with exposure to heavymetals present in food products is considered as a serious threat to human health (Saei-Dehkordi and Fallah, 2011).

These metals enter the human body mainly by two routes namely : inhalation and ingestion. The intake of heavy metals through ingestion depends on the food habit (Tripathi et al. 1997),Thus, information on the intake of heavy metals through food chain is important in assessing risk to human health. Here, the boundary between the essential and toxic effects is somewhat problematic (Thomas 2006). A simple and rapid method for the direct determination of cadmium, lead and copper in milk and fermented milk products by potentiometric stripping analysis (PSA) with oxygen as an oxidant and with inverse current imposed through the stripping step is described. The contents of cadmium, lead and copper in milk samples were in the range of 2.13–4.82, 54.3–95.2 and 112.2–124.7 lg/kg, respectively, whereas in the samples of fermented milk products in the range of 6.30–24.1, 210.1–463.6 and 260.0–320.7 lg/kg, respectively (Suturovic et al., 2014). Shahbazi et al.(2016) determined the concentrations of some heavy metals in dairy products, collected from five industrial regions in Iran during winter and summer in 2013, the results demonstrated that the concentration of metals were different either regionally or seasonally. Actually, the winter metal concentration amount was higher than its summer amount.

Determination of the residual concentrations of metals in milk could be an important "direct indicator" of the hygienic status of the milk, as well as an "indirect indicator" of the degree of pollution of the environment in which the milk was produced (Licata et al. 2004; González- Montaña et al., 2012).One of the main problems with metals is their ability to bioaccumulate. Metal residues in milk are of particular concern because milk is largely consumed by infants and children (Tripathi et al., 1999). The content of essential micronutrients and trace elements in milk depends mainly on external factors, i.e. given content of elements element content in soil, feed and water as well as its assimilability. To a lesser extent, concentration of mineral components is conditioned by factors related to secretion of milk, i.e. a cow's breed, stage of lactation, animal health (Cashman 2006; Dobrzanski et al., 2005; Gabryszuk et al., 2010; Malbe et al., 2010; Larranaga and Blascoi, 2009; Vidovic et al., 2005). both too low and too high content of micro and macro elements can cause adverse health effects in humans and animals; knowledge about dietary minerals in food is important (Malbe et al. 2010).Therefore, this research aims to know the effect of different environment factors (Feed - the study area - quality of the plants and soils ... etc.) on the mineral contents in camel and sheep's milk in some locations at Qassim and Riyadh regions, KSA.

MATERIAL AND METHODS

Sampling

Milk (sheep and camel), Riyadh wildplants (*Plantago ovate* and *Haloxyylonsalicornicum*), Qassim wild plants (*Schismusarabicusnees* and *Heliotropiumcrispum*) and soil samples (root zone) were collected from Al-Qassim and Riyadh regions at Kingdom of Saudi Arabia at April ,2016. Soil samples were collected from the root zone of each plant (five samples from different sites at each region). The samples were then dried at 105 °C in an electric oven for 48 h and sieved through a 2-mm sieve to remove large debris and stones. The soil samples from each region for each plant mixed in order to obtain representative samples, and were subsequently stored in plastic bags prior to laboratory analysis for the content of metals. Riyadh Plant Samples (*P. ovate*, *H. salicornicum* and *H. crispum*) were collected from the same sites as the soil samples. Each plant samples were repeatedly washed with tap water until no macroscopic soil particles were observed in the liquid phase, and subsequently washed with deionized water and separated into different parts (leaves, stems and roots). All parts of plant samples were dried at 110°C in an electric oven for 48 h. Dried plant samples were crushed and powdered in an agate mortar prior to digestion. The milk samples for sheep and camel (five samples from each region)were obtained by hand in 100-ml acid-washed glass vials and immediately placed in a cooler box, then transported to the laboratory.

Analytical methods

Milk samples

The mineralization were carried out by wet oxidation (Konuspayeva et al., 2011) to destroy the organic matter in presence of mixture from nitric, sulphuric and perchloric acids(2:1:2 v/v). The samples of milks (10 ml of each kind) with acids (in Teflon beakers) were placed in sand bath on hot plate up to 150 °C, until near the dryness of samples, then volumes of nitric acids were added again then evaporated on the heating plate, this step repeated several times until total destruction of the organic matter. When the solutions became clear, the dilutions were carried out with deionized water containing 1% nitric acid. each sample transferred to 25 ml measuring flask and completed to the mark by deionized water as a prelude for metal analysis

Soil Samples

Chemical parameters in soil samples were determined using methods from a textbook of soil analysis (Baruah and

Barthakur 1997).Single-step leaching techniques were used to partition the heavy metals in the soil samples

A-Total metal concentrations:

One gram of each soil sample was digested with a mixture of HF, HNO_3 and HCl in a Teflon beaker. Digestion was repeated three times to ensure complete dissolution; the residue was dissolved in 5 ml 2M HNO_3 and rewarmed at 80°C for 20 minutes (residual phase). All extracted solutions were filtered off through Whatman No. 42 filter paper and then used for analysis.

(B) Soluble metal Concentrations

10 gram of each soil sample was suspended in 50 mL distilled water (1 : 5 soil : water mixture) and shaking for 24 hrs., then, the clear liquid phase was obtained using a centrifuge at 3000 rpm for 15 minutes.

Plant Samples

Plant samples were digested according to Allen(1989). One-gram portions of plant (leaves and stems) were digested with 10 ml of a conc. HNO_3:$HClO_4$ mixture (3:1) in a Teflon reactor under pressure (Allen 1989) to prevent any atmospheric contamination or loss of volatile elements that might have occurred during dry ashing. After complete digestion and cooling, the solution was diluted with 2% nitric acid solution and then with bidistilled water to a final volume of 25 ml.

Instrumental techniques

Metal-ion concentrations (Cu, Zn, Cd, Pb, and Ca) in the different leachates and reference materials (National Institute of Standards and Technology 1993)were determined by flame atomic absorption spectrophotometry (Model Solaar 969, ATI Unicam Comp.) equipped with a digital direct concentration read out and an air–acetylene burner. Single-element hollow-cathode lamps (ATI Unicam Comp.) and standard instrumental conditions were used for each element. To validate the method for accuracy and precision, certified reference materials were analyzed for each element. Suitable precautions were takento minimize interference when necessary. Background absorption can be troublesome, so the traditional and simplest methods are used to monitor absorbance of the continuum output of a deuterium lamp beam and to correct the analyzed signal for any absorption detected.

Quality Control

Accurate analysis of heavy and toxic elements is dependent upon the prevention of element contamination. Quality control was achieved by analyzing reference materials independently prepared from the standards. All chemicals used were purchased from BDH, Sigma, Aldrich and E. Merck (A.R., 99.9%). All vessels were made of Pyrex and high-density polyethylene, washed with 30% HNO_3, then rinsed three times with bidistilled water and dried in an oven. The accuracy of the methods was verified by subjecting standard reference material to the overall analytical procedures. Analysis of reference material yielded metal concentrations within acceptable limits. The mean coefficient of variation of the metal concentrations was calculated from a triplicate analysis of individually digested subsamples of plant or soil.

Atomic absorption spectroscopic standard solutions (1mg ml^{-1}) for the elements Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (BDH, UK) were prepared by diluting stock solutions using deionized water. The standard curves were verified after 10 successive runs by analysis of one standard solution within the linear range for each sample. All stages of samples preparation, analyzing and measuring were carried out in a clean environment.

RESULTS AND DISCUSSION

The mean concentrations of some elements in milk (Camel and Sheep), feeder plant (wild plant)and soil samples are recorded in Table (1). The results in the above Table refers to obvious high concentrations for some elements such as nickel and lead compared to the results of previous published research's. Also, the results showed different concentrations of elements in milk samples as a result of the difference of studied areas and quality of the feeders, these results demonstrates the influence of environmental factors on the mineral content of the milk. Some previous research (Konuspayeva et al. 2011; Meldebekova et al. 2009) attributed the high concentrations of some elements in the milk samples to grazing areas near highways teeming with vehicles and affecting the soil and the feeder plants for animals, other studies refers to the responsibility of sewage and agricultural drainage on the soil pollution and the feeder plants (Rahimi, 2013;Gaucheron, 2013). Bhati and Choudhry (1996), Dey and Swarup (1996) and Simsek et al. (2000) considered that cattle reared close to manufacturing or roads produced a milk containing significantly higher levels of lead. However, in all these studies, lead concentration in milk was very variable, with higher value between 0.032 ppm and 7.20 ppm (Bhati and Choudhry, 1996; Swarup et al., 2005). Taking in consideration all these information's, it was possible that the highest lead concentration in milk from some farms could be due to the proximity of road with high traffic. Lead occurs naturally from the decomposition of parent rocks and may accumulate from anthropogenic sources, including traffic exhaust, lead–zinc smelters, dumps and other sites receiving industrial and household lead, e.g., paints and batteries (Mulligan et al., 2001). Therefore it is best to choose areas far from cities as pastures for these animals in order to avoid the risk of contaminants.

The accumulation factor of elements in feeder plants for both Camel and sheep's is recorded in Table (2). These values indicates that the plants are considered as hyper accumulator for lead element, despite that the solubility of lead in soil samples is low (0.02– 0.05 %)as in Table (4), although the solubility of cadmium, zinc and iron are high

Table 1. The concentration of elements (mean of 5 samples) in plants , soil, and milk samples (ppm) in Riyadh and Qassim (Saudi Arabia)

Element Sample	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe
Plantago ovate	4.4	44	24.5	6	15	12	75.1	219.1
Soil of Plantago ovate	1.6	31.8	14.5	4.5	9.2	8.3	46.9	305.4
Soil of Plantago ovate (1:5)	0.02	0.01	0.03	0.03	0.03	0.2	0.2	2.5
Riyadh camel milk	0.013	0.54	1.51	0.038	0.27	1.19	0.46	0.68
H. salicornicum	4.4	48.9	30	7.5	19.2	18.9	64.1	143.8
Soil of H. salicornicum	1.6	31.8	14.5	4.5	9.2	8.3	46.9	305.4
Soil of H. salicornicum	0.02	0.01	0.03	0.03	0.03	0.2	0.2	2.5
Riyadh sheep milk	0.026	0.68	0.80	0.068	0.20	0.95	0.19	0.93
H. crispum	4.2	36.7	27.3	7.1	9.2	18.2	62.9	118.7
Soil of H. crispum	0.81	29.3	40.9	3	37.5	7.7	52.8	321.8
Soil of H. crispum (1:5)	0.03	0.005	0.025	0.04	0.03	0.10	0.20	2.35
Qassim camel milk	0.026	0.59	2.1	0.075	0.18	1.13	0.12	0.79
Schismusarabicusnees	4.8	34.2	29.1	6.75	16.4	18.4	51.8	196.3
Soil of Schismusarabicusnees	0.97	19.6	70	3	12.5	13.2	86.3	342.4
Soil of Schismusarabicusnees (1:5)	0.025	0.01	0.04	0.02	0.03	0.19	0.25	2.54
Qassim sheep milk	0.026	0.88	2.21	0.053	0.38	1	.065	3.2

Table 2. Bioaccumulation coefficient of elements in the feeder plants (wild plants) for camel and sheep in Riyadh and Qassim regions (concentration of the element in the plant / concentration of the element in the soil extract (5: 1))

Element Plant	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe
Plantago ovate	220	4400	816	200	500	60	354	87
H. salicornicum	220	4890	1000	250	640	94	320	57
H. crispum	140	3740	1092	177	306	128	314	50
Schismusarabicusnees	092	3420	727	337	546	96	207	77

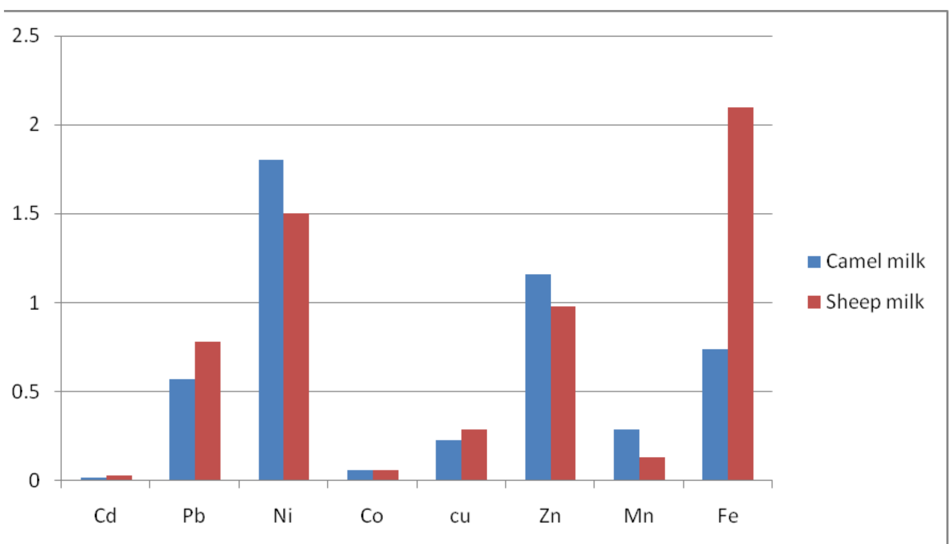
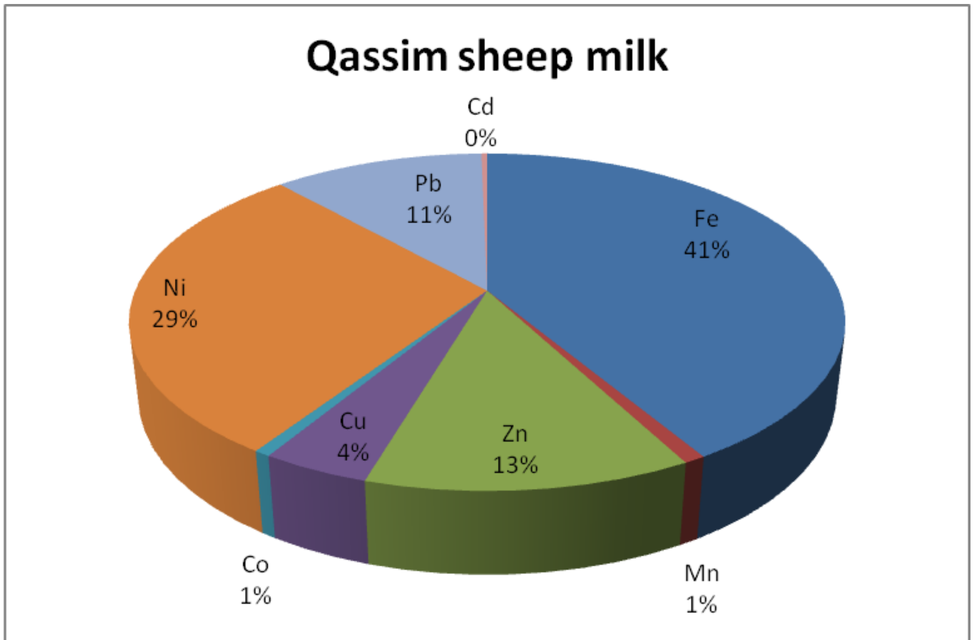


Figure 1: The average concentrations of elements (ppm) in milk samples of camel and sheep's at Riyadh and Qassim (Saudi Arabia)

(Table 4), but the accumulation factors for them rather low and this refers to the plants selectivity for some elements. Some plants are considered a bio indicator of the presence of some elements, so they are grown in contaminated land to remove or reduce the concentration of these elements (Panich-Pat et al., 2010).

Figure (1) shows the average concentrations of various elements in the milk samples for camel's and sheep's. As



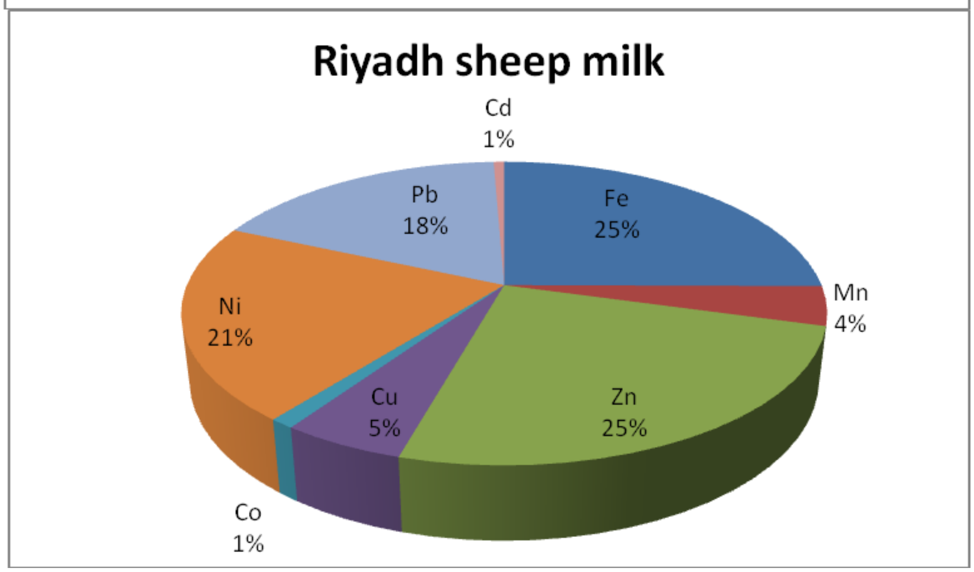


Figure 2: Graphs illustrate the percentage of elements in the sheep's milk for the total elements that were estimated

shown as in the above Figure, the concentrations of elements in the kinds of milk exhibited Convergence in the results , but in the case of iron, where iron concentration rises in the milk of sheep, this may be due to the extra feed from the iron-rich grass which brought from other places. We also note the high concentrations of zinc, one of the key elements in the milk and its limits within the international levels, while nickel concentrations high and this is due to the geology of the plant soil and concentrating in plant tissues (Table 1), also note a clear dropping of the cadmium concentrations and this confirms the selectivity of animal tissues to the needed elements. Figures (2 and 3) illustrates the percentage of elements in the sheep's and camel milk for the total elements that were estimated. These Figures show different ratios of metallic elements in milk samples depending on changing environmental factors (Feed - the study area - quality of the plants and the different components - the age group for animal ... etc.).

The Percentage to extract metallic elements in milk (the concentration of the element In milk / concentration in the plant) are recorded in Table 3. The above table exhibited high extractable ratios of zinc, manganese, copper , which is the key elements in milk components, in addition to nickel, which its concentration coming as a result of its richness in the soil and the plant, on other hand we note the low values of lead , may be as a result of the selectivity of animal tissues .

Solubility percentage of metals in soil samples in Riyadh

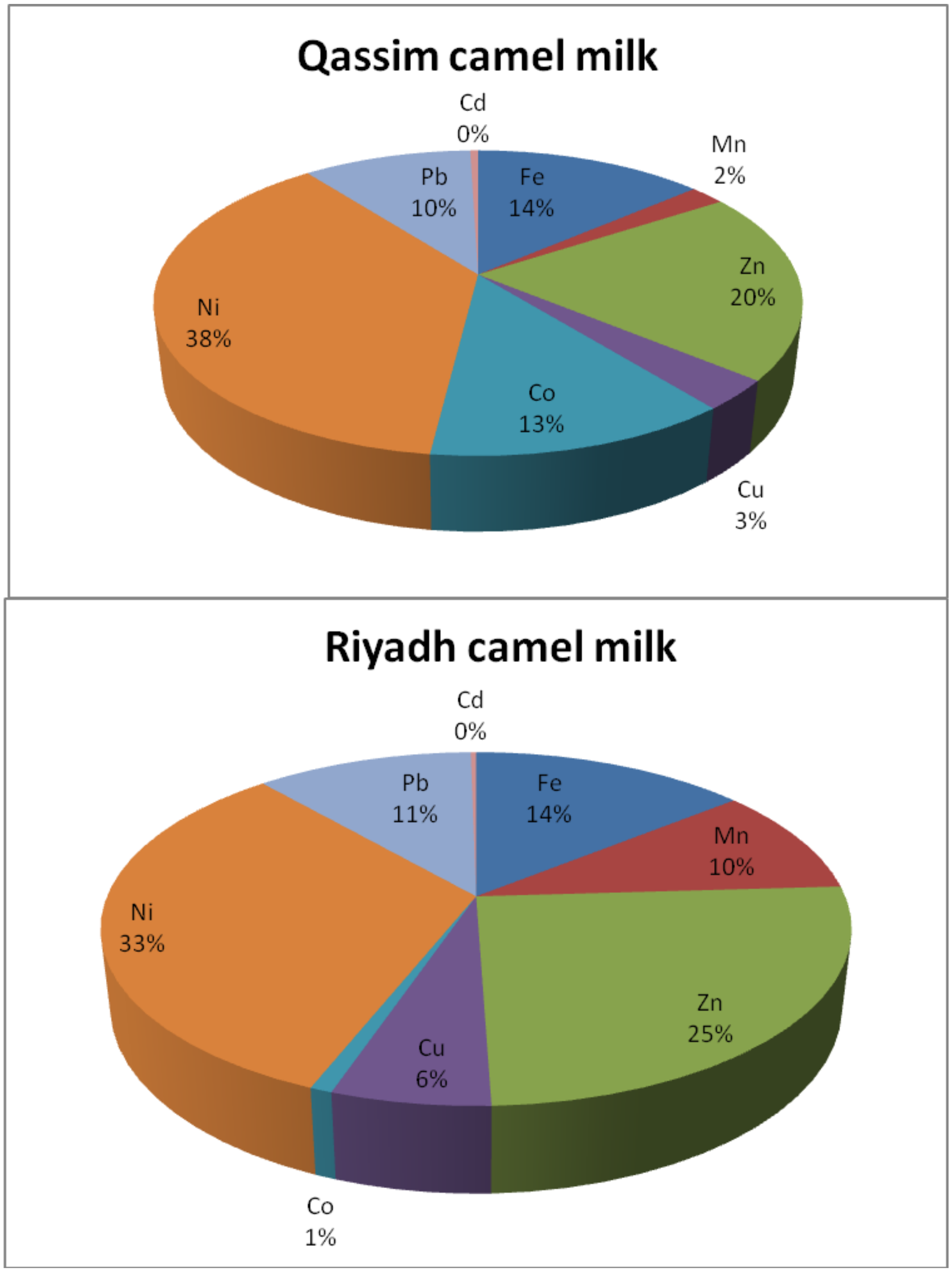


Figure 3: Graphs illustrate the percentage of elements in the camel milk for the total elements that were estimated.

Table 3. Percentage to extract metallic elements in milk (the concentration of the element in milk / concentration in the plant)

Element Sample	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe
Riyadh camel milk	0.3	1.2	6.1	0.6	1.8	9.9	3.8	0.3
Qassim camel milk	0.6	1.6	7.7	1.1	1.9	6.2	0.19	0.6
Riyadh sheep milk	0.6	1.39	2.7	0.91	1.04	5	0.30	0.65
Qassim sheep milk	0.54	2.57	7.6	0.79	2.32	5.4	0.13	1.63

and Qassim regions are recorded in Table (4). The solubility of elements is considered as an indicator for the form of the element in the soil, the slightly soluble elements are often present in the form of carbonate or

Table 4. Solubility percentage of metals in soil samples in Riyadh and Qassim regions(element concentration in the extract (5:1) / total concentration of the element in the soil)

Milk specie	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe
Soil of Riyadh(Camel & sheep)	1.25	0.03	0.21	0.67	0.33	2.41	0.43	0.82
Soil of Qassim (camel)	3.7	0.02	0.06	1.33	0.08	1.30	0.38	0.73
Soil of Qassim (sheep)	2.57	0.05	0.06	0.67	0.24	1.44	0.29	0.74

Table 5. Comparison of the results of current study with the previous studies

Milk species	Cd	Pb	Ni	Co	Cu	Zn	Mn	Fe
Sheep [7]	-----	----	**0.054**	**0.004**	**0.11-09**	**4.15**	**0.053**	**0.62-1**
Sheep [16]	-----	----	----	----	**0.4**	**5.7**	**0.07**	**0.80**
Sheep [17]	-----	-----	-----	----	**0.4-0.68**	**5.2-7.4**	**0.05-0.1**	**0.7-1.2**
Sheep [18]	-----	----	-----	----	**1**	**7**	Trace	**0.30**
Sheep [19]	**0.001-0.01**	**0.030.01**	-----	-----	-----	-----	----	-----
Sheep [20]	------	-----	----	----	**0.04-0.05**	**5.4-6**	**0.01-0.02**	**0.09-0.1**
Sheep of Qassim	**0.026**	**0.88**	**2.21**	**0.053**	**0.38**	**1**	**0.065**	**3.2**
Sheep of Riyadh	**0.026**	**0.68**	**0.80**	**0.068**	**0.20**	**0.95**	**0.19**	**0.93**
Camel [21]	----	----	----	----	-----	**5.3**	**0.5**	**2.9**
Camel [22]	----	----	----	----	**0.11-1.5**	**2.8-4.4**	**0.2-1.9**	**0-3.7**
Camel [23]	----	**0.025**	----	----	**0.07**	**5.16**	**0.08**	**1.48**
Camel [24]	**0.001-0.003**	**0.01-0.06**	----	----	**0.05-0.07**	**4.07-5.3**	----	----
Camel of Qassim	**0.026**	**0.59**	**2.1**	**0.075**	**0.18**	**1.13**	**0.12**	**0.79**
Camel of Riyadh	**0.013**	**0.54**	**1.51**	**0.038**	**0.27**	**1.19**	**0.46**	**0.68**

silicate or oxide or sulphate or sulphide, while the soluble elements with highly extent are in the form of nitrate or chloride, and whenever the element is more soluble whenever It was the available concentrations much larger for plant, but this depends on plant selectivity at the same time.

Comparing the results of the study with the results of previous studies (Table 5), we have shown that iron and zinc concentrations are low in camel milk compared to previous research, while the concentrations of manganese and copper in the rate of the previous studies concentrations, while noting a sharp rise in the concentration of lead and cadmium. The food chain is an important source of Cd and Pb accumulation, especially for plants grown on polluted soils. Significant amounts of Cd and Pb can be transferred from contaminated soil to plants and grass, causing accumulation of these potentially toxic metals in grazing ruminants (Lopez et al., 2003). In the case of sheep milk, moderate concentrations of zinc, while a clear increase in the concentrations of nickel, lead and cadmium appears. We conclude from the previous comparisons that there is a common factor between Qassim and Riyadh in the soil and then the concentration of these elements concentrated in the plants, and in the end these concentrations transmitted to the milk.

CONCLUSIONS

The results showed different concentrations of elements in milk samples as a result of the difference of animals and studied areas. Also, the concentration of elements in milk samples in study areas are often correlated with their concentrations in the soil and their plants (feeders), thus, these results demonstrates the influence of environmental factors on the mineral content of the milk. High concentrations of some elements in milk samples attributed to the grazing areas near highways teeming with vehicles and affecting the soil and plants (feeders) , for example, The concentration of high lead in milk can be due to the proximity of roads with high traffic exhausts from the farms and can accumulate from human sources including lead smelters, zinc and other sites that receive the effluents such as paints and batteries, while the high concentrations of nickel may be due to the geology of the plant soil and its concentrating in plant tissues. high concentrations of zinc are detected in the milk samples, which is one of the key elements in the milk and its limits within the international levels, The results exhibited high extractable ratios of zinc, manganese, copper in milk samples which are the key elements in milk components, in addition to nickel, which its concentration coming as a result of its richness in the soil and plant. On other hand, the low extractable ratio of lead, may be as a result of selectivity of animal tissues. The solubility of elements is considered as an indicator for the form of the element in the soil, where the slightly soluble elements are often present in the form of carbonate or silicate or oxide or sulphate or sulphide, while the highly soluble elements are present in the form of nitrate or chloride, and whenever the element is more soluble whenever It was the available concentrations much larger for plant, but this depends on plant selectivity at the same time. The study recommends that they should not rely on animal feed entirely on herbs and the need to diversify nutrients so that it can reduce the concentration of undesirable elements in milk, and may be added concentrations from low elements , such as zinc and iron into the nutrients or in animal drinking water, Also, the study recommends the need to take samples periodically for analysis of milk and components to take precautions in order to preserve the public health of the citizens.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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