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Macro Minerals and Trace Elements in Milk of Dairy Buffaloes and Cows Reared in Mediterranean Areas

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Abstract: Aim of this study was to evaluate the differences in Ca, P, K, Na, Mg, Zn, Fe, Cu, Mn, Se, Mo, Co, Li, B, Ti, Rb, and Sr concentrations in milk from buffaloes and cows reared in the same farm in Mediterranean areas and fed diets including the same ingredients. Individual milk samples were obtained from 32 Mediterranean buffaloes and 29 Italian Friesian cows and samples of milk, dietary ingredients and drinking water were analyzed for the investigated chemical elements by inductively coupled plasma-mass spectrometry. Data about milk element concentrations were processed by one-way analysis of variance. Buffalo milk contains higher concentrations of Ca, P, Mg, Zn, Fe, Cu, B, Ti, and Sr, and lower concentrations of K, Na, Mo, Li, and Rb compared to cow milk, whereas milk from both species contains similar concentrations of Mn, Se, and Co. The concentrations of the investigated elements in the diet were similar for both species and the differences observed between buffalo and cow milk were not dependent on environmental factors.

Keywords: buffalo milk; cow milk; macro minerals; essential trace elements; non-essential trace elements; diet

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1. Introduction

Buffalo milk production in 2020 was the second largest globally and accounted for approximately 134 million tons, following cow milk production of 718 million tons [1]. Most buffalo milk is produced in Asia (India and Pakistan as major producers), where it is consumed fresh (usually after skimming, and sometimes mixed with cow milk) or used as milk derivatives [1–3]. Buffalo milk can be processed to obtain derivatives, such as cream, butter, yogurt, and many types of cheeses, often related to the historical tradition of each buffalo milk-producing country [1–3]. In Italy, the major producer in Europe [1], buffalo milk is used for cheese manufacturing, and Mozzarella cheese and Ricotta from buffalo milk produced in a specific area of Southern Italy (mainly in Campania region) have obtained the label of Protected Designation of Origin [3]. Moreover, about ten traditional cheeses from buffalo milk are officially recognized in Italy, and innovative soft cheeses, similar to Stracchino and Taleggio, and yogurt from buffalo milk are also developed for the Italian market [3].

Interspecies differences in gross composition exist between buffalo and cow milk. Buffalo milk has a higher content of fat (approx. 6.8 to 8.8 g/100 g milk), protein (3.6 to 4.9 g/100 g milk), and ash (0.71 to 0.85 g/100 g milk), and similar content of lactose (4.8 g/100 g milk) [4,5] compared to cow milk (3.7 g, 3.4 g, 4.8 g and 0.7 g of fat, protein, lactose, and ash, respectively, for 100 g milk) [6]. Approximately 80% of total protein is represented by caseins both in buffalo and cow milk [2,5].

The mineral fraction of buffalo milk received less attention than major milk components, and the literature data deal mainly with macro minerals and with some essential trace elements [2]. Chemical elements in milk are of great nutritional and technological importance [5,7]. Milk contains nutritionally essential macro minerals and trace elements whose biological role is well established, i.e., structural components of body tissue and components of many enzymes and other biologically active compounds [7,8]. Milk also contains other trace elements, whose role is not known, that are not defined essential, but data from animal and human nutrition studies suggest that Li, B, Ti, Rb, and Sr, among other elements, exert beneficial bioactive effects [9–12]. In experimental conditions, a suboptimal biological function due to dietary deprivation of a specific non-essential element may be prevented or reversed by an intake of physiological amounts of the element [9–11].

The published data on chemical element concentrations in milk show variations, particularly wide for trace elements [4,6]. The available literature data on milk composition are derived from experimental observations carried out in different locations, therefore reflecting differences in breeds, management, and environmental conditions [4]. Breed, stage of lactation, and health status of the mammary gland are the main factors influencing the concentration of macro minerals in milk, whereas diet is reported to have relatively little effect on the concentration of most elements [5,6]. However, according to Stocco et al. [13], diet is an important factor in determining the differences in macro mineral contents in milk from different buffalo herds. Furthermore, the variability in the literature data also depends on different methods of analysis implemented in the published studies. The concentration of essential trace elements in buffalo milk is not well characterized as it mainly focuses on Zn, Fe, and Cu concentrations and data on most non-essential trace elements are lacking in the available literature.

The aim of this study was to evaluate the differences in Ca, P, K, Na, Mg, Zn, Fe, Cu, Mn, Se, Mo, Co, Li, B, Ti, Rb, and Sr concentrations in milk from buffaloes and cows reared in the same farm in Mediterranean areas and fed diets including the same ingredients.

2. Materials and Methods

2.1. Animals, Diet, and Sampling

This study was carried out on milk samples obtained from routine production practice in farming conditions, in accordance with the Italian law on the protection of farm animals, including dairy buffaloes and cows (D. Lgs. 146/2001). The ethical approval of the research protocol was waived in accordance with the European Commission legislation (Dir. No. 2010/63/EU).

Individual milk samples were obtained from 32 Mediterranean buffaloes (averaging approx. 1.5 months from calving and 4.5 parity) and 29 Italian Friesian cows (averaging approx. 3.5 months from calving and 2.5 parity). Buffaloes and cows were reared in the same commercial dairy farm located in rural areas of Jesi municipality (Ancona province, Italy) and were housed in two freestall systems separated by the feeding area, with continuous access to water. The animals were fed specific total mixed rations. Common dietary ingredients for the two dairy species were alfalfa hay, meadow hay, corn silage, corn, soybean meal, calcium carbonate, sodium chloride, sodium bicarbonate, and a commercial mineral (iron carbonate, manganese oxide, zinc sulfate, copper sulfate, sodium selenite, and cobalt carbonate) and vitamin (Vit A, Vit D, Vit E, Riboflavin, Niacin, Pyridoxine, Biotin, and Cobalamin) supplement also including rumen-protected methionine.

Daily rations for cows (22.7 kg dry matter/head) and buffaloes (14.6 kg dry matter/head), respectively, included (g/100 g dry matter) 34.6 vs. 22.5 corn silage, 5.76 vs. 29.9 meadow hay, 19.2 vs. 20.9 alfalfa hay, 15.5 vs. 18.1 corn, 14.4 vs. 7.25 soybean meal, 0.71 vs. 0.48 calcium carbonate, 0.31 vs. 0.34 sodium chloride, 0.53 vs. 0.34 sodium bicarbonate and 0.15 vs. 0.17 mineral/vitamin supplement. Daily ration for cows also included 8.53 g/100 g dry matter of barley and 0.31 g/100 g dry matter of a commercial probiotic (live yeast *Saccharomyces cerevisiae*) supplement. Representative samples of each ingredient included in the total mixed rations and of drinking water were collected. Based on the concentrations of the investigated chemical elements in feedstuffs and on the proportion of inclusion in total mixed rations for buffaloes and cows, mineral concentrations were then calculated for both diets.

The milking system was a 2 × 9 herringbone-milking parlor, and buffaloes and cows were milked twice a day (at 4:00 h and 16:00 h) at identical intervals between morning and afternoon milking. The working vacuum was 40 kPa for both species. Aliquots of individual milk samples representative of the whole milking obtained using milk meters (Milko-Scope MK II. Foss, Hillerød, Denmark) during the routine afternoon milking were frozen and stored at −21 °C until analysis. The milk somatic cell count (Fossomatic 360, Foss, Hillerod, Denmark) averaged approximately 160 × 10^3/mL and 260 × 10^3/mL in fresh buffalo and cow milk, respectively. All glasses and polyethylene tubes used for collection, storage, and analysis of samples were previously washed with 3% HNO_3 (Suprapur quality, Merck, Darmstadt, Germany) solution.

2.2. Milk, Feedstuffs, and Drinking Water Analyses

All solutions were prepared using ultrapure water obtained from a Millipore Milli-Q system (resistivity 18.2 MΩ·cm). Mineralization of milk samples was carried out by placing 1 mL of milk sample in a Teflon digestion vessel, followed by 3 mL of HNO_3 (65%). Fifty microliters of Te solution (5 mg/L) were added as a recovery standard [14]. The vessel was then placed in a microwave closed vessel system (Berghof Speedwave four, Berghof, Eningen, Germany) for mineralization. Mineralized solutions were transferred to a 10 mL volumetric flask and diluted with ultrapure water for the measurements of trace elements. Mineralized solutions were further diluted 1:10 with ultrapure water for the measurement of macro minerals and Zn [15,16]. Mineralization solution for feedstuffs was made of 0.15 g of ground samples, 3.5 mL of HNO_3 (65%) (Suprapur quality, Merck), and 3.5 mL of H_2O_2 (30%; Suprapur quality, Merck).

The concentrations of Ca, P, K, Na, Mg, Zn, Fe, Cu, Mn, Se, Mo, Co, Li, B, Ti, Rb, and Sr in the mineralized solution and in acidified (1% HNO_3) drinking water were measured by inductively coupled plasma-mass spectrometry (Agilent Technologies, 7500 cx series, Santa Clara, CA, USA). The operating conditions were as previously described [15].

Calibration curves for the investigated elements were obtained using aqueous (1% HNO_3) standard solutions prepared with appropriate dilution of stock standards (Fluka Analytical, Sigma-Aldrich, Milano, Italy). The accuracy of the analytical procedure was checked within each batch analysis by analysis of blanks and of certified reference material, skim milk powder ERM-BD151 (European Reference Material, Geel, Belgium). Recovery of certified elements was in good agreement with the certified values (86 to 110%).

2.3. Statistical Analysis

Data about milk concentration of the investigated elements were processed by one-way analysis of variance (SPSS version 25, IBM Corp. Armonk, NY, USA), and differences were considered significant for $p < 0.05$. Results are expressed as least squares means ± SEM.

3. Results and Discussion

3.1. Essential Macro Minerals in Milk

Results on macro mineral concentrations in milk from Mediterranean buffaloes and Italian Friesian cows are given in Table 1. Higher ($p < 0.05$) concentrations were observed in buffalo milk for Ca, P, and Mg, but the concentrations of K and Na were significantly lower ($p < 0.05$) than in cow milk, confirming what was reported in previous studies with a direct comparison between buffalo and cow milk [17,18]. The differences in concentrations for Ca, P, and K observed in our study were also in agreement with results by Ahmad et al. [19] and Chen et al. [20]. However, Ahmad et al. [19] reported 16% higher Na concentration in buffalo milk than in cow milk, and Chen et al. [20] reported significantly lower Mg concentration in buffalo milk than in cow milk but no significant differences in Na in the two types of milk. The Ca/P ratio was not different between buffalo and cow milk (Table 1), consistently with findings by Islam et al. [18].

Table 1. Essential macro mineral concentrations (mg/L) and Ca:P ratio in buffalo and cow milk.

Element	Buffalo n = 32	Cow n = 29	SEM	*p*-Value
Ca	1598	1153	31.1	<0.001
P	1340	975	19.9	<0.001
K	1021	1461	29.9	<0.001
Na	333.9	391.7	17.0	0.02
Mg	154.6	104.0	4.1	<0.001
Ca/P	1.21	1.18	0.03	0.49

SEM = standard error of the mean.

In our study, the concentrations of Ca, P, and Mg in buffalo milk were respectively 38.6%, 37.4%, and 48.6% higher than in cow milk, in agreement with previously published data for Ca [17–20], P [17–19], and Mg [18,19]. The concentrations of K and Na were respectively 30.0% and 15% lower in buffalo milk than in cow milk, in agreement with previously published data for K [17–20] and Na [18].

The average macro mineral concentrations observed in cow milk (Table 1) were consistent with the literature data [6,7]. Our results on Ca in buffalo milk (Table 1) were similar to those observed by Stocco et al. [13], Benincasa et al. [17], Islam et al. [18], and Ariota et al. [21]. Other studies reported higher (approx. 1900 to 2015 mg/L) [19,22] or lower values (approximately 750 to 1120 mg/L) [20,23]. The concentration of P in our study was generally higher than those previously reported for buffalo milk [13,17–19,22,23] but similar to that observed by Ariota et al. [21]. The Mg concentration in buffalo milk was in close agreement with data by Stocco et al. [13], Islam et al. [18], and Ahmad et al. [19], but others reported lower (approx. 60 to 80 mg/L) [20,23] or higher concentrations (235 mg/L) [22]. The concentration of K was in the range reported for buffalo milk [19,22,23], but lower values were also observed (approx. 640 to 860 mg/L) [13,17,18,20]. Our results on Na concentrations were similar [18,20] or lower than published data in buffalo milk [19,22,23].

3.2. *Essential Trace Elements in Milk*

Results on essential trace elements in buffalo and cow milk are presented in Table 2. Higher ($p < 0.05$) concentrations were observed for Zn (44.9%), Fe (51%), and Cu (96.4%) in buffalo milk than in cow milk, whereas the opposite was observed for Mo concentration, resulted significantly ($p < 0.05$) lower (32%) in buffalo than in cow milk. The concentrations of Mn, Se, and Co were not statistically different between the two species.

Table 2. Essential trace element concentrations (μg/L) in buffalo and cow milk.

Element	Buffalo n = 32	Cow n = 29	SEM	*p*-Value
Zn	4978	3435	0.14	<0.001
Fe	321.9	212.7	14.6	<0.001
Cu	109.8	56.0	11.2	0.005
Mn	30.1	25.8	1.71	0.087
Se	26.9	25.4	0.74	0.166
Mo	49.9	73.8	2.15	<0.001
Co	0.94	0.78	0.06	0.063

SEM = standard error of the mean.

Previous studies dealing with a direct comparison between buffalo and cow milk also reported significantly higher Zn [17,18] and Cu [20] concentrations in buffalo milk compared to cow milk, but Chen et al. [20] did not observe significant differences for Zn. Published data on Fe are also variable. Benincasa et al. [17] found similar Fe concentrations in milk from both species, but Chen et al. [20] observed significantly higher (43%) Fe concentration in cow milk than in buffalo milk. Similarly to our study, Chen et al. [20] did not report significant differences in Mn concentrations in milk from both species, but others reported significantly higher Mn concentrations for cow [17] or buffalo milk [18]. The concentration of Se was reported to be higher in cow than in buffalo milk [20], and those of Mo and Co were similar in milk from both species [17]. Although based on raw data, Enb et al. [24] and Zhou et al. [25] reported higher concentrations of Zn, Fe, Cu, Mn, and Co in buffalo than in cow milk.

The average essential trace element concentrations observed in cow milk (Table 2) were consistent with reference data indicated by Fox et al. [5], except for Fe and Cu found lower in our experiment.

Regarding the average essential trace element concentrations in the current study (Table 2), the concentration of Zn in buffalo milk was consistent with results available in the literature which indicates a range of concentration from approximately 4000 to 6000 μg/L in buffalo milk [4,17–19,23–26]. Ample variations of concentration are reported in the literature for Fe (approx. 300 to 4000 μg/L), Cu (approx. 50 to 600 μg/L), and Mn (approx. 3 to 300 μg/L) in buffalo milk [4,17,20,23–26]. However, the concentration of Fe in our study was similar to that observed by Benincasa et al. [17] and Zhou et al. [25], that of Cu was similar to those reported by Zhou et al. [25] and Esposito et al. [26], and that of Mn was generally lower than most of the published values on such element [4,17,20,23–26]. The concentration of Se and Mo substantially agreed with the few available literature data [20,25,26]. Available published studies on Co are also limited and reported higher (approx. 2 to 8.3 μg/L) [17,24,26] concentration than in the current study, except for Zhou et al. 2016 [25], who observed 0.40 μg/L in buffalo milk.

3.3. Non-Essential Trace Elements in Milk

Results on the investigated non-essential trace elements in buffalo and cow milk are presented in Table 3. Significantly higher ($p < 0.05$) concentrations were observed in buffalo milk for B, Ti, and Sr, but the concentrations of Li and Rb were found to be significantly lower ($p < 0.05$) than in cow milk.

Table 3. Non-essential trace element concentrations (μg/L) in buffalo and cow milk.

Element	Buffalo n = 32	Cow n = 29	SEM	*p*-Value
Li	2.98	8.03	0.52	<0.001
B	342.3	277.6	8.48	<0.001
Ti	426.8	301.1	11.6	<0.001
Rb	391.9	793.5	18.6	<0.001
Sr	1139	563.8	33.09	<0.001

SEM = standard error of the mean.

In the rare studies dealing with direct comparison of buffalo and cow milk in terms of non-essential trace elements, significantly higher concentrations of Rb were reported for cow milk [17] as in the current study, but similar concentrations were observed for Sr in both species [17,20]. On the contrary, raw means published by Enb et al. [24] indicate higher Rb and lower Sr concentrations in buffalo milk than in cow milk.

To the authors' knowledge, published data about the investigated non-essential trace elements in buffalo milk are limited to few results on Rb and Sr, and no data are available on Li, B, and Ti. Moreover, little attention was devoted to the concentrations of Li, B, Ti, Rb, and Sr even for the highly characterized cow milk. Our data showed that Sr, Ti, Rb, and B represent, respectively, the 2nd to 5th largest concentration among the investigated trace elements in buffalo milk, following that of Zn. In cow milk, the descending order Zn > Rb > Sr > Ti > B was observed (Tables 2 and 3).

In the current study, the average Li concentration in cow milk (Table 3) was comparable to the values reported by Dobrzanski et al. [27] and Bilandzic et al. [28]. Besides its therapeutic role in the treatment of people with manic-depressive psychosis at therapeutic amounts, it has been suggested that dietary Li may have a role in the regulation of some endocrine function [10]. Feeding goats with a diet deficient in Li negatively affected fertility, birth weight, and lifespan, and altered activity of several liver and blood enzymes [9]. Moreover, negative effects on fertility, birth weight, litter size, and weaning weight have been reported for rats fed a diet deficient in Li [10].

The average B concentration in cow milk (Table 3) was lower than those reported by Anderson (approx. 330 μg/L) [29] and Zwierzchowski and Ametaj (approx. 350 μg/L) [30]. Findings from in vitro and in vivo animal studies indicate that insufficient dietary B results in altered bone development, brain function, trace elements metabolism, energy substrate utilization, immune function, and insulin secretion, as reviewed by Nielsen [31].

Compared to our results (Table 3), Dobrzanski et al. [27] and Anderson [29] reported a lower concentration of Ti (50 to 110 μg/L) in cow milk. About apparent signs of dietary deprivation for Ti, findings from lactating goats fed a diet deficient in Ti showed increased mortality and reduced growth of kids, as well as reduced Ti content of milk [9].

The milk concentration of Rb in the current study (Table 3) was considerably lower than that reported in previous studies on buffalo (approx. 1440 to 2960 μg/L) and cow milk (1800 to 2440 μg/L) [17,25,30,31]. Decreased feed intake and growth and increased spontaneous abortions have been observed in goats fed a diet deficient in Rb [10].

Results from the current study on Sr in buffalo milk (Table 3) showed generally higher concentrations than those reported in the literature (approx. 410 to 750 μg/L) [17,20,25], except for data reported by Esposito et al. [26], that were similar. The concentration of Sr in cow milk was consistent with results available in the literature (approx. 410 to 700 μg/L) [17,20,25,28,30]. It has been reported that Sr determines beneficial effects on teeth and bones at supranutritional or pharmacological amounts. However, it has also been reported that growing pigs fed a diet supplemented with 50 mg Sr/kg dry matter showed enhanced breaking strength, mineral content, and mineral density of metatarsals and femurs [11].

3.4. Macro Minerals and Trace Elements in the Diet of Buffaloes and Cows

The concentrations of the investigated minerals in dietary ingredients (Table S1) were in the range reported in the literature [12,32,33], and the calculated chemical element concentrations of the two diets are summarized in Table 4. The concentrations of essential macro minerals and trace elements of the diets meet or exceed the dietary requirements reported in the literature for lactating dairy cows, except for P, Mg, and S, which resulted marginally lower [34,35].

Table 4. Chemical elements composition of diets fed to buffaloes and cows.

	Buffalo	**Cow**
Essential macro minerals, g/100 g DM		
Ca	0.88	0.78
P	0.24	0.29
K	1.80	1.48
Na	0.24	0.29
Mg	0.18	0.19
S	0.16	0.18
Essential trace elements, mg/kg DM		
Zn	110.7	112.6
Fe	142.1	147.8
Cu	15.9	16.3
Mn	59.5	61.5
Se	0.31	0.31
Mo	5.53	3.62
Co	0.26	0.25
Non-essential trace elements, mg/kg DM		
Li	0.51	0.37
B	20.3	18.2
Ti	1.83	1.86
Rb	10.4	10.2
Sr	37.1	17.9

DM = dry matter.

It appears that the diets fed to buffaloes and cows were substantially similar for most elements. However, the different proportions of ingredients in the two diets resulted in higher Mo, Li, and Sr in the diet fed to buffaloes. Nevertheless, conversely, the concentrations of Mo and Li were lower in buffalo than in cow milk (Tables 2 and 3). Therefore, in the current experimental conditions, the concentrations of chemical elements in buffalo and cow milk were not dependent on the diet or by environmental factors and should be ascribed to physiological differences between the lactating buffalo and cow, at the mammary gland level and likely at the systemic level. Most of the available studies reporting results on chemical elements in buffalo and cow milk derived from animals reared in different locations and diets are not often mentioned. Benincasa et al. [17] collected milk samples from 6 buffaloes and 12 cows reared on the same farm and fed the same feedstuffs and did not observe a significant correlation between the concentration of chemical elements in feedstuffs and milk, suggesting that the differences in chemical elements between cows and buffalo milk were not due to differences of diets. However, in the latter paper, the concentration of chemical elements was not presented for diet nor feedstuffs. Although not in all experimental conditions, Se in milk is reported to be dependent on dietary intake in humans and animals [5,36]. Zhou et al. [25] observed significant correlations between Cu, Se, and Co in the diet and in milk from buffaloes and cows and concluded that elements in feedstuffs might contribute to the elements in milk. In our study, the concentrations of Se and Co were similar in the diets and milk of both species (Tables 2 and 4).

4. Conclusions

The current study contributes to knowledge advances on essential macro mineral and trace element concentrations in buffalo milk and provides further data on some non-essential trace element contents in both buffalo and cow milk. The results show that buffalo milk contains higher concentrations of Ca, P, Mg, Zn, Fe, Cu, B, Ti, and Sr and lower concentrations of K, Na, Mo, Li, and Rb compared to cow milk, whereas milk from both species contains similar concentrations of Mn, Se, and Co. In the current experimental conditions, the differences observed in milk concentration of chemical elements cannot be considered dependent on environmental factors in buffaloes and cows, clinically healthy and in early lactation, raised on the same farm and fed diets including the same ingredients.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/article/10.3390/beverages8030051/s1, Table S1: Macro mineral and trace element concentrations in feedstuffs and drinking water.

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References

1. FAO. FAOSTAT. Available online: https://www.fao.org/faostat/en/#data/QCL (accessed on 12 July 2022).
2. Ahmad, S. Buffalo milk. In *Milk and Dairy Product in Human Nutrition: Production, Composition and Health*; Park, Y.W., Haenlein, G.F.W., Eds.; John Wiley & Sons: Oxford, UK, 2013; pp. 519–553. https://doi.org/10.1002/9781118534168.ch24.
3. Tripaldi, C.; Amatiste, S.; Giangolini, G.; Palocci, G.; Borghese, A. Milk quality and products. In *Buffalo Livestock and Products*; Borghese, A., Ed.; Consiglio Ricerca Sperimentazione Agricoltura: Roma, Italy, 2013; pp. 234–260, ISBN 978-88-97081-27-2.
4. Abd El-Salam, M.; El-Shibiny, S. A comprehensive review on the composition and properties of buffalo milk. *Dairy Sci. Technol.* **2013**, *29*, 663–699. https://doi.org/10.1007/s13594-011-0029-2.
5. Fantuz, F.; Salimei, E.; Papademas, P. Macro- and micro-nutrients in non-cow milk and products and their impact on human health. In *Non-Bovine Milk and Milk Products*; Tsakalidou, E., Papadimitriou, K., Eds.; Academic Press: London, UK, 2016; pp. 209–261. https://doi.org/10.1016/B978-0-12-803361-6.00009-0.
6. Fox, P.F.; Uniacke-Lowe, T.; McSweeney, P.L.H.; O'Mahony, J.A. *Dairy Chemistry and Biochemistry*, 2nd ed.; Springer International Publishing: London, UK, 2015; pp. 241–270. https://doi.org/10.1007/978-3-319-14892-2.

7. Gaucheron, F. Milk minerals, trace elements and macroelements. In *Milk and Dairy Product in Human Nutrition: Production, Composition and Health*; Park, Y.W., Haenlein, G.F.W., Eds.; John Wiley & Sons: Oxford, UK, 2013; pp. 172–199. https://doi.org/10.1002/9781118534168.ch9.
8. Hunt, C.D.; Nielsen, F.H. Nutritional aspects of minerals in bovine and human milk. In *Advanced Dairy Chemistry, Lactose, Water, Salts and Minor Constituents*, 3rd ed.; McSweeney, P.L.H., Fox, P.F., Eds.; Springer: New York, NY, USA, 2009; pp. 391–456, Volume 3. https://doi.org/10.1007/978-0-387-84865-5_10.
9. Haenlein, G.F.W.; Anke, M. Mineral and trace element research in goats: A review. *Small Rumin. Res.* **2011**, *95*, 2–19. https://doi.org/10.1016/j.smallrumres.2010.11.007.
10. Nielsen, F.H. Ultratrace elements in nutrition: Current knowledge and speculation. *J. Trace Elem. Exp. Med.* **1998**, *11*, 251–274. https://doi.org/10.1002/(SICI)1520-670X(1998)11:2/3<251::AID-JTRA15>3.0.CO;2-Q.
11. Nielsen, F.H. Manganese, molybdenum, boron, chromium, and other trace elements. In *Present Knowledge in Nutrition*, 10th ed.; Erdman, J.W., Macdonald, A., Zeisel, S.H., Eds.; Wiley-Blackwell: Oxford, UK, 2012; pp. 586–607. https://doi.org/10.1002/9781119946045.ch38.
12. Suttle, N.F. *The Mineral Nutrition of Livestock*, 4th ed.; CAB International: Wallingford, UK, 2010.
13. Stocco, G.; Cipolat-Gotet, C.; Bonfatti, V.; Schiavon, S.; Bittante, G.; Cecchinato, A. Short communication: Variations in major mineral contents of Mediterranean buffalo milk and application of Fourier-transform infrared spectroscopy for their prediction. *J. Dairy Sci.* **2016**, *99*, 8680–8686. https://doi.org/10.3168/jds.2016-11303.
14. Fantuz, F.; Ferraro, S.; Todini, L.; Piloni, R.; Mariani, P.; Malissiova, E.; Salimei, E. Minor and potentially toxic trace elements in milk and blood serum of dairy donkeys. *J. Dairy Sci.* **2015**, 98, 5125–5132. https://doi.org/10.3168/jds.2015-9404.
15. Fantuz, F.; Ferraro, S.; Todini, L.; Cimarelli, L.; Fatica, A.; Marcantoni, F.; Salimei, E. Distribution of calcium, phosphorus, sulfur, magnesium, potassium, and sodium in major fractions of donkey milk. *J. Dairy Sci.* **2020**, *103*, 8741–8749. https://doi.org/10.3168/jds.2020-18251.
16. Fantuz, F.; Ferraro, S.; Todini, L.; Spurio, R.; Fatica, A.; Marcantoni, F.; Salimei, E. Distribution of selected trace elements in the major fractions of donkey milk. *J. Dairy Sci.* **2022**, *105*, 6422–6430. https://doi.org/10.3168/jds.2022-21901.
17. Benincasa, C.; Lewis, J.; Sindona, G.; Tagarelli, A. The use of multi element profiling to differentiate between cow and buffalo milk. *Food Chem*. **2008**, *110*, 257–262. http://doi.org/10.1016/j.foodchem.2008.01.049.
18. Islam, M.A.; Alam, M.K.; Islam, M.N.; Khan, M.A.S.; Ekeberg, D.; Rukke, E.O.; Vegarud, G.E. Principal milk components in buffalo, Holstein cross, indigenous cattle and Red Chittagong cattle from Bangladesh. Asian Australasian. *J. Anim. Sci*. **2014**, *27*, 886–897. https://doi.org/10.5713/ajas.2013.13586.
19. Ahmad, S.; Gaucher, I.; Rousseau, F.; Beaucher, E.; Piot, M.; Grongnet, J.F.; Gaucheron, F. Effect of acidification on physico-chemical characteristics of buffalo milk: A comparison with cow milk. *Food. Chem.* **2008**, *106*, 11–17. https://doi.org/10.1016/j.foodchem.2007.04.021.
20. Chen, L.; Li, X.; Liab, Z.; Deng, L. Analysis of 17 elements in cow, goat, buffalo, yak, and camel milk by inductively coupled plasma mass spectrometry (ICP-MS). *R. Soc. Chem. Adv*. **2020**, *10*, 6736–6742. https://doi.org/10.1039/d0ra00390e.
21. Ariota, B.; Campanile, G.; Potena, A.; Napolano, R.; Gasparrini, B.; Neglia, G.L.; Di Palo, R. Ca and P in buffalo milk: Curd yield and milk clotting parameters. *Ital. J. Anim. Sci*. **2007**, *6* (Suppl. S1), 497–499. http://doi.org/10.4081/ijas.2007.1s.497.
22. Singh, M.; Sharma, R.; Ranvir, S.; Gandhi, K.; Mann, B. Profiling and distribution of minerals content in cow, buffalo and goat milk. *Indian J. Dairy Sci.* **2019**, *72*, 480–488. https//doi.org/10.33785/IJDS.2019.v72i05.004.
23. Patino, E.M.; Pochon, D.O.; Faisal, E.L.; Cedrès, J.F.; Mendez, F.I.; Stefani, C.G.; Crudeli, G. Influence of breed, year, season and lactation stage on the buffalo milk mineral content. *Ital. J. Anim. Sci.* **2007**, *6* (Suppl. S2), 1046–1049. https://doi.org/10.4081/ijas.2007.s2.1046.
24. Enb, A.; Abou Donia, M.A.; Abd-Rabou, N.S.; Abou-Arab, A.A.K.; El-Senaity, M.H. Chemical composition of raw milk and heavy metal behaviour during processing of milk products. *Glob. Vet.* **2009**, *3*, 268–275.
25. Zhou, X.; Qu, X.; Zhao, S.; Wang, J.; Li, S.; Zheng, N. Analysis of 22 elements in milk, feed, and water of dairy cow, goat, and buffalo from different regions of China. *Biol. Trace Elem. Res*. **2017**, *176*, 120–129. https://doi.org/10.1007/s12011-016-0819-8.
26. Esposito, M.; Miedico, O.; Cavallo, S.; Pellicanò, R.; Rosato, G.; Baldi, L.; Chiaravalle, A.E. Trace elements in raw milk of buffaloes (*Bubalus bubalis*) from Campania, Italy. *Food Chem.* **2017**, *233*, 378–384. https://doi.org/10.1016/j.foodchem.2017.04.124.
27. Dobrzanski, Z.; Kolacz, R.; Górecka, H.; Chojnacka, K.; Bartkowiak, A. The content of microelements and trace elements in raw milk from cows in the Silesian region. *Pol. J. Environ. Stud*. **2005**, *14*, 685–689.
28. Bilandžić, N.; Sedak, M.; Dokic, M.; Bozic. D. Determination of macro- and microelements in cow, goat, and human milk using inductively coupled plasma optical emission spectrometry. *Spectrosc. Lett.* **2015**, *48*, 677–684. https://doi.org/10.1080/00387010.2014.962704.
29. Anderson, R.R. Comparison of trace elements in milk of four species. *J. Dairy Sci.* **1992**, *75*, 3050–3055. https://doi.org/10.3168/jds.S0022-0302(92)78068-0.
30. Zwierzchowski, G.; Ametaj, B.N. Mineral elements in the raw milk of several dairy farms in the province of Alberta. *Foods* **2019**, *8*, 345. https://doi.org/10.3390/foods8080345.
31. Nielsen, F.H. Update on human health effects of boron. *J. Trace Elem. Med. Biol.* **2014**, *28*, 383–387. https://doi.org/10.1016/j.jtemb.2014.06.023.
32. McDowell, L.R.; Valle, G. Major minerals in forages. In *Forage Evaluation in Ruminant Nutrition*; Givens, D.I., Owen, E., Axford, R.F.E., Omed, H.M., Eds.; CABI Publishing: Wallingford, UK, 2000; pp. 373–397.

33. Van Paemel, M.; Dierick, N.; Janssens, G.; Fievez, V.; De Smet, S. Selected Trace and Ultratrace Elements: Biological Role, Content in Feed and Requirements in Animal Nutrition—Elements for Risk Assessment. EFSA-Publications Connexes-Technical Report. 2010. Available online: https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903/sp.efsa.2010.EN-68 (accessed on 25 July 2022).
34. Erickson, P.S.; Kalscheur, K.F. Nutrition and feeding of dairy cattle. In *Animal Agriculture*; Bazer, F.W., Lamb, G.C., Wu, G., Eds.; Academic Press: San Diego, CA, USA, 2020; pp. 157–180. https://doi.org/10.1016/B978-0-12-817052-6.00009-4.
35. Weiss, W.P. Recommendations for trace minerals for dairy cows. In Proceedings of the Herd Health and Nutrition Conference, Ithaca, NY, USA, 12 April 2017. Available online: https://ecommons.cornell.edu/handle/1813/48026 (accessed on 25 July 2022).
36. Fantuz, F.; Ferraro, S.; Todini, L.; Mariani, P.; Piloni, R.; Salimei, E. Essential trace elements in milk and blood serum of lactating donkeys as affected by lactation stage and dietary supplementation with trace elements. *Animal* **2013**, *7*, 1893–1899. https://doi.org/10.1017/S175173111300133X.