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Analysis of 22 Elements in Milk, Feed, and Water of Dairy Cow, Goat, and Buffalo from Different Regions of China

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Abstract The objectives of this study were to measure the concentrations of elements in raw milk by inductively coupled plasma-mass spectrometry (ICP-MS) and evaluate differences in element concentrations among animal species and regions of China. Furthermore, drinking water and feed samples were analyzed to investigate whether the element concentrations in raw milk are correlated with those in water and feed. All samples were analyzed by ICP-MS following microwave-assisted acid digestion. The mean recovery of the elements was 98.7 % from milk, 103.7 % from water, and 93.3 % from a certified reference material (cabbage). Principal component analysis results revealed that element concentrations differed among animal species and regions. Correlation analysis showed that trace elements Mn, Fe, Ni, Ga, Se, Sr, Cs, U in water and Co, Ni, Cu, Se, U in feed were significantly correlated with those in milk ($p < 0.05$). Toxic and potential toxic elements Cr, As, Cd, Tl, Pb in water and Al, Cr, As, Hg, Tl in feed were significantly correlated with those in milk ($p < 0.05$). Results of correlation analysis revealed that elements in water and feed might contribute to the elements in milk.

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Introduction

Milk and milk products represent an important source of macro and micronutrients, including minerals. Trace elements such as iron (Fe), zinc (Zn), copper (Cu), and selenium (Se) are essential in human metabolism, growth, and development [1], while toxic elements such as lead (Pb) and cadmium (Cd) induce mental retardation and cardiovascular diseases [2, 3]. Therefore, element concentration in milk and milk products are indicative of their safety and nutritional value.

The concentrations of trace and toxic elements in raw cow milk vary significantly by region [4–6]. For example, Pb, Cd, and Cu concentrations are 47.45, 1.68, and 890.15 μg/L, respectively, in raw milk from Croatia [7], and 5.23, 0.40, and 51.8 μg/L, respectively, in raw milk from Spain [8]. Additionally, element concentration in milk varies by animal species [3, 9, 10]. Najarnezhad et al. have studied the concentration of Pb and Cd in ewe and cow milk; the results showed that Pb and Cd in ewe milk were significantly higher than those in cow milk [10]. Lin Bo [11] reported that the concentrations of Fe and Zn in buffalo milk were higher than those in cow milk.

The concentrations of elements in raw milk are also affected by animal forage, feed, and water [12–14]. Concentrations of health-beneficial elements, e.g., cobalt (Co), Fe, Zn, in milk are dependent on the animal species, feed, milk sample collection time, environmental conditions, and manufacturing processes [15, 16]. Arsenic (As) and Fe in cow milk are possibly related to a higher consumption of concentration feed [6]. Potortì et al. have reported that elements in donkey milk were related with those in feed and water [17]. Cu levels in milk are attributed to feed Cu concentrations [18].

In China, cattle represents a vital part of the economy. Cattle breeding stock reached 14.9 million in 2012, contributing to approximately 38.75 million tonne of cow milk [19]. In 2014, the population of dairy goats was approximately 1.2 million, and goat milk was the second most important type of milk in China [20]. Buffalo milk, which represents an important source of income in southern China, had a yield of approximately 33,000 t in Guangxi province in 2012 [21].

There is little information on the concentrations of trace, potentially toxic, and toxic elements in goat and buffalo milk in China. The correlations of elements content between milk and feed, drinking water are also little. Therefore, the objectives of this study were to measure the concentrations of elements in raw milk by inductively coupled plasma-mass (ICP-MS) and evaluate differences in element concentrations among animal species and regions. Furthermore, drinking water and feed samples were analyzed to investigate whether the element concentrations in milk are correlated with those in drinking water and feed.

Materials and Methods

Instrumentation

Vanadium (V), manganese (Mn), Fe, Co, nickel (Ni), Cu, Zn, gallium (Ga), Se, rubidium (Rb), strontium (Sr), silver (Ag), caesium (Cs), barium (Ba), uranium (U), aluminum (Al), chromium (Cr), As, Cd, mercury (Hg), thallium (Tl), and Pb were measured by ICP-MS (7700x, Agilent, USA), which was equipped with a quadrupole hyperboloid, Scott double pass spray chamber, concentric nebulizer, and high matrix introduction (HMI) sample introduction system. A microwave dissolver (CEM Corporation, USA) with PTFE tubes was used for milk and feed sample digestion; the operating conditions of ICP-MS are presented in Table 1. Vessels used in the digestion were previously immersed in 20 % HNO_3 (*v*/*v*) for at least 12 h and rinsed with ultrapure water.

Preparation of Standard Solutions

A mercury calibration solution was prepared from 10 mg/L mercury standard solution (SPEX, USA), while the calibration solutions of the other 21 elements were prepared from 10 mg/L multi-element stock standard solution (SPEX). An internal standard solution was an aqueous multi-element standard solution containing 100 mg/L of Li, Sc, Ge, Rh, In, Tb, Lu, and Bi (SPEX). The internal stock standard solution was further diluted and used to correct any fluctuations of the instrument due to the matrix. Cabbage certified reference material (CRM) was obtained from the National Institute of Metrology (GBW10014, China). Nitric acid (65 %, Sigma, USA) and hydrogen peroxide (30 %, Merck, Germany) were used in sample digestion. To maintain the same percentage of acid in the samples, the calibration solutions were diluted with 6 % (*v*/*v*) HNO_3 for milk, 10 % (*v*/*v*) HNO_3 for feed, and 1 % (*v*/*v*) HNO_3 for water.

Table 1 Operating conditions and measurement parameters for the ICP-MS

Parameter	
Nebulizer	Concentric nebulizer
Spray chamber	Dual channel Scott type
Mass analizator	Quadruple
RF power	1550 W
Ar gas flow rates	
Plasma	15 L/min
Auxiliary	1.10 L/min
Lens voltage	12.2 V
Scanning mode	Peak hopping
Dwell time	45 s
Sample uptake rate	0.15 mL/min
Isotopes	^{45}Sc, ^{72}Ge, ^{103}Rh, ^{115}In, ^{159}Tb, ^{175}Lu, ^{209}Bi

Sample Collection and Digestion

A total of 299 samples were analyzed, including 100 milk samples (20 cow milk samples from Shandong, 20 cow milk samples from Shaanxi, 20 goat milk samples from Shandong, 20 goat milk samples from Shaanxi, and 20 buffalo milk samples from Guangxi), 100 feed samples, and 99 water samples (feed and water samples were collected from the same sites as the milk samples). Feed samples were total mixed ration (TMR) and collected from where the animal feeding. All samples were collected in April and July of 2014.

Milk and water samples were stored in 200 mL polypropylene bottles at −20 °C. Water samples were preserved by acidification with 2 mL HNO_3. Feed samples were oven dried at 65 °C for 48 h and ground to a particle size of 1 mm.

Milk (1 mL) was digested with 3 mL HNO_3 (65 %) and 4 mL H_2O_2 (30 %) in polytetrefluoethylene (PTFE) tubes. Feed (0.5 g) was first added with 1 mL of ultrapure water, then digested with 5 mL HNO_3 (65 %) and 2 mL H_2O_2 (30 %). Water was mixed with 1 % *v*/*v* HNO_3 prior to ICP-MS analysis. Sample digestion was performed at room temperature in open vessels.

A MARS 6 microwave sample digestion system (MARS 6, CEM Corporation, USA) with a power of 1600 W was used for the digestion of milk and feed samples. The milk samples were digested according to the following program: (1) ramp time 5 min, temperature 90 °C, hold time 5 min; (2) ramp time 5 min, temperature 150 °C, hold time 10 min; and (3) ramp time 5 min, temperature 180 °C, hold time 20 min. The feed samples were digested according to the following program: (1) ramp time 5 min, temperature 90 °C, hold time 5 min; (2) ramp time 5 min, temperature 150 °C, hold time 10 min; and (3) ramp time 5 min, temperature 200 °C, hold time 20 min. Digested samples were allowed to cool to room temperature, transferred to polypropylene tubes (Corning, USA), and diluted to 50 mL with ultrapure water. Blanks, devoid of samples, were subjected to similar digestion procedures.

Quality Assurance

Limit of detection (LOD) and limit of quantification (LOQ) were calculated from three and 10 times, respectively, the standard deviation of the sample blank relative to the slope of the analytical curve. The digestion procedures were different for milk, water, and feed samples; therefore, LOD and LOQ were calculated separately. The digested milk, feed, and water samples were used in the calculation of LOD and LOQ [22], as shown in Table 2.

To assess the accuracy of the method, cabbage CRM and spiked samples were analyzed. The recovery of the elements from cabbage CRM and spiked samples is shown in Table 3. The recovery of 22 elements in water and milk samples was 94.3–123.3 % and 91.4–113.4 %, respectively, except for Hg (86.5 % in water and 71.0 % in milk). For cabbage CRM, the recovery of 18 elements was 71.2–114.8 %. The results of recovery accord with precision of quantitative methods [23].

Statistical Analysis

Element concentrations below LOD were replaced by half the value of the respective detection limits. The data were not normally distributed; therefore, non-parametric test was used in the analysis. Spearman rank correlation was used to determine the magnitude of the correlation among elements in milk, water, and feed samples. Data analyses were performed using SPSS 17.0 (IBM, USA). Statistical significance was set at $p < 0.05$. Principal component analysis (PCA) was performed with Canoco 5.0.

Table 2 Detection limits of 22 elements in milk, feed, and water

Element	Milk (μg/L)		Feed (μg/kg)		Water (μg/L)	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
V	1.35×10^{-2}	0.04	0.05	0.16	0.04	0.12
Mn	1.83	6.11	0.19	0.64	1.47	4.91
Fe	9.83	32.76	9.40	31.33	6.25	20.85
Co	0.03	0.11	0.06	0.21	1.15×10^{-2}	0.04
Ni	0.12	0.41	0.15	0.51	0.13	0.43
Cu	1.16	3.86	1.71	5.71	0.16	0.52
Zn	3.16	10.53	1.51	5.02	1.65	5.50
Ga	9.73×10^{-3}	0.03	0.04	0.12	5.49×10^{-3}	0.02
Se	0.13	0.44	0.11	0.38	0.09	0.29
Rb	4.03	13.45	1.44	4.82	0.05	0.15
Sr	0.32	1.08	3.92	13.07	15.75	52.49
Ag	0.20	0.66	0.05	0.16	0.03	0.10
Cs	0.03	0.11	0.06	0.19	0.02	0.08
Ba	0.29	0.97	0.59	1.96	11.26	37.52
U	0.08	0.27	0.03	0.08	0.02	0.08
Al	1.69	5.64	1.53	5.11	2.91	9.71
Cr	0.82	2.74	0.39	1.28	0.07	0.24
As	0.09	0.30	0.18	0.61	0.15	0.51
Cd	2.89×10^{-3}	0.01	3.35×10^{-3}	0.01	2.88×10^{-3}	0.01
Hg	0.22	0.73	0.47	1.57	0.09	0.32
Tl	1.33×10^{-2}	0.04	4.13×10^{-3}	0.01	1.07×10^{-2}	0.04
Pb	0.28	0.94	0.16	0.53	0.05	0.16

Table 3 Spike recovery and quality control of certified reference material, cabbage

Element	Recovery (%)		Certified reference material		
	Water	Milk	Certified values (μg/kg)	Observed values (μg/kg)	Recovery (%)
Al	123.3	103.6	– [b]	– [b]	– [b]
V	105.1	100.1	– [b]	– [b]	– [b]
Cr	103.7	97.4	1800	1616.80	89.8
Mn	107.1	99.1	18,700	19,366.70	103.6
Fe	111.8	96.7	98,000	89,836.62	91.7
Co	96.2	97.7	89	63.34	71.2
Ni	95.3	97.1	930	922.70	99.2
Cu	94.3	94.7	2700	2190.18	81.1
Zn	107.3	94.0	26,000	23,543.38	90.5
Ga	100.3	99.6	– [a]	– [a]	– [a]
As	100.6	104.2	62	56.82	91.7
Se	101.3	113.4	200	229.66	114.8
Rb	105.3	91.4	19,600	18,882.77	96.3
Sr	114.3	98.5	48,000	48,460.21	101.0
Ag	103.2	103.3	– [a]	– [a]	– [a]
Cd	100.1	99.7	35	36.60	104.6
Cs	105.1	101.5	82	74.87	91.3
Ba	112.3	104.1	12,000	11,321.96	94.3
Hg	86.5	71.0	10.9	10.56	96.9
Tl	102.4	101.1	6.3	4.63	73.4
Pb	103.2	100.6	190	173.92	91.5
U	102.1	103.2	20	19.42	97.1
Mean ± SD	103.7 ± 7.45	98.7 ± 7.49			93.3 ± 10.25

[a] Certified value not available

[b] Measured value not available

Results and Discussion

Concentrations of Trace Elements in Milk Samples

Mn, Fe, Cu, Zn, Se, Rb, Sr, Cs, and Ba were present in all milk samples (positive rate 100.0 %). In buffalo milk, Ga had a positive rate of 100.0 % (Table 4). V was present in 50–100 % of all milk samples, and Ga and U were present in 50–100 % of cow and goat milk samples (Table 4). Other elements had lower positive rates: Ni, Co, and U were present in 10.0 to 50.0 % of all milk samples, goat milk, and buffalo milk, respectively. Ag had positive rate was lower than 10.0 % in all milk samples. As a result of the large percentage range, the mean values were affected by the high concentrations of the elements, which contributed to mean values that were higher than the median values.

Mean values were compared with those previously reported. Values above LOD were used for mean value calculation. Fe and Zn concentrations in our cow milk samples were similar to those reported in cow milk from Northern Spain [6], but lower than those reported from Turkey [24]. In this study, Zn concentrations in cow milk were similar to those in cow milk from Silesia [14] and higher than those from Pakistan [25]. Mostly, Cu, Co, and Mn concentrations were lower than those previously reported. In our study, Cu and Co concentrations were lower than those measured in cow milk from Northern Spain [6] and Turkey [14]. Similarly, Cu concentrations in cow milk from Croatia and Pakistan [7, 25], and Mn concentrations in cow milk from South Africa [2] were higher than those obtained in our study (Table 4). On the other hand, Mn concentrations were comparable to those obtained in cow milk from Northern Spain [6].

The trace elements in goat milk were lower than those previously reported (Table 4). Fe, Cu, and Zn concentrations in our goat milk samples were lower than those from Turkey [26] and Saudi Arabia [12]. Additionally, the concentrations of most elements in goat milk were higher than those in cow milk (Table 4), as previously reported [27–29]. In the present study, Zn concentration in buffalo milk was five times higher than that in buffalo milk from India, while Fe concentrations were similar between the two studies [30].

Table 4 Concentration of 22 elements in raw milk from different species

Element	Cow (n = 40)				Goat (n = 40)				Buffalo (n = 20)			
	Positive rate	Median	p75	Mean	Positive rate	Median	p75	Mean	Positive rate	Median	p75	Mean
V	75.0	0.12	0.32	0.29	80.0	0.21	0.58	0.39	75.0	0.15	0.30	0.26
Mn	100.0	20.58	27.10	23.35	100.0	33.78	40.26	36.32	100.0	56.30	61.29	51.49
Fe	100.0	230.15	329.80	352.08	100.0	361.15	525.19	462.96	100.0	497.60	567.47	421.33
Co	80.0	0.21	0.30	0.29	27.5	0.02	0.04	0.14	85.0	0.25	0.53	0.40
Ni	20.0	0.06	0.06	5.76	50.0	1.75	5.84	5.60	15.0	0.06	0.06	1.05
Cu	100.0	25.42	32.08	32.02	100.0	81.52	113.30	84.67	100.0	32.11	61.89	48.42
Zn	100.0	3307.37	3623.15	3233.96	100.0	2983.43	3281.77	2953.93	100.0	4689.09	5504.16	4629.55
Ga	80.0	0.05	0.07	0.08	60.0	0.05	0.08	0.09	100.0	0.09	0.17	0.25
Se	100.0	19.50	23.53	20.72	100.0	17.67	22.23	17.34	100.0	19.59	24.69	20.21
Rb	100.0	1659.44	1861.72	1828.84	100.0	2670.54	3418.40	2982.71	100.0	2757.65	3848.80	2965.06
Sr	100.0	518.79	658.39	589.20	100.0	1242.59	1827.51	1357.31	100.0	374.35	552.25	409.82
Ag	2.5	0.10	0.10	0.23	7.5	0.10	0.10	0.45	5.0	0.10	0.10	0.55
Cs	100.0	6.57	7.61	6.74	100.0	7.04	9.87	8.43	100.0	26.15	33.73	26.78
Ba	100.0	34.47	57.88	60.94	100.0	92.28	132.09	98.06	100.0	184.30	278.53	209.55
U	80.0	1.03	1.53	2.07	75.0	0.79	1.56	1.60	45.0	0.04	0.46	0.69
Al	92.5	48.22	74.54	56.91	92.5	69.40	138.62	102.54	50.0	0.99	101.64	89.18
Cr	15.0	0.41	0.41	12.52	35.0	0.41	2.36	5.26	ND	NC	NC	NC
As	82.5	0.48	0.81	0.86	45.0	0.05	0.44	1.26	100.0	2.30	2.73	2.49
Cd	32.5	0.00	0.02	0.07	27.5	0.00	0.02	0.05	ND	NC	NC	NC
Hg	47.5	0.11	1.74	5.20	15.0	0.11	0.11	5.07	15.0	0.11	0.11	0.33
Tl	77.5	0.03	0.06	0.07	80.0	0.14	0.27	0.20	5.0	0.01	0.01	0.02
Pb	95.0	1.16	2.10	1.46	100.0	1.52	2.40	1.75	100.0	6.77	8.84	7.16

Cr and Cd were not detected in buffalo milk. Concentrations expressed in microgram per liter

ND not detected, *NC* not computable, *n* number of samples

Concentrations of Trace Elements in Drinking Water and Feed Samples

The concentrations of trace elements in drinking water are presented in Table 5. Buffalo drinking water had higher trace element concentrations than those of cows and goats. Buffalo drinking water samples were collected from different province; therefore, region might account for such differences [31, 32]. The concentrations of V, Co, Ni, Cu, Ga, Se, Rb, and Cs in drinking water were lower than 10 μg/L; Ag was not detected in any of the samples. The concentrations of Mn, Cu, and Zn in all drinking water samples were lower than those reported in northern Pakistan [32].

V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Se, Rb, Sr, Cs, and Ba were present in 100 % of all feed samples. Both Ag and U had positive rates of 100 % in buffalo feed samples (Table 6). The concentrations of trace elements in feed samples were higher (tenfold) than those in drinking water (Tables 5 and 6).

Concentrations of Toxic and Potential Toxic Elements in Raw Milk, Water, and Feed Samples

The concentrations of toxic and potentially toxic elements (Al, Cr, As, Cd, Hg, Pb, and Tl) in milk samples are presented in Table 4. In cow milk, Pb had the highest positive rate (95.0 %), followed by Al, As, and Tl. Cr, Cd, and Hg had positive rates less than 50.0 %. In goat milk, Pb had the highest rate, followed by Al and Tl, for Cr, Cd, As, and Hg had the positive rate less than 50 %. In buffalo milk, Pb and As were detected in all samples (100.0 %), Al, Hg, and Tl were detected in less than 50 % of the samples, and Cr and Cd were not detected.

The concentrations of toxic and potentially toxic elements in water and feed samples are presented in Tables 5 and 6, respectively. Cr was detected in all drinking water samples, and Hg was not detected. Tl had the lowest positive rate in cow and goat drinking water. The positive rate of the other elements in cow and goat drinking water was 47.5–87.5 %. Al, Pb, and Cd were present in 100.0 % of buffalo water samples. For feed samples, Al, Cr, As, Cd, and Pb showed the highest positive rates. Tl had the highest positive rate in buffalo feed.

The results in Table 4 showed that Cd, Cr, and Pb concentrations in our cow milk samples were lower than those reported in Pakistan and Turkey, whereas As concentrations in our cow milk samples were higher than that reported in Turkey [24, 25, 33]. There were higher Cd concentrations in our cow milk samples than those reported in cow milk from South Africa [2]. Additionally, the concentrations of Al, Cd, Cr, and Pb in goat milk were lower than those reported by Coni [15]. The concentrations of As in all drinking water samples were lower than those reported in Argentina [34]. Most of the toxic and potentially toxic elements detected in our samples were lower than those from other regions. Concentrations of Pb, Cr, Hg, and As in all milk samples were below MRL established by China and the European Union (EU) [35]. Therefore, the raw milk samples used in this study had no health risks.

Difference Analysis by Principal Component Analysis

Figure 1 showed principal component 1 × principal component 2 plots, where loadings and scores were simultaneously represented. PCA allowed the reduction of 17 variables to four PCs, which explained 68.12 % of the total variance. The samples were collected from different animal species and regions. Element concentrations in milk and drinking water were analyzed by PCA to evaluate the effect of animal species and regions on raw milk element concentration.

The PCA results revealed that the concentrations of elements differed among animal species and regions (Fig. 1b), in agreement with the findings of Rahimi [3]. Similar results were obtained with drinking water. Element concentrations in water samples differed among regions. Element concentrations in buffalo water samples were different to those in cow and goat water samples, with no significant differences between cow and goat water samples (Fig. 1a). These results might be attributed to the location of sample collection. Cow and goat drinking water samples were collected from the same provinces, while buffalo water samples were collected from another distant region. The concentrations of elements in underground water from different regions are considerably different [32]. Differences in element concentrations in underground water might contribute to differences in element concentration in milk, water, and feed. PCA for feed samples revealed no significant differences among animal species or regions (data not shown).

Correlation Analysis of Milk, Water, and Feed

Trace elements Mn, Fe, Ni, Ga, Se, Sr, Cs, and U in milk were significantly correlated with those in drinking water, while Co, Ni, Cu, Se, and U were significantly correlated ($p < 0.05$) with those in feed (Table 7). Similarly, toxic and potentially toxic elements in milk were significantly correlated ($p < 0.05$) with those in water and feed. Cr, As, Cd, Tl, and Pb in milk had significant correlations with those in drinking water, while Al, Cr, As, Hg, and Tl in milk samples were significantly correlated with those in feed samples ($p < 0.05$, Table 7).

Therefore, elements in drinking water and feed might contribute to the elements in milk. This result was consistent with previously reported correlations between elemental mass fractions in milk and ingested feed and water [16]. Fe contamination in drinking water may directly affect cow milk Fe

Table 5 Concentration of 22 elements in drinking water from different species

Element	Cow (n = 40)				Goat (n = 39)				Buffalo (n = 20)			
	Positive rate	Median	p75	Mean	Positive rate	Median	p75	Mean	Positive rate	Median	p75	Mean
V	100.0	2.05	7.61	4.26	100.0	3.86	7.67	5.12	80.0	0.09	0.16	0.26
Mn	17.5	0.74	0.74	5.30	30.8	0.74	2.27	16.50	100.0	16.85	98.47	69.09
Fe	80.0	7.24	28.58	93.98	79.5	11.12	25.61	54.45	95.0	18.93	53.55	37.95
Co	85.0	0.02	0.06	0.06	100.0	0.07	0.12	0.11	100.0	0.51	3.17	1.89
Ni	35.0	0.06	0.19	0.44	61.5	0.18	0.30	0.69	100.0	0.72	3.11	1.78
Cu	40.0	0.08	0.30	1.19	71.8	0.24	0.60	1.81	95.0	1.04	2.93	1.82
Zn	65.0	2.44	4.64	9.54	71.8	2.59	6.88	17.07	95.0	7.44	10.52	8.52
Ga	27.5	0.00	0.00	0.01	23.1	0.00	0.00	0.02	90.0	0.02	0.28	0.62
Se	95.0	0.90	3.06	2.07	100.0	0.99	3.40	4.85	100.0	0.18	0.50	0.74
Rb	100.0	0.43	0.54	1.02	100.0	0.48	0.89	1.29	100.0	4.98	8.53	6.15
Sr	100.0	512.63	1517.11	1159.69	100.0	813.77	1428.44	1096.84	45.0	7.87	18.15	24.73
Ag	ND	NC	NC	NC	ND	NC	NC	NC	ND	NC	NC	NC
Cs	15.0	0.01	0.01	0.38	10.3	0.01	0.01	0.12	95.0	0.18	0.55	0.41
Ba	90.0	20.11	32.10	31.87	89.7	28.50	40.19	43.30	65.0	23.14	52.34	47.11
U	100.0	2.50	18.96	9.24	100.0	7.95	14.95	17.20	45.0	0.02	0.04	0.23
Al	57.5	3.18	5.36	9.61	61.5	3.69	7.24	20.17	100.0	17.75	45.93	139.88
Cr	100.0	9.60	83.03	45.34	100.0	1.55	28.54	22.63	100.0	0.25	0.40	0.45
As	77.5	0.52	2.47	1.76	87.2	1.03	2.64	1.65	70.0	0.27	0.50	0.69
Cd	55.0	0.00	0.01	0.01	76.9	0.01	0.01	0.03	100.0	0.03	0.06	0.05
Hg	ND	NC	NC	NC	ND	NC	NC	NC	ND	NC	NC	NC
Tl	7.5	0.01	0.01	0.02	2.6	0.01	0.01	0.02	95.0	0.03	0.11	0.08
Pb	47.5	0.02	0.09	0.10	71.8	0.10	0.17	0.24	100.0	0.48	1.23	2.93

One water samples of goat is missed, the corresponding milk and feed sample was used when calculated mean values, while dropped when correlation test. Ag and Hg were not detected in water samples. Concentrations expressed in microgram per liter

ND not detected, *NC* not computable, *n* number of samples

Table 6 Concentration of 22 elements in feed from different species

Element	Cow (n = 40)				Goat (n = 40)				Buffalo (n = 20)			
	Positive rate	Median	p75	Mean	Positive rate	Median	p75	Mean	Positive rate	Median	p75	Mean
V	100.0	1.00	1.45	1.26	100.0	1.01	1.97	1.37	100.0	0.29	0.99	0.97
Mn	100.0	102.74	128.30	117.96	100.0	97.39	139.82	115.77	100.0	123.15	176.77	124.37
Fe	100.0	573.35	802.76	664.16	100.0	428.06	791.66	687.38	100.0	387.67	574.80	624.28
Co	100.0	0.56	1.00	0.84	100.0	0.37	0.62	0.53	100.0	0.18	0.97	0.45
Ni	100.0	1.06	1.40	1.18	100.0	1.20	1.65	1.44	100.0	1.11	1.42	1.29
Cu	100.0	15.57	18.26	19.52	100.0	7.91	12.62	10.68	100.0	6.83	17.57	10.85
Zn	100.0	77.85	92.27	98.42	100.0	45.90	67.65	58.75	100.0	45.54	110.64	70.00
Ga	100.0	0.12	0.17	0.14	100.0	0.14	0.25	0.19	100.0	0.07	0.08	0.12
Se	100.0	0.33	0.42	1.50	100.0	0.18	0.33	0.25	100.0	0.12	0.36	0.21
Rb	100.0	8.98	10.75	9.16	100.0	7.98	10.45	9.01	100.0	18.48	30.98	21.04
Sr	100.0	31.57	41.73	34.28	100.0	16.43	55.57	38.60	100.0	9.29	12.49	10.46
Ag	50.0	0.00	0.00	0.01	77.5	0.00	0.01	0.01	100.0	0.00	0.01	0.01
Cs	100.0	0.12	0.14	0.12	100.0	0.11	0.17	0.12	100.0	0.09	0.12	0.13
Ba	100.0	11.22	14.14	10.99	100.0	8.59	26.95	15.84	100.0	8.63	13.22	13.53
U	97.5	0.05	0.11	0.08	82.5	0.03	0.12	0.10	100.0	0.02	0.05	0.03
Al	100.0	453.19	663.61	492.00	100.0	474.10	798.54	626.34	100.0	266.59	381.42	454.08
Cr	100.0	3.16	6.34	5.23	100.0	1.30	5.13	6.89	100.0	1.48	4.45	6.19
As	100.0	0.29	0.38	0.34	100.0	0.21	0.45	0.34	100.0	0.22	0.37	0.33
Cd	100.0	0.05	0.06	0.06	100.0	0.05	0.18	0.15	100.0	0.10	0.13	0.11
Hg	75.0	0.01	0.01	0.01	85.0	0.00	0.01	0.01	90.0	0.01	0.01	0.01
Tl	97.5	0.01	0.01	0.01	92.5	0.01	0.02	0.02	100.0	0.01	0.02	0.02
Pb	100.0	0.87	1.27	0.99	100.0	0.72	1.34	1.08	100.0	0.85	1.32	1.26

Concentrations expressed in milligram per kilogram

n number of samples

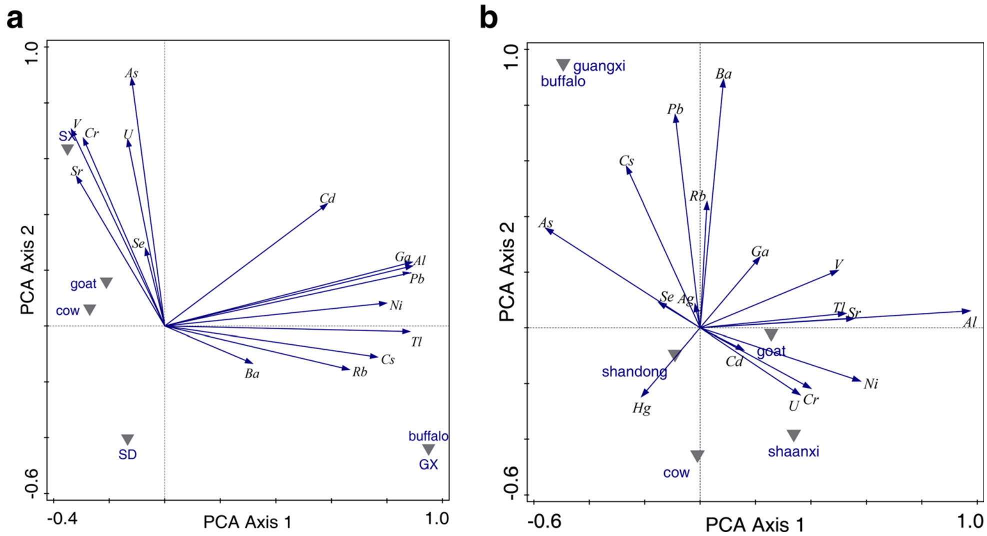

Fig. 1 The result of difference analysis by PCA for milk and water. *SD* Shandong province, *SX* Shaanxi province, *GX* Guangxi province. *X*-axis is principal component 1 and *Y*-axis is principal component 2. **a** The result of PCA for water samples. **b** The result of PCA for milk samples. Variables used in the principal component analysis were V, Se, Ni, Ga, Rb, Sr, Ag, Cs, Ba, U, Al, Cr, As, Cd, Hg, Tl, and Pb in water and milk samples

concentrations [36]. Deka [37] reported that Cr concentrations in milk is increased by adding Cr to the feed; however, As in drinking water showed a low biological transference to cow milk [34]. Compared to water, fewer elements in feed were significantly correlated with those in milk (Table 7). The feed of dairy animals is more likely to be collected from different regions rather than locally produced. On the other hand, drinking water is usually local.

Table 7 Correlation analysis of elements in milk with that in drinking water and feed

Element	Water		Feed	
	R	*p*	*R*	*p*
Mn	0.421	0.000	–	–
Fe	0.237	0.018	–	–
Co	–	–	0.238	0.018
Ni	−0.369	0.000	−0.321	0.001
Cu	–	–	−0.206	0.041
Ga	0.261	0.009	–	–
Se	−0.210	0.037	0.365	0.000
Sr	0.431	0.000	–	–
Cs	0.512	0.000	–	–
U	0.207	0.040	0.218	0.030
Al	–	–	−0.075	0.005
Cr	0.481	0.000	−0.228	0.023
As	−0.398	0.000	0.199	0.048
Cd	−0.252	0.012	–	–
Hg	–	–	0.297	0.003
Tl	−0.483	0.000	−0.237	0.018
Pb	0.434	0.000	–	–

R correlation coefficient

p statistically significant at $p < 0.05$

–*p* > 0.05, no relationship between milk and water or feed

Conclusion

There were differences in element concentrations based on animal species and regions. Drinking water samples from different regions had different element concentrations. On the other hand, there were no significant differences in element concentrations in feed samples among animal species or regions. Correlation analysis revealed that the concentrations of elements in water and feed might contribute to those in milk. From the correlation results, toxic and potentially toxic elements in raw milk were associated with those in feed and drinking water, which emphasizes the importance of element control in the feed and drinking water of dairy animals. However, further longitudinal studies are requires to clarify the way that element in drinking water and feed secreted into milk, especially toxic elements.

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Compliance with Ethical Standards

Conflict of Interest All authors have approved the submission and none of the author declares any conflict of interest in the work performed or in the submission of the manuscript.

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