The Effect of Environmental Factors on Heavy Metal and Mineral Compositions of Raw Milk and Water Samples

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In this research, the concentrations of essential metals (Mn, Zn, Cr, Cu, Co), toxic metals (Cd, Pb) and some minerals (Al, Ca, K, Na, Fe, Mg) were determined in raw cow's milk and water samples collected from 3 different regions at 3 different periods (November-December, February-March and April-May). The regions from those areas are close to heavy industry plants (Yeniçiftlik), food producing plants (Gümüşçay) and highways (Şakirbey) in Biga county of Çanakkale province, Turkey. Metals and mineral contents of the samples were determined by using inductively coupled plasma-atomic emission spectrometry (ICP-AES).

This study showed that heavy metal concentrations in the two most important liquid food were found to differ from region to region due to environmental factors such as rainfall and industrialization. However, for mineral concentrations in the water and milk samples, no change was observed according to regional pollution parameters.

Keywords: heavy industry; highways; liquid food; mineral; heavy metal; ICP-AES

Çiğ Süt ve Su Örneklerinin Ağır Metal ve Mineral Kompozisyonları Üzerine Çevresel Faktörlerin Etkisi

Bu çalışma, üç farklı bölge ve dönemde (Kasım-Aralık, Şubat-Mart, Nisan-Mayıs) toplanan çiğ inek sütü ve içme suyu örneklerinin metal (Mn, Zn, Cr, Cu, Co), toksik metal (Cd, Pb) ve mineral madde (Al, Ca, K, Na, Fe, Mg) düzeylerine bölgesel kirlilik parametreleri ve mevsimsel değişimin etkisini belirlemek amacıyla yapılmıştır. Bölgeler; Çanakkale'de gıda işletmeleri, ağır sanayi tesisleri ve karayollarına olan yakınlığını göz önünde bulundurularak seçilmiş olan Gümüşçay, Yeniçiftlik ve Şakirbey'den oluşmuştur. Örneklerin metal ve mineral madde içeriği İndüklenmiş Eşleşmiş Plazma Atomik Emisyon Spektroskopi (ICP AES) ile belirlenmiştir. Bu çalışmada, çiğ süt ve su örneklerinin metal düzeylerinde yağış ve sanayileşme gibi çevresel faktörler nedeniyle bölgeden bölgeye farklılık belirlenirken, mineral madde düzeylerinde ise bölgesel kirlilik parametrelerine göre bir değişim belirlenmemiştir.

Anahtar Kelimeler: ağır sanayii; karayolları; sıvı gıda; mineral; ağır metal; ICP-AES

Introduction

Rapid urbanisation and industrial development have caused environmental pollution all over the world. Technical progress, various industrial activities and increased roadway traffic resulted in significant increase of environmental contamination. Heavy metals can be toxic for humans when they are not metabolized by the body and accumulate in the soft tissues. A concern with the metals is their concentration in domestic and industrial waste products because the elements are indestructible (IDF 1979; Staniskiene and Garaleviciene, 2004). Fortunately, animals may act as a very efficient biological filter against heavy metal contamination in milk when the animals are grazing near motorways and roads with heavy car traffic (Carl, 1991).

Lead (Pb) and cadmium (Cd) are widely dispersed in the environment. They are generally considered as the most toxic elements to humans and animals. The adverse human health effects associated with exposure to them even at low concentrations are diverse and at least include neurotoxic and carcinogenic actions as Agency for Toxic Substance and Disease Registry declared (ATSDR, 2007, 2012; Tokar et al., 2011).

Essential metals beside basic nutrients have a vital role in the functioning of a human organism. “Essential metals” term is widely recognized and usually applied to the elements such as Cu, Fe, Mn, Cr and Zn which is commonly associated with pollution and toxicity problems (Alloway and Ayres, 1993). Nevertheless, Fe, Cu, Zn and Mn play a crucial role in protection of a human body against the negative effect of toxic free radicals (Cashman, 2006). They can be toxic when taken in excess; both toxicity and necessity vary from element to element (Tripathi et al., 1999). Milk and dairy products are staple components of a daily diet of contemporary consumers like children. Thus, it is crucial to monitor regularly milk quality in terms of toxic metals’ content. Their concentration in milk, especially near industrial regions may serve as a direct bio-indicator of the milk quality and its products but can also be an indirect indicator of contamination in milk (Licata et al 2004). Although milk is an ideal source of macro elements (Ca, K and P) and microelements (Cu, Fe, Zn, Se), additional amounts of contaminant metals might enter milk and dairy products reaching levels that are harmful to humans (Qin et al., 2009).

There are two most essential liquid food, milk and water, for human health. Therefore, the aim of this study was to determine and understand the effects of environmental factors such as areas’ pollution parameters or seasonal changes on the concentration levels of toxic, essential heavy metals (Cd, Pb, Mn, Zn, Cr, Cu and Co) and mineral matter (Al, Ca, K, Na and Mg) in raw cow’s milk and drinking water samples. By finding possible relations between these parameters, it would be possible to take some measures to prevent contamination in milk and water which are indispensible for healthy diet.

Materials and Methods

Milk and drinking water sampling

Rraw milk and water (about 100 mL each) were collected at three time intervals (November–December, February-March and April-May) from these areas namely; Yeniçiftlik, Gümüşçay and Şakirbey. Three parallel milk samples were collected at each season from a collective tank in each area. Cows are put out to pasture in April-May season, therefore, they consume the grass in these areas. For the other seasons, all cows consume food ration containing fixed amount of pellet food, straw, barley, wheat and oat paste. The collected milk samples were immediately transported to the laboratory in a cooler with ice packs and stored below -20°C prior to analysis. Regarding the drinking water samples, three parallel samples were taken from tap water located in farms and this was for both human and animal use. These areas were characterized by different ecological features.

Site characteristics

The selected study areas are located in the northwest part of Turkey in Çanakkale province. Average rainfall and temperature values are similar for each study areas. Average rainfall gradually decreases from November to May and changes between (90-106), (67-79) and (30-50) mm for November-December, February-March and April-May period, respectively. For the same periods, average temperatures range between (5.3-15.9), (3.4-12.4) and (8.5-22.6) °C. Geographical longitude, latitude and site pollution parameters are shown in Table 1. There is an important point in choosing these areas which is that although pollution parameters are different for each study areas, their average temperature and rainfall parameters are similar. This enabled studying the effects of site pollution parameters and seasonal changes independently.

Table 1. Geographical coordinates (longitude latitude) and pollution parameters of study area

Çizelge 1. Çalışma alanının coğrafi koordinatları (enlem boylam) ve kirlilik parametreleri

The name of site	Longitude	Latitude	Pollution parameters
Yeniçiftlik	27° 10′ 60′′	40° 17′ 60′′	Close to heavy
Gümüşçay	27° 16′ 50	40° 16′ 59′′	Close to small dairies
Şakirbey	27° 15′ 25′′	40° 14′ 45′′	Close to highways

Reagents and solutions

All reagents used were of analytical reagent grade (Merck). The ultrapure de-ionised water was used for the preparation of all solutions. The nitric acid (65 %) and hydrogen peroxide solutions were ultrapure grade and obtained from Merck. The used standard solutions were prepared by diluting the stock solutions (1000 mg L^{-1}) in 10 % hydrochloric acid and then stored in colored glass bottles. All calibration standards were prepared by appropriate dilution of stock solutions (1000 mg L^{-1}) in 2 % HNO_3. Multi elemental standard solutions were used for the calibration of Pb, Cd, Cr, Mn, Zn, Cu, Co, Al, Ca, K, Na, Fe and Mg standard solutions. The calibration range was adjusted depending on the sensitivity of the selected element. The instrument was calibrated by 0.5–500 µg L^{-1} concentrations of ICP multi element Standard solution VIII (Merck, 24 elements).

Digestion procedure for ICP-AES

A microwave system was used for acid digestion of the samples. All samples were dried at 100°C in a forced stove until reaching a constant weight. For the determination of toxic, essential heavy metals and minerals, cow's milk and drinking water samples were initially digested with a closed–pressurized system microwave oven (MARS 5 CEM Corporation) at 650 W. Approximately 1 g of samples were weighed in TEFLON-vessels, mixed with 5 ml of HNO_3 (65 %, Merck) and 2 ml of H_2O_2 (% 30, Merck) and digested by microwave radiation by increasing power from 250 to 650 W at 5 min increments. Within 15 min, completely clear and colourless solutions were obtained which were subsequently diluted with double-distilled water. Samples were prepared in triplicate runs. Toxic, essential heavy metals and mineral contents were determined by inductively coupled plasma-atomic emission spectrometry (Liberty AX sequential, USA) with a concentric glass type nebulizer

Analytical determination of trace elements

For the quantitative analysis of samples, the calibration technique was followed. Standard solutions were prepared by diluting multi-element standard solution containing all the analyte elements. The calibration curves for the analytes were built on five different concentrations to determine the limit of detection (LOD). All the measurements were carried out using the full quantitative model analysis. The correlation coefficients of all calibration curves were at least equal or higher than 0.995.

For the assessment of concentration accuracy of trace elements determined in milk and water samples, reference materials (NIST-1549) and (NIST-1643e) were used respectively for quality control purposes.

Statistical analysis

The data obtained from three replicate experiments were analyzed by ANOVA using the SPSS 18 software and the differences between the means were compared using the Duncan's multiple range test at the significance level of 0.05.

Results and Discussion

Toxic heavy metals and essential metals contents

The concentration range (mean ±SD) of the analyzed toxic heavy metals and essential metals in milk and water samples were shown in Table 2 at different periods and areas.

The average concentration of lead was determined as 1.011±0.36 mg L^{-1} (ranging between 0.503-1.859 mg L^{-1}) for the milk samples (Table 2). The highest lead concentration was found in Şakirbey region which was close to highways. This can be attributed to the high amount of lead emission for years from vehicles using leaded fuel. This caused accumulation of lead on pasture lands of this region. However, for the water samples, the highest lead concentration was determined as 0.038 mg L^{-1} in Yeniçiftlik in November-December period. Heavy industry lead emissions along with high rainfall rates resulted in high concentrations of lead in the water samples. The reason might be that emitted Pb was deposited onto the earth and water sources were contaminated by rains. Lead concentrations in cow's milk samples were higher than the maximum permitted level in the Codex standard (2003). The tolerable weekly intake (TWI) was set at 25 µg kg^{-1} body weight in terms of lead contents FAO/WHO (2000). These results were similar to those obtained by Maas et al., (2011) and lower than those reported by Ayar et al., (2009).

The average concentration of cadmium was 0.124±0.11 mg L^{-1} (ranging between 0.027-0.397). The same trend was found as lead concentrations for the milk and water samples. Cadmium concentrations decreased with decreasing rainfalls. The highest concentration in the milk samples (0.397 mg L^{-1}) was found in Şakirbey region (Table 2). Cadmium was emitted mainly from industrial plants and conveyed to soil by the action of wind. Heavy traffic caused continuous release of contaminated dust to air and pasture lands which might be the source of milk contamination. For the water samples, closeness to industrial facility increased cadmium concentrations which might result from industrial wastes carried by rains (0.063 mg L^{-1}). The European Food Safety Authority (EFSA 2009a) has established a TWI of 2.5- 8.54 µg kg^{-1} body weight for cadmium. If we consider a daily intake of 200 g/day from milk and milk products, this represents an intake of 0.55 µg/week of cadmium. Thus the value is in the range of the TWI for an average adult weight of 70 kg. The levels of Cd obtained in the present study were higher than the results determined by Maas et al., (2011).

Chromium is an important mineral that the body must have to function properly. For the milk samples, the chromium values obtained in this study varied between 0.051 and 0.669 mg L^{-1} (Table 2) with a mean value of 0.36 mg L^{-1}. The highest value was detected as 0.669 mg L^{-1} in Yeniçiftlik region. This could be due to presence of industrial processes in this region as the main sources of chromium were generally the emissions from chemical manufacturing industry and combustion of oil and coal. Regarding the water samples, the highest level was found as 0.15 mg L^{-1} in Gümüşçay region which was close to small dairies. The contamination might result from wastewater of these plants since contamination of chromium also originated from industrial wastes in the rivers as well as the application of phosphatic fertilizers, used refrigeration brines and detergents containing compounds of chromium in the production of dairy products (Jarrett 1979). The differences among the regions were statistically significant ($p<0.05$).

The results obtained for all regions and periods were higher than dietary reference intakes (DRI). The acceptable daily intake of Cr is 50-200µg/day. The results for cow's milk (0.36 mg L^{-1}) were higher than the values reported by Soares et al., (2010) (0.014 mg L^{-1}). However, the chromium results of this research were lower than the values reported by Temurci and Güner (2006) in some regions of Ankara, Turkey. They found an average concentration of 1.016 mg kg^{-1} in cow's milk within the range of 0.184-7.484 mg kg^{-1}.

Manganese concentrations of the samples varied between 0.043 mg L^{-1} and 1.693 mg L^{-1} (Table 2). The average was found as 0.081 mg L^{-1} in the analyzed milk samples. The highest concentrations for both water and milk samples were determined in Yeniçiftlik region which was close to heavy industrial plants. This can be expected as manganese compounds are generated from coal-burning industrial plants. Manganese compounds can be present as dust particles in the air and dissolved in ground and drinking water. The difference was statistically significant ($P<0.05$) between both regions and periods. International Dairy Federation (IDF, 1979) accepted maximum limit of 0.025 mg L^{-1} for manganese. The estimated safe and adequate daily dietary intake of Mn is 2-5 mg/day for adults and 2.5-25 µg per kilogram body weight for infants. The values were higher than those found by Lant et al., (2006) who reported a range of 0.0291-0.06 mg L^{-1} Mn in cow's milk. In contrast, the results were lower than that detected by Ogabiela et al., (2011), Coni et al., (1995) in cow's milk (average of 0.13 mg L^{-1}, and 0.109 mg kg^{-1}, respectively).

Table 2. Essential and toxic metal (X± SD) contents of cow's milk and feeding water samples collected from different regions of Çanakkale at different periods (mg L^{-1}).

Çizelge 2. Çanakkale'nin farklı bölgelerinden farklı periyotlarda toplanan inek sütü ve içme suyu örneklerinin toksik ve toksik olmayan metal içerikleri (X± SD) (mg L^{-1}).

Samples	Element (mg L^{-1})	Yeniçiftlik			Gümüşçay			Şakirbey		
		Nov-Dec	Feb-Mar	Apr-May	Nov-Dec	Feb-Mar	Apr-May	Nov-Dec	Feb-Mar	Apr-May
Milk	Pb	0.773±0.051^{aA}	1.038±0.049^{cA}	0.503±0.036^{bA}	0.990±0.052^{aB}	1.015±0.047^{cB}	0.921±0.069^{bB}	0.763±0.067^{aC}	1.859±0.089^{cC}	1.237±0.042^{bC}
	Cd	0.193±0.014^{cA}	0.056±0.004^{aA}	0.059±0.004^{bA}	0.194±0.013^{cB}	0.078±0.003^{aB}	0.056±0.011^{bB}	0.397±0.025^{cC}	0.027±0.002^{aC}	0.058±0.004^{bC}
	Cr	0.284±0.021^{bC}	0.051±0.004^{aC}	0.669±0.044^{cC}	0.139±0.009^{bA}	0.069±0.005^{aA}	0.052±0.003^{cA}	0.154±0.029^{bB}	0.137±0.006^{aB}	0.054±0.003^{cB}
	Mn	1.693±0.079^{cB}	0.079±0.007^{aB}	0.219±0.013^{bB}	1.190±0.057^{cC}	0.086±0.006^{aC}	0.968±0.056^{bC}	1.224±0.059^{cA}	0.116±0.005^{aA}	0.043±0.002^{bA}
	Zn	0.936±0.042^{bA}	1.027±048^{cA}	1.540±0.044^{aA}	2.093±0.103^{bB}	2.009±0.101^{cB}	0.755±0.038^{aB}	1.397±0.067^{bC}	3.046±0.120^{cC}	0.774±0.042^{aC}
	Cu	0.600±0.034^{aB}	0.648±0.047^{bB}	0.619±0.022^{cB}	0.573±0.032^{aC}	0.655±0.005^{bC}	1.564±0.060^{cC}	0.517±0.029^{aA}	0.591±0.045^{bA}	0.624±0.016^{cA}
	Co	0.037±0.002^{aC}	0.211±0.014^{cC}	0.006±0.001^{bC}	0.004±0.001^{aA}	0.053±0.004^{cA}	0.023±0.001^{bA}	0.018±0.001^{aB}	0.039±0.003^{cB}	0.039±0.003^{bB}
Water	Pb	0.038±0.003^{cC}	0.019±0.001^{aC}	0.017±0.001^{bC}	0.038±0.002^{cB}	0.017±0.001^{aB}	0.017±0.002^{bB}	0.022±0.001^{cA}	0.010±0.001^{aA}	0.019±0.001^{bA}
	Cd	0.063±0.005^{cC}	0.001±0.000^{aC}	0.001±0.000^{bC}	0.033±0.002^{cB}	0.001±0.000^{aB}	0.013±0.001^{bB}	0.003±0.002^{cA}	0.003±0.002^{aA}	0.011±0.002^{bA}
	Cr	0.091±0.006^{cB}	< 0.001±0.001^{aB}	< 0.001±0.001^{bB}	0.053±0.004^{cC}	0.107±0.006^{aC}	< 0.001±0.001^{bC}	0.031±0.002^{cA}	ND	< 0.001±0.001^{bA}
	Mn	2.003±0.075^{cC}	0.002±0.000^{bC}	0.001±0.000^{aC}	0.133±0.008^{cB}	0.001±0.000^{bB}	0.001±0.000^{aB}	0.004±0.001^{cA}	0.012±0.001^{bA}	0.003±0.000^{aA}
	Zn	0.697±0.039^{bC}	< 0.001±0.001^{aC}	0.003±0.001^{aC}	0.189±0.012^{bB}	0.003±0.000^{aB}	0.003±0.001^{aB}	0.024±0.001^{bA}	ND	0.002±0.001^{aA}
	Cu	0.153±0.012^{cC}	0.004±0.001^{aC}	0.011±0.001^{bC}	0.019±0.001^{cA}	0.011±0.001^{aA}	0.011±0.003^{bA}	0.045±0.003^{cB}	< 0.002±0.001^{aB}	0.009±0.001^{bB}
	Co	0.002±0.001^{cB}	ND	ND	0.011±0.006^{cC}	0.001±0.000^{bC}	ND	0.001±0.000^{cA}	ND	ND

^{abc} Letters indicate differences among periods ($p \leq 0.05$). ^{ABC} Letters indicate differences among regions ($p \leq 0.05$). ND Not Detectable

Only a few studies investigating the content of zinc in cow's milk have been published to date and the factors affecting its concentration in milk have not been described thoroughly. The highest concentration in water samples was determined in Yeniçiftlik region (0.697 mg L^{-1}). This might be due to the presence of large quantities of zinc in the wastewater of industrial plants. However, for the milk samples, the highest concentration was found in Şakirbey region. This could be due to heavy traffic since Wuana and Okieimen (2011) stated that zinc and cadmium can also be found on soil adjacent to roads resulting from tyres and lubricant oils of vehicles. Zinc contents varied between 0.755-3.046 mg L^{-1} (Table 2). The mean concentration in the analyzed fresh cow's milk samples was found as 1.9005 mg L^{-1}. The provisional tolerable daily intake for zinc is 60 mg L^{-1} for an average adult of 60 kg body weight. The maximum permissible levels of metals recommended by IDF (1979) standard for zinc is 0.328 mg kg^{-1}. The results showed that most of the milk samples from the different regions contained higher concentrations of zinc than those recommended by IDF (1979) and Codex (2003). According to the results, the highest and the lowest zinc levels were determined in winter and spring months, respectively. Therefore, the amount of rainfall increased zinc concentrations in both water and milk samples. Citek et al., (1994) reported that zinc concentration in raw milk were slightly higher in summer period than winter.

The highest copper content of the milk samples was found as 1.564 µg kg^{-1} in Gümüşçay region at April-May period. The sources of copper can be mainly related to fertilizers, pesticides, biosolids and manures (Basta et al., 2005). Therefore, it is normal to expect that the samples collected from Gümüşçay region where is close to small dairies have the highest amount of copper concentrations (Table 2). Concerning the water samples, the highest concentration was determined as 0.153 mg L^{-1} at November-December period in Yeniçiftlik region. Industrial wastes and high rainfalls might influence the copper content of water in this area. According to analysis of variance, the differences between three regions were statistically significant ($p<0.05$). The copper concentrations detected at summer period were higher than those for winter period. Herbicide used in agriculture can increase the amount of copper in milk. Therefore, the copper amount of milk might increase by both industrial emissions and used herbicides at the summer season.

The results for copper concentrations of milk (average of 0.71 mg L^{-1}) were lower than the results reported by Temurci and Güner (2006) and higher than the results reported by Şimşek et al., (2000) and by Licata et al., (2004). Provisional tolerable daily intake (PTDI) level, dietary reference intakes (DRI) and upper level (UL) for copper are 0.05-0.5 mg kg^{-1}, 0.7-0.9 mg kg^{-1} and 3-10 mg kg^{-1}, respectively reported by FAO/WHO (2000) and Food and Nutrition Board. The FAO/WHO has set a limit for heavy metals intake based on body weight. For an average adult weight (60 kg), PTDIs for copper is 3 mg (FAO/WHO 1999). Considering a daily intake of 500 g/day from milk and milk products, this makes an intake of 0.35 mg. Thus, when the copper values found in this study were compared with PTDI, DRI, and UL values, the results were approved by the literature limits. However, milk is not the only source of this metal. Therefore, it can be concluded that consuming large amounts of milk may cause toxic effects in human beings.

Cobalt is an important trace element in nature and can be either essential or toxic for many biological systems depending on its concentration range (Underwood, 1977). The maximum cobalt concentration was found as 0.211 mg L^{-1} in Yeniçiftlik region and 0.011 mg L^{-1} in Gümüşçay region for the milk and water samples, respectively (Table 2). Industrial emissions due to burning of fossil fuels in these industrial areas might influence cobalt concentration in the samples. The toxicity of cobalt is relatively low compared to many other metals (EFSA ,2009b).

Iron is a potent problem in dairy technology because of its catalytic effect on oxidation of lipids. It is generally emitted as a result of wear and tear of brake pads and other automobile parts. Therefore, the samples collected from the area close to highways should have the highest iron contents. Thus, for both milk and water samples, the highest iron concentrations were found as 4.207 and 0.843 mg L^{-1}, respectively in Şakirbey region due to presence of heavy traffic (Table 2). According to analysis of variance, the differences between three regions were statistically significant ($p<0.05$).

The FAO/WHO has set a limit for heavy metal intake based on body weight. For an average adult weight, the provisional tolerable daily intakes

(PTDIs) for iron is 48 mg (FAO/WHO, 1999). Consumption of daily 500 g of milk and milk products causes an intake of 1.46 mg iron. Thus, the levels of iron in this study are lower than the recommended daily allowance. Consumption of cow's milk from these regions therefore pose no danger to iron toxicity. The average value of 2.92 mg kg^{-1} in this study was higher than that found by Lant et al., (2006) who reported a concentration of 0.3 mg kg^{-1} in cow's milk.

Mineral contents

Concentration ranges (mean ±SD) of the analyzed minerals at different periods and areas were shown in Table 3 for both milk and water samples. The most important result is that different from the heavy metal results, the highest concentrations of all minerals were only determined in Gümüşçay region for both milk and water samples. As regards milk samples, the highest content of aluminum was found as 22.5 mg L^{-1} in the heavy rainfall season, however, the highest contents of other minerals, calcium, potassium, sodium and magnesium was found as 861.3, 884.6, 532.5 and 248.7 mg L^{-1}, respectively in the medium rainfall season. On the other hand, for water samples the highest contents of all minerals, aluminum, calcium, potassium, sodium and magnesium was found as 0.739, 137.2, 15.09, 129.9, 12.53 mg L^{-1}, respectively in the heavy rainfall season.

It was observed that heavy metal concentrations of the milk and water samples were mostly influenced by the man-made factors like industrial activities and heavy traffic rather than natural factors such as rainfall. Therefore, depending on the activity type, the highest heavy metal concentrations were found to differ from region to region. However, concerning the mineral concentrations in the samples, no change was observed from region to region. In other words, it was notably realized that different man-made activities did not affect the mineral compositions. Same behavior was also observed by Johansen et al., (2002). They studied the regional variations in the composition of whey. They selected three study regions; southern region, middle region and northern region of Norway. Man-made activities happening in these regions did not affect the mineral concentrations and the highest concentrations of phosphorus, calcium, potassium, sodium and magnesium were exclusively found in the northern region of Norway.

Interestingly the highest mineral contents were found in only Gümüşçay region for both milk and water samples. Cows consume water and fodder and it is the feeding of cows which directly affects the mineral compositions of milk. Although there is no direct relation between water and milk samples, it can be deduced that there is at least some effect of the location where cows are bred on the mineral compositions of milk.

Table 3. Mineral matter (X± SD) contents of cow's milk and feeding water samples collected from different region of Çanakkale at different periods (mg L^{-1}).

Çizelge 3. Çanakkale'nin farklı bölgelerinden farklı periyotlarda toplanan inek sütü ve içme suyu örneklerinin mineral madde içerikleri (X±SD) (mg L^{-1}).

Samples	Element (mg L^{-1})	*Yeniçiftlik*			*Gümüşçay*			*Şakirbey*		
		Nov-Dec	*Feb-Mar*	*Apr-May*	*Nov-Dec*	*Feb-Mar*	*Apr-May*	*Nov-Dec*	*Feb-Mar*	*Apr-May*
Milk	Al	19.53±0.185^{cA}	5.485±0.271^{bA}	5.485±0.271^{aA}	22.50±0.234^{cB}	6.224±0.309^{aB}	6.224±0.309^{aB}	15.38±0.153^{cC}	17.32±0.340^{bC}	12.36±0.489^{aC}
	Ca	622.7±5.227^{cA}	405.6±3.980^{bA}	405.6±3.997^{aA}	701.4±6.025^{cC}	861.3±7.002^{bC}	861.1±7.985^{aC}	811.0±7.140^{cB}	725.9±6.980^{bB}	163.7±1.024^{aB}
	K	19.86±0.387^{aA}	330.4±3.011^{cA}	330.4±2.470^{bA}	596.9±4.940^{aC}	884.6±8.011^{cC}	884.6±7.980^{bC}	665.6±5.950^{aB}	733.9±6.950^{cB}	137.5±0.998^{bB}
	Na	199.9±1.024^{aA}	92.95±1.856^{cA}	92.95±0.870^{bA}	108.5±0.994^{aC}	532.5±4.970^{cC}	532.5±4.975^{bC}	211.8±1.985^{aB}	193.8±1.011^{cB}	38.77±0.710^{bB}
	Fe	1.597±0.038^{bA}	2.607±0.122^{cA}	2.607±0.079^{aA}	2.736±0.185^{bC}	4.048±0.200^{cC}	4.048±0.201^{aC}	4.207±0.164^{bB}	3.517±0.169^{cB}	0.963±0.054^{aB}
	Mg	60.09±0.599^{aA}	25.49±0.495^{cA}	25.49±0.495^{bA}	42.85±0.845^{aC}	248.7±1.985^{cC}	248.7±1.998^{bC}	66.47±0.540^{aB}	56.96±0.269^{cB}	12.44±0.371^{bB}
Water	Al	0.673±0.053^{bB}	0.019±0.001^{aB}	< 0.015±0.001^{aB}	0.739±0.042^{bC}	0.017±0.001^{aC}	0.019±0.001^{aC}	0.094±0.008^{bA}	0.010±0.00^{aA}	0.011±0.007^{aA}
	Ca	41.12±0.140^{cA}	41.81±0.834^{aA}	41.65±0.829^{bA}	137.2±1.285^{cC}	45.81±0.902^{aC}	58.40±0.576^{bC}	59.83±0.596^{cB}	49.81±0.992^{aB}	40.35±0.801^{bB}
	K	4.183±0.204^{cA}	1.600±0.095^{bA}	1.021±0.049^{aA}	15.09±0.295^{cC}	1.673±0.097^{bC}	1.245±0.056^{aC}	3.730±0.067^{cB}	1.572±0.085^{bB}	1.978±0.079^{aB}
	Na	48.53±0.479^{cB}	24.77±0.492^{bB}	21.02±0.416^{aB}	129.9±0.970^{cC}	28.77±0.571^{bC}	24.65±0.487^{aBC}	32.87±0.579^{cA}	23.57±0.469^{bA}	24.56±0.475^{aA}
	Fe	0.157±0.006^{bB}	< 0.001±0.001^{aB}	< 0.001±0.001^{aB}	0.093±0.007^{bA}	< 0.001±0.001^{aA}	< 0.001±0.001^{aA}	0.843±0.063^{bC}	< 0.001±0.001^{aC}	< 0.001±0.001^{aC}
	Mg	33.58±0.652^{cC}	5.815±0.287^{bC}	4.211±0.204^{aC}	12.53±0.247^{cB}	6.815±0.337^{bB}	5.356±0.263^{aB}	8.402±0.250^{cC}	5.816±0.279^{bC}	5.642±0.279^{aC}

^{abc} Letters indicate differences among periods ($p \leq 0.05$). ^{ABC} Letters indicate differences among regions ($p \leq 0.05$).

Conclusion

Investigation of bioelements in the two essential liquid food for human health showed that mainly anthropogenic factors affected the heavy metal concentrations of the cow's milk and water samples. The highest toxic metal (lead and cadmium) concentrations in the milk samples were found in the region close to highways. However, the highest concentrations of chromium, manganese and cobalt were determined in the industrial region. Copper was mainly found near the area close to small dairies. For the water samples, the highest concentrations of lead, cadmium, manganese, zinc and copper were observed in the industrial region whereas chromium and cobalt were mostly determined near the small dairies. On the other hand, concerning the all studied minerals, the highest concentrations in both milk and water samples were determined in the one region which notably indicated that anthropogenic factors did not influence the mineral contents. Although the main factor is cows' feed for bioelements compositions of milk, this study shed lights on how important to select mineral rich areas to raise cattle for the production of good quality milk. This study indicated that future research should move on to investigate relation between environmental factors and feeding on the bioelement composition of milk. Nevertheless, this work provided important information on the relation between environmental effects and quality standards of two essential liquids, milk and water.

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