

## Comparison of Selected Toxic Elements in Cow Serum and Milk Samples from Industrial and Rural Regions

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Received: 30 June 2003/Accepted: 21 January 2004

Pollution of the environment with toxic elements is a serious problem for animal and human, which is recognized in most countries of the world. Arsenic (As) cadmium (Cd) and lead (Pb) are widespread and persistent environmental pollutants. The extensive distribution of aluminum (Al) and its compounds in the environment, as it is the third most copious element in the world, and its widespread use have provoked great interest in the toxicity of this metal. Al accumulates in blood if not filtered by the kidney and is distributed in bone and the brain (Erasmus et al. 1993). Arsenic is used mainly in agriculture in herbicide and pesticide formulations (Fowler et al. 1979). Lead is one of the most ubiquitous toxic metals and primarily affects the peripheral and central nervous systems. Nickel (Ni) is an essential element for some animal species, but toxicity results from exposure to high dose of Ni or its compounds (Barceloux 1999). Environmental sources of Ni include emissions from coal- and oil-fired boilers, coke ovens, diesel-fuel burning and gray-iron foundries.

Minerals in food and animal products such as milk depend on a large number of factors, such as geography, animals' nutrition, environmental contamination and manufacture process (Alonso et al. 2000). Milk, whether human, cow, or formula based, is an essential food for especially baby's life and an important component of human diet thereafter (Garcia et al. 1999; Krachler et al. 2000). With increasing environmental pollution toxic and heavy metal exposure assessment study is necessary. The aim of present study is to evaluate the effects of heavy industrial activities on blood and milk of cows grazing around the iron steel-processing region (Payas-Iskenderun) in Southern Turkey and to compare them with concentrations in cows distant (Antakya) from the main sources.

### MATERIALS AND METHODS

Element levels were determined in serum and milk samples (n=112) from cows in summer and winter seasons. Blood and milk samples were collected from lactating healthy cows from around the industrial and non-industrial regions. Milk samples were collected into clean polyethylene tubes by manual expression and blood samples were taken by jugular puncture in vacutainers then serums were separated and stored frozen until analysis.

Serum and milk samples were acid digested according to the methods of Lai and Jamieson (1993) and Krachler et al. (1998), respectively. The determinations of elements were carried out in an inductively coupled plasma-atomic emission spectrometry, ICP-AES (Liberty Series-II Varian, USA). The wavelengths used were 396.152 nm for Al, 193.696nm for As, 228.802 nm for Cd, 283.306 nm for Pb and 352.454 nm for Ni. Multielement calibration standards were prepared by appropriate dilution of single element standard solutions (Merck, Darmstadt, Germany). For all analysis, control standard solutions were run at the start, during and at the end of sample runs to ensure continued accuracy. Preparations of samples and all standard manipulations were carried out with suprapure nitric acid (Merck) and ultrapure water (Barnstead EASYpure RF 1051, USA).

Recovery tests were made during the analysis of each sample type. For this, indium (Merck, Darmstadt, Germany) was used as internal standard at concentrations of 0.1 and 5.0 µg/L and the results of the recovery tests ranged from 98.0 – 101.5%. The blank levels were monitored throughout the investigation period and were deducted from the readings before the results were calculated. The reliability of the method for estimation of selected elements in samples was checked by analyzing the multi-elemental reference material CRM063 (skim milk powder-natural) from BCR (Brussels, Belgium). The results agreed within  $\pm 3\text{-}5\%$  of the certified values.

Statistical analysis was performed using the Statistical Package for Social Sciences (SPSS) for Windows. One-way ANOVA was used to determine statistically significant levels for differences in mean values of measured variables among subjects grouped by region and seasons.

## RESULTS AND DISCUSSION

Concentrations of Al, As, Cd, Pb and Ni in serum and milk samples are given in Table 1. Samples collected from cows that were breeding in the Payas-Iskenderun region are indicated as having come from an industrial region whilst the Antakya region is specified as non-industrial. Values of zero, or less than zero, were not used in the calculation.

Aluminum was found in all of milk and 75 of serum samples. The mean concentration of Al in serum and milk samples analyzed were 189.4 and 338.7 µg/L, respectively and no significant differences was observed either between the two region or seasons (Table 1). These results are comparable and lower than to the previous reports, where the level of cow milk Al level were 460 µg/L (Abollino et al. 1998), 796 µg/kg (Vinas et al. 1997) and 0.955 µg/L in goat milk (Park 2000).

Arsenic was detected in 21 and 41 serum and milk samples of 112 ranged from non-detectable to 12.8 and 42.8 µg/L, respectively and no statistical differences were found between the two regions in the both seasons (Table 1). The average

**Table 1.** Analysis of Al, As, Cd, Pb and Ni in serum and milk samples in cows grazing in two different regions

	Antakya (non-industrial)				Iskenderun-Payas (industrial)				<i>p</i>	<i>Total mean</i>
	Summer		Winter		Summer		Winter			
	<i>n</i>	Mean	<i>n</i>	Mean	<i>n</i>	Mean	<i>n</i>	Mean		
<b>Al</b>										
Serum	25 (14)	209±59.2 (ND-731.4)	25 (11)	190.6±27.6 (ND-344.1)	32 (26)	190.5±42.4 (ND-390.0)	30 (24)	170.4±65.5 (ND-790.3)	NS	189.4±28.0 (n=75)
Milk	27 (27)	286.5±15.1 (180.2-510.7)	25 (25)	390.6±41.4 (128.2-1169.3)	35 (35)	320.8±20.6 (186.5-755.9)	25 (25)	366.2±25.7 (188.8-753.3)	NS	338.7±13.5 (n=112)
<b>As</b>										
Serum	25 (4)	11.4±1.4 (ND-12.8)	25 (5)	7.5±2.0 (ND-12.7)	32 (7)	7.3±1.5 (ND-12.6)	30 (5)	8.5±1.3 (ND-12.8)	NS	8.3±0.8 (n=21)
Milk	27 (12)	18.6±2.8 (ND-35.3)	25 (14)	17.1±3.1 (ND-42.8)	35 (10)	16.7±4.0 (ND-35.8)	25 (5)	18.0±5.4 (ND-34.3)	NS	17.5±1.7 (n=41)
<b>Cd</b>										
Serum	25 (13)	0.31±0.04 (ND-0.64)	25 (12)	0.64±0.34 (ND-4.39)	32 (17)	0.31±0.05 (ND-0.69)	30 (23)	0.31±0.07 (ND-1.69)	NS	0.3±0.06 (n=65)
Milk	27 (15)	1.1±0.1 <sup>b</sup> (ND-2.7)	25 (13)	1.1±0.2 <sup>b</sup> (ND-2.7)	35 (23)	1.7±0.2 <sup>a</sup> (ND-3.7)	25 (11)	1.8±0.1 <sup>a</sup> (ND-2.7)	<0.05	1.4±0.13 (n=62)

**Table 1.** ContinuedAnalysis of Al, As, Cd, Pb and Ni in serum and milk samples in cows grazing in two different regions

<b>Pb</b>										
Serum	25 (22)	27.6±5.5 (ND-52.0)	25 (10)	26.6±4.2 (ND-46.2)	32 (22)	20.7±2.5 (ND-52.0)	30 (18)	26.3±3.8 (ND-57.7)	NS	24.5±1.9 (n=60)
Milk	27 (23)	23.1±3.2 (ND-63.5)	25 (19)	32.5±4.5 (ND-80.7)	35 (26)	27.2±3.8 (ND-86.4)	25 (17)	23.4±2.6 (ND-46.2)	NS	26.6±0.13 (n=62)
<b>Ni</b>										
Serum	25 (12)	8.3±3.4 (ND-44.5)	25 (12)	8.4±3.3 (ND-41.9)	32 (20)	6.1±1.2 (ND-21.5)	30 (21)	7.1±1.1 (DD-22.5)	NS	7.2±1.0 (n=65)
Milk	27 (24)	4.3±0.7 (ND-15.5)	25 (22)	6.6±0.9 (ND-15.9)	35 (33)	5.7±0.6 (ND-14.7)	25 (21)	7.2±0.8 (ND-15.7)	NS	5.8±0.4 (n=100)

Ranges are given in the bracket below the means. The value for *n* in parenthesis is the number of samples above the limit of detection. ND: Not determined. NS: Not significant. Concentrations in milk and serum are indicated in µg/L.

As content of milk concentrations was 2 times higher than the serum. The mean serum As concentration was found to be higher than 2.92 µg/L measured in Spain (Alonso et al. 2000). Data reported in the literature for As levels in cow milk varies from 0.14 - 77 µg/L (Cervera et al. 1994; Simsek et al. 2000). The mean As concentrations detected in the milk samples are comparable to the previous findings.

Cadmium was found in 65 and 62 of 112 serum and milk samples, respectively. The mean Cd level of serum samples was not affected by either season or region and was similar to reference ranges of 0.44 µg/L (Alonso et al. 2000). However, summer and winter milk samples from the industrial region contained higher levels of Cd than the non-industrial region ( $p < 0.05$ ). Although these levels exceed previously reported result (0.07 µg/L) for cow milk (Tripathi et al. 1999), it is lower than 0.47 and 6.08 µg/L measured in Spain (Martino et al. 2001; Garcia et al. 1999).

No significant differences were observed between the two regions either in serum or in milk Pb concentrations. Mean levels of Pb in serum and milk ranged from 20.7 - 27.6 and 23.1 - 32.5 µg/L, respectively. Serum Pb level are slightly higher than the result from a previous study giving 12.2 µg/L for cows (Alonso et al. 2000). The contents of milk Pb are in good agreement with 34, 40 and 32 µg/L demonstrated by Garcia et al. (1999), Abollino et al. (1998) and Simsek et al. (2000) for cow milk. However, the mean concentration is higher than 1.4 and 1.7 µg/L (Martino et al. 2001; Tripathi et al. 1999); but lower than milk samples those from the industrial region (Simsek et al. 2000).

Nickel is not a cumulative toxin and it is an essential element for several animal species which is involved in lipid metabolism, especially the regulation of lipid content in tissues and synthesis of phospholipids (Barceloux 1999). Ni concentrations were measured in 65 serum and 100 milk samples ranged from non-detectable to 44.5 and 15.9 µg/L, respectively. The concentrations of Ni in cow serum and milk in the present study are well within the reference range of 9.5 - 73 µg/L, respectively (Garcia et al. 1999; Martino et al. 2001).

Analyzed toxic and highly toxic elements appeared in milk and serum samples in amounts not exceeding the literature. No significant effect was observed by industrial actions Al, As, Cd, Pb and Ni concentrations of serum or milk. Moreover, seasonal differences did not alter the selected toxic element concentrations of samples examined in this study.

*Acknowledgments.* This research was supported by grants from The Scientific and Technical Research Council of Turkey, TUBITAK (Project no: VHAG-1606).

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