The trace metal levels in milk and dairy products consumed in middle Anatolia—Turkey

Ahmet Ayar · Durmuş Sert · Nihat Akın

Received: 12 October 2007 / Accepted: 9 April 2008 / Published online: 14 May 2008 © Springer Science + Business Media B.V. 2008

Abstract In this study, aluminium (Al), lead (Pb), cadmium (Cd), selenium (Se) and arsenic (As) contents in milk and different dairy product samples were measured. Pb, Cd, As, Al and Se contents in the milk and different dairy products ranged from 0.054 mg/kg (milk powder)-1.100 mg/kg (Kaşar cheese), 0.009 mg/ kg (whey powder and yogurt)-0.051 mg/kg (Tulum cheese), 0.010 mg/kg (whey powder)-0.146 mg/kg (butter), 2.848 mg/kg (ice cream)-8.778 (drained yogurt) and n.d. (ice cream, milk and whey powder, yogurt, ayran and Lor cheese)-0.434 mg/kg (Tulum cheese), respectively. The 75% of White and Kaşar cheeses, 50% of Lor and 12.5% of Tulum cheese samples contained higher Pb according to the legal limits established by the Turkish Food Codex and European Communities regulation and 12.5% of Tulum cheese sample contained Cd. It was concluded that Pb contents of milk and dairy products from this region might be highly hazardous to human

Keywords Milk · Dairy products · Trace metal · ICP-AES · Turkey

A. Ayar (⊠) • D. Sert • N. Akın Food Engineering Dep., Selçuk University, Kampus, Konya, Turkey e-mail: aayar@selcuk.edu.tr e-mail: eerayar@hotmail.com

Introduction

In recent years, there has been a growing interest in microelements, as their presence in foods is the indicator of qualitative parameters such as processing conditions, environmental pollution, sanitation and husbandry, and may affect the chemical and functional properties of milk. Elements such as Al, Pb, Cd and As are important as they can contaminate foods from the tools and machines used in the production of dairy products. Al, Pb and Cd are bound to lipids together with casein, and an increase in acidity enables their release from curd. This is called demineralization of casein micelles. Salting results in the loss of these elements by osmosis (Coni et al. 1996).

As trace metals, some minerals are essential to maintain the metabolic systems of the human body. However, at higher levels they can lead to poisoning. Some toxic elements are introduced into animals and human organisms through plants. The mammary glands are the most physiologically active part of dairy cows, and therefore the input and output of toxic elements in these organisms are clearly reflected in the milk. Monitoring the route of toxic elements in relation to the soil–fodder–milk pathway is important since the consequences of their activity have a great impact on both the environment and people' health (Markert and Friese 2000).

Trace metals such as Pb, Cd, Zn, Cu, Cr and As are potential bioaccumulative toxins production system of the milk and dairy products (Li et al. 2005). The trace metal contents in milk depend on the genetic properties of the cow, environmental conditions, lactation time and feed type. Trace metals in dairy products also vary with the processing methods and technologies applied (Merdivan et al. 2004). The trace metal content of the milk and dairy products, however, remains poorly documented, particularly in Turkey. Because milk and dairy products are some of the most widely consumed foods in the human diet, they can contribute a large fraction of the intake of trace and toxic elements. Strict control of trace and toxic element levels in these foods is therefore advisable. Many of the dairy products produced from cow milk may expose to trace metal contamination. Several trace metals in dairy products may cause severe health problems in animals and human beings. Therefore, limitations on trace metal contents in foods are included in recent food legislation and regulations (Şimşek et al. 2000).

Milk and dairy products are a source of many valuable nutrients and minerals for humans in Turkey. It is roughly estimated that 30% of total milk is consumed locally (home/farm), 30% is processed in small traditional local dairies, 20% is sold as a raw milk in the street, and remaining 20% is processed by modern dairy plants in Turkey (DPT, 2001). The milk, cheese, yogurt, butter, ice cream and milk powder consumptions were determined as 68.8, 30.6, 58.6, 8.3, 6.0 and 1.5 kg/year for each family member, respectively. Milk and dairy products formed approximately 30% of daily diet in Turkey (Karkacıer 2000; Ayar and Sert 2005).

According to the notifications in the Turkish Food Codex (TFC) and European Communities regarding the determination of the maximum levels of contaminants in food products, Al, Pb, Cd and As amounts should not exceed 15, 0.02 (milk)–0.20 (milk powder and cheese), 0.01–0.50 and 0.10–1.00 mg/kg, respectively. No limitation was imposed for elemental Se (TFC 2002).

The aim of this study is to determination of various trace metal contaminants in milk and dairy products, which play an important role in nutrition of Turkish society and in the investigation of potential health risks for humans.

Materials and methods

Collection of samples

The selection of dairy products was based on estimates on their potential consumption in Turkey. In Table 1 the general characteristics of the milk and the dairy products are reported. Monthly samples were collected for 4 months (from July to October during 2004). The samples were collected that they were high probability contamined by heavy metals The collected cheese samples were homogenized. Cheese and raw milk samples were kept in clear polyethylene cups. 200 g sample was taken from each product. Yogurt, ayran and butter samples were purchased in their original packages. All samples were stored below -18° C prior to analysis. Sampling procedure was performed according to FIL/IDF recommendations (FIL/IDF 1980).

Analysis of minerals

A microwave system was used for acid digestion of all the samples. All the samples (Milk and Dairy products) were dried at 100°C in a forced stove until dry weight. For the determination of element contents, milk and dairy products samples were preliminarily digested with a closed-pressurized system microwave oven, using MARS 5 CEM Corporation, rated at 650 W, featuring programmable time, power and a rotating sample carousel. Approximately 1.0 g of milk, yogurt, ayran, butter, and 0.5 g of other dairy products samples were weighed into the TEFLON-vessels, mixed with 5 ml of HNO₃ (65%, Sigma) plus 2 ml of H₂O₂ (% 30, Sigma) and digested by microwave irradiation in steps, increasing power from 250 to 650 W by 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 (Anonymous 1998).

Mineral contents were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (VARIAN-CCD Simultaneous ICP-AES, Australia) with an automatic sampler system. The working conditions for ICP-AES are given in Table 2.

 Table 1 The general characteristics of the milk and dairy product

	Description	Protein (%)	Fat (%)	Dry matter (%)	No. of brands in the analytical sample
Milk	Raw cow milk, obtained from individual farms in traffic intensity and industrial regions of Konya, Aksaray, Karaman, Niğde (non brand)	2.9–3.0	3.5-4.0	11.5–13.0	4
Butter	Produced from cow milk cream from local dairy plants in Konya, Karaman Aksaray, Niğde (non brand)	0.50-0.70	80-82	82.0-85.0	4
Ice cream	With vanilla, full fat, taken from retail outlets in Konya, Karaman, Aksaray, Niğde	3.57-4.35	3.95-4.16	32.46-37.12	4
Milk powder	Skim milk powder, obtained from local dairy plants in Konya	34.02	0.08	96.0	4
Whey powder	Cow whey powder, obtained from local dairy plants in Konya	75.00	6.00	97.0	4
Yogurt	Fermented cow milk, not ripened, obtained from local dairy plants in Konya, Aksaray, Karaman, Niğde	4.5–6.0	5.0-6.8	17.00–19.54	4
Drained yogurt	Drained yogurt, obtained from local dairy plants and retail outlets in Konya, Karaman (non brand)	7.54-8.64	6.49–7.91	19.38-21.69	4
Ayran	Drinkable yogurt, from local dairy plants in Konya, Karaman, Aksaray, Niğde (non brand)	2.4–2.6	2.2–2.7	8.5–9.0	4
White cheese	Fresh cheese made from cow milk. semi soft. a grainy appearance, obtained from local plants in Konya, Karaman, Aksaray, Niğde (non brand and non package)	12.0–12.5	17–18	36–37	4
Kaşar cheese	Produced from cow milk, without a ripening process and sold as fresh, taken from dairy plants in Konya, Karaman, Aksaray, Niğde (non brand and non package)	12.0–15.45	20.80-23.50	40.35-43.16	4
Tulum cheese	A white or cream colour, a high fat content, a crumbly semi-hard texture and a buttery pungent flavour, obtained retail outlets (non brand and non package)	19.54–24.14	30.90-38.00	60.15-67.48	4
Lor cheese	Soft. not ripened, made from cow's cheese whey, obtained from local dairy plants and retail outlets in Konya, Karaman, Aksaray, Niğde (non brand and non package)	11.11–14.38	11.16–16.00	29.47-42.05	4

Statistical analysis

The experimental data on trace metal contents in milk and dairy products were tested by ANOVA (One way ANOVA randomized complete blocks); the determination of the differences between means was achieved using the Duncan multiple range test (Costat 1990).

Results and discussion

The mineral contents of milk and dairy products are given in Tables 3, 4, 5, 6 and 7. However, the orders

of the mean metal contents in the milk and dairy products are given in Table 8.

Aluminum content

There were statistically significant differences between the Al contents of milk and dairy products (Table 3) (P<0.01). The highest (8.78 mg/kg) and the lowest (2.85 mg/kg) Al amounts were determined in süzme (drained) yogurt and ice cream samples as the average, respectively (Table 8). In Turkey, an industrial production method for drained yogurt has not yet been developed. It is still produced by local methods

Table 2 The working conditions for ICP-AES Condition Value Wavelengths Detectable Recovery

		used for the monitoring (nm)		Corrected (%)
Power	1,400 W			
Gas exit	13.50 L/min			
Gas flow rate	1.50 ml/min			
Nebuliser gas flow rate	0.90 ml/min			
Sample intake (aspiration) rate	2.25 ml/min			
Preflow time	45 s			
Reading time	3×24 s			
Al		396.15	0.0015	83.6
Pb		220.35	0.003	82.5
Cd		228.80	0.0004	87.9
Se		196.03	0.005	107.2
As		188.98	0.005	90.7

in dairy houses in Turkey. Large amounts of Al contamination result from the uncontrolled use of low quality materials made from Al. The acidity of yogurt can give rise to corrosion of Al in pots. In addition, the traditional production of drained yogurt, which is peculiar to Middle Anatolia, and the soil type of this region may influence its high Al content. The other yogurt types, butter and milk samples were also found to contain high amounts of Al and probably arise from the same reason. Whey powder was produced in Konya as the soils of Konya region contain high contents of Al. The low Al content in ice cream is attributed to its technological production conditions and use of low-Al-containing materials in the process. The additives used in ice-cream production such as sugar are also effective in reducing Al contents.

Tulum cheese had the highest Al content among the cheese types (Table 3). Tulum cheese is mostly a home-produced cheese type and its production is not controlled. As the malaxation stage of the process is carried out on surfaces made from Al materials, the contamination ratio increases. These Tulum cheese samples were also produced in Middle Anadolu Region. Lor cheese (4.266 mg/kg) and White cheese Sp c c e

Table 3 Co.	ntents of Al (r	ng/kg) in milk	Table 3 Contents of Al (mg/kg) in milk and dairy product samples	uct samples							
Milk	Butter	Ice cream	Ice cream Milk powder Whey powder Ayran	Whey powder	Ayran	Yogurt	Drained yogurt White cheese Kaşar cheese Tulum cheese Lor cheese	White cheese	Kaşar cheese	Tulum cheese	Lor cheese
$8.27 \pm 0.37a^{a}$ $8.92 \pm 0.16a$	8.27±0.37a ^a 8.66±0.23a 2.22±0.17b 3.12±0.17c 8.92±0.16a 6.95±0.07b 3.31±0.16a 3.63±0.18bc	2.22±0.17b 3.31±0.16a	8.27±0.37a ^a 8.66±0.23a 2.22±0.17b 3.12±0.17c 8.92±0.16a 6.95±0.07b 3.31±0.16a 3.63±0.18bc	9.29±0.41a 7.74±0.20b	6.73±0.04c 7.33±0.04c	$\begin{array}{rll} 6.73\pm0.04c & 5.22\pm0.03b^{b} \\ 7.33\pm0.04c & 8.06\pm0.08a \end{array}$	$9.34\pm0.48b$ $8.35\pm0.28b$	2.61±0.16b 3.66±0.08a	4.71±0.16b 8.21±0.30a	5.04±0.06c 2.22±0.17c 9.34±0.19b 2.73±0.11c	2.22±0.17c 2.73±0.11c
$5.65 \pm 0.07c$	$5.65 \pm 0.07c$ $8.34 \pm 0.48a$ $2.38 \pm 0.11b$ $6.48 \pm 0.12a$	2.38±0.11b	6.48±0.12a	5.12±0.17c	$9.17 \pm 0.24b$	9.17±0.24b 7.90±0.14a	11.19±0.27a	2.88±0.11b	$4.80{\pm}0.14b$	12.67±0.24a	7.76±0.08a
$6.88 \pm 0.25b$	$6.88 {\pm} 0.25b 6.59 {\pm} 0.13b 3.48 {\pm} 0.11a 3.88 {\pm} 0.11b$	3.48±0.11a	3.88±0.11b	6.19±0.27c	10.62±0.28a 3.52±0.03c	3.52±0.03c	6.23±0.33c	4.10±0.14a	$5.45 {\pm} 0.18b$	5.45±0.14c	4.36±0.08b
^a Different le	tters indicate a	significant diff	^a Different letters indicate significant differences among themselves of milk and dairy products (P<0.01)	themselves of m	nilk and dairy p	products $(P < 0)$.	01)				
^b Values repr	esent the mean	n of triplicate	$^{\rm b}$ Values represent the mean of triplicate determinations \pm SD for each sample	± SD for each si	ample						

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.10±0.06b 0 0.10±0.05b 0 0.15±0.11a 0 0.11±0.05ab 0 0.11±0.05ab 0 able ers indicate sign ers indicate sign	0.08±0.11bc 0 0.05±0.11bc 0 0.18±0.08a 0 0.02±0.04c n ftriplicate deterr pificant differer	0.11±0.07a ^a 0.10±0.06b 0.08±0.11b 0.08±0.06a 0.11±0.1 0.09±0.08a 0.10±0.05b 0.05±0.11bc 0.07±0.08a 0.03±0.0 0.11±0.18a 0.15±0.11a 0.18±0.08a 0.07±0.05a 0.13±0.0 0.11±0.11a 0.11±0.05ab 0.02±0.04c n.d. 0.07±0.0 Values represent the mean of triplicate determinations ±SD for each <i>n.d.</i> not detectable ^a Different letters indicate significant differences among themselves c ^a Different letters indicate significant differences among themselves c ^a Different letters indicate significant differences among themselves c	0.11±0.17a C 0.03±0.03b (C 0.13±0.03a (C 0.07±0.04b (C for each sample mselves of milk amselves of milk t samples	0.10±0.04c (0.11±0.05c (0.15±0.09b (0.19±0.04a (e and dairy pre	0.06 \pm 0.08c 0.14 \pm 0.04a 0.09 \pm 0.04b 0.08 \pm 0.05bc roducts (P <0.01	0.15±0.05a 0.12±0.12a 0.12±0.04a 0.14±0.07a	0.60±0.00bc 2.20±0.02a n.d. 0.90±0.00b	2.50±0.05a 0.90±0.00b 0.10±0.00b 0.90±0.00b	n.d. n.d. 2.50±0.04a	n.d. 0.30±0.00a n.d. 1.50±0.00b
Values represent th <i>n.d.</i> not detectable ^a Different letters in	e mean of t idicate sign	triplicate detern ufficant differer	minations ±SD nces among the nd dairy produc	for each sample mselves of milk t samples	and dairy pr	roducts $(P < 0.01)$					
<i>i.a.</i> not detectable ^a Different letters ir	ndicate sign	uificant diffèren	nces among the	mselves of milk t samples	and dairy pr	oducts (<i>P</i> <0.01)	<u> </u>				
			nd dairy produc	t samples							
			nd dairy produc	t samples							
			and dairy produc	t samples							
Table 5 Contents	of Cd (mg/.	/kg) in milk an		·							
Milk But	Butter	ice cream	Milk powder	r Whey powder Ayran	Ayran	Yogurt	Drained yogurt	White cheese	White cheese Kaşar cheese	Tulum cheese	Lor cheese
$0.019\pm0.002a^{a}$ 0.021±0.001b 0.041±0.004b 0.042±0.002a n.d.	21±0.001b	0.041 ± 0.004	b 0.042±0.002	a n.d.	0.036±0.00	0.036±0.00b 0.033±0.00a	$0.031 \pm 0.00b$	0.004±0.00b	0.038± 0.005ab	0.004± 0.00b	n.d.
$0.030\pm0.001a$ $0.003\pm0.00c$ $0.004\pm0.00c$	03±0.00c	0.004±0.00c		$0.017\pm0.024a$ $0.002\pm0.00c$	0.035 ± 0.001	$0.035\pm0.00b$ $0.003\pm0.00b$	$0.005 \pm 0.00c$	$0.038\pm0.005a$	0	0.094± 0.0655	0.010± 0.000±
$0.020 \pm 0.004 a 0.038 \pm 0.005 a 0.065 \pm 0.007 a 0.001 \pm 0.00 a$	38±0.005a	$0.065 \pm 0.007_{6}$	a 0.001±0.00a	0.000±0.00b	0.075±0.01a n.d.	a n.d.	0.043±0.004a n.d.	n.d.	0.058±	0.106±	0.082±
0.002±0.00b n.d.		0.005±0.00c		0.037±0.009a 0.027±0.002a 0.014±0.00c n.d.	0.014±0.00c	lc n.d.	n.d.	0.006±0.00b	0.007a n.d.	0.008a n.d.	0.002a n.d.

						-					
Milk	Butter	Ice cream	Milk powder	Whey powder	Ayran	Yogurt	Drained yogurt	White cheese	Kaşar cheese	Tulum cheese	Lor cheese
$0.23\pm0.05a^a$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.78±0.00a	0.54±0.05b	n.d.
n.d.	0.74±0.05a	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	$0.26{\pm}0.05b$	n.d.
$0.35{\pm}0.08a$	$0.42{\pm}0.02b$	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	$0.09 {\pm} 0.03 b$	n.d.	$0.46{\pm}0.08b$	n.d.
$0.35{\pm}0.07a$	0.10±0.55c	n.d.	n.d.	n.d.	n.d.	n.d.	0.33±0.04a	0.55±0.07a	$0.33{\pm}0.00b$	0.48±0.07a	n.d.

Table 6 Contents of Se (mg/kg) in milk and dairy product samples

Values represent the mean of triplicate determinations \pm SD for each sample.

n.d. not detectable

^a Different letters indicate significant differences among themselves of milk and dairy products (P<0.01)

(3.312 mg/kg) samples showed the lowest Al contents among the other cheese types. One sample of Lor cheese was also particularly high (7.760 mg/kg). Lor cheese is produced from whey and this usually leads to low Al contents. However, in the case of Lor cheese production by boiling milk, from direct acidified milk, on dairy farms and by family companies, the Al content increases. White cheese is an industrial product which is produced under controlled conditions. Besides, the low dry matter content and non-Al-containing package materials of this type of cheese (e.g. plastic) help to maintain low Al content.

Al contents of milk samples, as well as the other dairy product samples, were found to be significantly different within their own groups (P<0.01) (Table 3). Different times and the diverse location used for collection of samples, different processing methods and tools used in production may be the reasons for these significant differences.

Fernandez et al. (1999) reported that the mean Al contents of cow milks and human milk were determined as 0.700 and 0.234 mg/kg, rspectively. The average Al contents of milk and cheese samples in Italy have been reported to be 0.200 and 0.300-0.500 mg/kg, respectively (Lante et al. 2006). These contents are lower than those found in the present study. Merdivan et al. (2004) reported the Al contents of White cheese samples to be between 2.23 and 11.82 mg/kg, which is higher than the contents found in the present study. In a study, the highest Al content among cow milk samples was in the aluminised carton box. Experiments showed that Al content in the high-Al milk could be reduced by more than 70% at the manufacturing stage, by using low-Al components (Şahin et al. 1995).

The Al has historically been considered to be relatively non-toxic in healthy individuals, who can tolerate oral daily doses of as much as 7.20 g of Al without any apparent harmful effects. Even without considering pharmaceutical sources, the typical daily dietary intake of Al varies widely, from 3 to 100 mg. However, there is now abundant evidence that Al may cause adverse effects on the nervous system. Moreover, high intakes of Al through such sources as buffered analgesics and antacids by susceptible individuals (especially, those with impaired kidney function including the elderly and low-birth-weight infants) may lead to pathological changes (Pennington and Schoen 1995; WHO 1996).

The Al contents in milk and dairy products determined in this study were below the limits of TFC. The Al content in daily diets of Turkish society is based on 24 mg/kg dry weight (Aras et al. 1996). Therefore, it was concluded that milk and dairy products are not significant contributor to the intake of Al in Turkey.

Lead content

The sources of contamination with lead are: lead piping and lead-lined tanks in domestic water supplies, canning and use of the pottery glaze for storing beverages. The Pb content of milk and dairy product samples showed significant differences (P< 0.01). Kaşar (1.10 mg/kg) and White cheese (0.92 mg/kg) samples had the highest Pb contents (Table 4). The lead results for cheese samples were notable for the marked inter-sample variability, which ranged from non-detectable to very high. The Pb contents of cheese (Kaşar cheese 1.10, White cheese 0.92 mg/kg) and yogurt (Ayran 0.136 mg/kg) samples were higher than the contents of milk samples (0.103 mg/kg). The Pb contents of cheese samples were significantly higher when compared with the contents of the other samples (P < 0.01) (Table 8). The Pb contents of

		;									
Milk	Butter	Ice cream	Milk powder	Ice cream Milk powder Whey powder Ayran		Yogurt	Yogurt Drained yogurt White cheese Kaşar cheese Tulum cheese Lor cheese	White cheese	Kaşar cheese	Tulum cheese	Lor cheese
n.d.	$0.17{\pm}0.03a^{a}$	$0.17\pm0.03a^{a}$ $0.09\pm0.08b$ n.d.	n.d.	n.d.	0.19±0.11a	0.15±0.12b	0.19±0.11a 0.15±0.12b 0.08±0.04bc		$0.01\pm0.00b$ $0.01\pm0.00b$	n.d.	$0.10 \pm 0.08a$
n.d.	0.05±0.01b n.d.	n.d.	$0.13\pm0.09ab$ $0.03\pm0.06a$	$0.03{\pm}0.06a$	$0.14{\pm}0.07bc$	$0.14\pm0.07bc$ $0.14\pm0.08b$	0.20±0.04a	$0.01 \pm 0.02b$	n.d.	n.d.	0.08±0.11a
n.d.	0.18±0.13a	$0.17 \pm 0.06a$	0.18±0.13a 0.17±0.06a 0.10±0.01b	n.d.	0.10±0.04c	$0.08{\pm}0.07c$	$0.01{\pm}0.01d$	0.08±0.12a	n.d.	$0.03 {\pm} 0.06a$	0.09±0.04a
$0.08 \pm 0.00a$	0.18±0.15a	$0.11{\pm}0.08b$	$0.08 \pm 0.00a 0.18 \pm 0.15a 0.11 \pm 0.08b 0.15 \pm 0.09a 0.01 \pm 0.01b$	$0.01 {\pm} 0.01 b$	0.15±0.12ab	$0.15\pm0.12ab$ $0.22\pm0.09a$	$0.11{\pm}0.08b$	$0.03\pm0.06b$ $0.07\pm0.13a$	$0.07{\pm}0.13a$	n.d.	n.d.
Values repre	sent the mean	of triplicate de	eterminations ±	Values represent the mean of triplicate determinations ±SD for each sample	ıple						
n.d. not detectable	sctable										
^a Different le	stters indicate s	significant diff	erences among	^a Different letters indicate significant differences among themselves of milk and dairy products (P<0.01)	nilk and dairy F	roducts $(P < 0)$.01)				

 Table 7 Contents of As (mg/kg) in milk and dairy product samples

7

cheese samples were high due to the Pb-binding characteristic of casein (Coni et al. 1996). The materials used for production and packaging purposes may be responsible for this increase in Pb. In a study, data showed that White brined cheese picked-up metals from tin containers and from the naturally contaminated salt, on the contrary brined cheese in preserved glass jars showed lower levels of metals (Ereifej and Gharaibeh 1993). Slight rises in the Pb content based on dry weight were shown to be mainly due to the retention of Pb by curd and, possible contamination occurring during the process (Zurera-Cosano et al. 1994).

The lowest Pb contents were determined in milk powder and whey powder samples. The Pb contents of dairy product samples except cheese samples were not statistically significant (Table 8). Pb concent showed significant variations within the same type of product group, but these were not as significant as the variations within Al contents.

The Pb contents of 75 milk samples from different locations in Turkey were reported to be between 0.02 and 0.05 mg/kg (Şimşek et al. 2000). Hejtmankova et al. (2002) reported the Pb contents of goat milk samples obtained between April-July from two farms in the Czech Republic to be in the range of 0.02-0.04 mg/kg. The Pb contents of 15 farm milk samples from Croatia were reported to be between 0.02 and 0.06 mg/L (Paclovic et al. 2004). 26% of milk samples in 1996 and 39.6% of milk samples in 1997 were reported to have Pb contents higher than the maximum permissible levels. The increase in Pb content in soil led to an increase in Pb contents of forage and milk (Vidovic et al. 2005). The Pb contents of milk samples from Yugoslavia ranged between 0.00 and 0.02 mg/kg. In the case of insufficiency for some elements such as Ca, Mg, Fe and Pb is highly absorbed in acidic conditions. The Pb contents detected in this study were higher than those reported in literature for milk from Turkey, Czech republic and Croatia, but lower than those of Italy, Brazil and Nigeria (mean Pb 0.53 mg/dm³) (Lawal et al. 2006).

The Pb contents of Italian milk and cheese samples were reported to range between 0.00 and 0.60 mg/kg (Lante et al. 2006). Anastasio et al. (2006) reported that the mean Pb contents of sheep milk, Ricotta, fresh cheese and mature cheese were 0.18, 0.39, 0.47, 0.58 mg/kg, respectively. In another study, the cheese samples from several regions of Romania were

	Al	Pb	Cd	Se	As	The orders of metals
Milk	$7.427^{a} \pm 1.362d^{b}$	0.103±0.14d	0.017±0.010d–f	0.232±0.124d	0.020±0.037f	Al>Se>Pb>As>Cd
Butter	7.635±0.965d	0.116±0.21d	0.015±0.016efg	0.315±0.356b	0.146±0.590a	Al>Se>As>Pb>Cd
Ice cream	2.848±0.601j	0.082±0.62d	0.028±0.027c	n.d.	$0.090 {\pm} 0.665 b$	Al>As>Pb>Cd>Se
Milk Powder	4.279±1.397h	0.054±0.33d	0.024±0.020cd	n.d.	0.095±0.620b	Al>Se>As>Pb>Cd
Whey Powder	7.085±1.699e	0.083±0.41d	0.009±0.011g	n.d.	$0.010 {\pm} 0.128 f$	Al>Pb>As>Cd>Se
Yogurt	6.175±2.036f	0.093±0.34d	0.009±0.014g	n.d.	0.145±0.526a	Al>As>Pb>Cd>Se
Drained yogurt	8.778±1.931a	0.133±0.15d	0.019±0.018de	0.082±0.153f	0.099±0.745b	Al>Pb>As>Se>Cd
Ayran	8.462±1.648b	0.136±0.40d	0.039±0.023b	n.d.	0.144±0.715a	Al>As>Pb>Cd>Se
White cheese	3.312±0.644i	$0.920 {\pm} 0.08b$	0.012±0.016fg	0.159±0.00e	0.032±0.313d	Al>Pb>Se>As>Cd
Kaşar cheese	5.793±1.531g	1.100±0.09a	0.029±0.023c	0.276±0.00c	0.021±0.307e	Al>Pb>Se>Cd>As
Tulum cheese	8.124±3.332c	0.610±0.11c	0.051±0.052a	0.434±0.751a	$0.070 {\pm} 0.131 f$	Al>Pb>Se>As>Cd
Lor cheese	$4.266 \pm 2.318 h$	$0.450 \pm 0.06c$	0.023±0.036cd	n.d.	$0.067 {\pm} 0.424 c$	Al>Pb>As>Cd>Se

Table 8 The average values of some trace metals in milk and dairy products (mg/kg)

n.d. not detectable

^a Values are mean of 4 month (4 samples)

^b Different letters indicate significant differences among the different types of milk and dairy products samples (P<0.01).

reported to contain 0.03–0.24 mg/kg elemental Pb (Hura 2002). Pb contents, exceeding the maximum limit of 0.20 mg/kg were found in samples. Previous research on two Turkish cheese types revealed Pb contents of 0.14 and 1.20 mg/kg for Çeçil and Çömlek cheese types, respectively (Mendil 2006). The research on Kaşar cheese revealed average Pb content of 0.09 mg/kg (Yüzbaşı et al. 2003). The determined Pb content in Kaşar cheeses by Yüzbaşı et al. (2003) was lower than our findings. The Pb contamination in milk and cheese could result from feeding cows with fodder collected from road sides and can be controlled by choosing the sours of the fodder without Pb contamination.

The total lead intake from food and beverages has been estimated for adults in various industrialised countries to be 0.25–0.30 mg/day. The Pb poisoning that is so severe as to cause evident illness is now very rare indeed in human beings. At intermediate contents, however, there is persuasive evidence that Pb can have small, subtle, subclinical effects, particularly on neuropsychological development in children (Anonymous 2003).

The Pb contents of all the milk samples and certain dairy product samples analyzed in this study exceeded the limit (0.02 mg/kg) in the TFC. The Pb contents of milk powder, butter, ice cream, whey powder, drained yogurt samples were below of the limit for dairy products (0.20 mg/kg) in the Codex. However, Pb content in daily diets in Turkey based on dry weight is 0.31 mg/kg (Aras et al. 1996). Namely, Pb content of

milk and dairy products very low for content in daily diets of Turkish society.

Cadmium content

Cd is found in low amounts in soil. It is transported via air and water from intensive industrial regions to the soil and sea. It is considered to be the most important contaminant in modern times. High contents in an ayran and a Tulum chese sample importantly increased the average contents of these two groups of samples (P < 0.01). Therefore, Tulum cheese had the highest average Cd content. Some of the Tulum cheese samples were produced under completely uncontrolled conditions and some of them were sold without being packaged. The high Cd content of ayran samples may also be attributed to uncontrolled production and the use of contaminated water in the production process. The average Cd content of raw milk samples was 0.017 mg/kg. The Cd contents in butter (0.015 mg/kg), whey powder (0.009 mg/kg) and yogurt (0.009) samples were lower than the contents in milk samples. The lowest average content was determined in whey powder and yogurt samples. This shows that Cd passes to whey at lower rates. In addition to this, contamination of whey powder is rare later in the manufacturing process due to the new technology and the controls on production. The differences between the Cd contents of milk samples and those between the other dairy products were significant (P < 0.01). The highest variation was observed in Tulum cheese samples (Table 5). The Cd results obtained in this study except for a Tulum cheese samples were below the limits of the Codex. Milk and dairy products were acceptable in the terms of their Cd contents.

Tripathi et al. (1999) reported very low contents (0.07-0.10 µg/kg) for the Cd contents of 75 milk samples. Goat milk samples obtained from the Czech Republic were reported to have Cd contents between 0.001 and 0.003 mg/kg (Heitmankova et al. 2002). The Cd contents of 15 farm milk samples from Croatia were reported to range between 0.003 and 0.006 mg/kg (Paclovic et al. 2004). The Cd contents of the milk samples analyzed in Yugoslavia were reported to be in the range of 0.001-0.016 mg/kg. Higher contents than the permissible limits were found in 32.3 and 26% of the milk samples in 1996 and 1997, respectively. A 30% decrease in the Cd content of soil represented a 17% of Cd decrease in forage and a 13% of Cd decrease in milk. This shows that soil and forage are not the only sources of Cd in milk (Vidovic et al. 2005). The content of Cd in milk samples in Nigeria was found to be higher (0.257 mg/L) than the recommended dietary intake of 0.02-0.06 mg/day (Lawal et al. 2006). Lante et al. (2006) reported that milk and cheese samples from Italy did not contain elemental Cd. The Cd contents of cheese samples from several regions of Romania were reported to be in the range of 0.003-0.24 mg/kg (Hura 2002). Yüzbaşı et al. (2003) determined that Kaşar cheeses contained Cd levels ranging from 0.0003 to 0.008 mg/kg in Turkey. It was concluded that Kaşar cheese is not significant contributor to the intake of Cd. Kilicel et al. (2004) reported the average Cd content of otlu Lor cheese samples as 0.20 mg/kg in Turkey. The results obtained by several researchers also show that the Cd contents in milk and cheese products vary over a wide range. A similar diversity in the Cd content of milk and dairy products was observed in this study.

The Cd derives its toxicological properties from its chemical similarity to zinc, an essential micronutrient for plants, animals and humans. Toxic contents of this element lead to renal insufficiency and metabolic abnormalities via enzyme inhibition (Hura 2002). The Cd content of milk and dairy products varied between 0.000 and 0.106 mg/kg.

The average daily Cd intake, from all sources, is in the range of 0.010–0.025 mg/day and has decreased steadily over the past 20 years. For the Turkish society, average daily Cd intake is 0.019 mg/kg (Aras et al. 1996). The tolerable daily Cd intake established by the World Health Organization (WHO 1996) is 0.060 mg/day for adult women and 0.070 mg/day for adult men. The contents of Cd in the milk and dairy products studied did not exceeded the permissible maximum daily intake recommended in the health criteria by WHO. The Cd contents of milk and dairy products samples are a little high for daily diet of Turkish society. But, this content was not above the tolerable levels.

Selenium content

The Se, as one of the important microelements, was recently reported to be a considerable antioxidant based on the latest knowledge of nutrition (Hejtmankova et al. 2002). Tulum cheese samples had significantly the higher average Se content (0.434 mg/kg) than those of other dairy products (P<0.01). Tulum cheeses have more dry matter and salt concentration, and they are salted as dry. The Se contents of butter samples were also high (0.315 mg/kg). The differences between the Se contents of milk and dairy products were also significant (P<0.01). The Se contents of ice cream, milk powder, whey powder and yogurt samples were below of detectable levels (Table 6).

The Se was used in a chelated form in a study for fortification of Turkish White cheese, so the chelating ability of casein did not make any remarkable effect on Se. Se stayed unbound in the curd structure and diffused to the brine during ripening (Gülbaş and Saldamlı 2005). The semi-hard cheese samples have been reported to have higher Se contents than milk. The Se contents in that study were reported as 0.013, 0.005, 0.073 and 0.152 mg/kg in milk, whey, fresh cheese and semi hard cheese, respectively (Garcia et al. 2006). The Se contents of yogurt and Groviera cheese were reported to be 0.11 and 1.10 mg/kg, respectively, in a study on Italian dairy products (Gambelli et al. 1999). Lante et al. (2006) reported the Se content of milk as 0.04 mg/kg and that of cheese to be between 0.21 and 0.26 mg/kg. The average Se content of Tulum cheese determined in this study was higher than that found in other studies. But this content was not above the tolerable levels.

The daily intake of Se depends on its content in food, the amount of food consumed, the chemical

form of the element, and its bioavailability. It varies from country to country, and for that reason, it is important to determine the Se content in different commonly consumed foods in order to estimate the daily intake of Se in each region. The average daily dietary intake content that is sufficient to meet the nutrient requirements of nearly all (97–98%) individuals in each life-stage and gender group/of Se is 0.55 mg/day (WHO 1996). The Se has a relatively narrow range of safety, and large amounts can lead to hair loss, brittle nails and other side effects.

Se daily intake in Turkey is around 0.020–0.053 mg Se/day, which is lower than recommended daily allowance (RDA) content of 0.055–0.070 mg Se/day (Aras et al. 2001). Table 6 indicates that the contents of Se in kilos of milk, butter, White cheese, Kaşar cheese and Tulum cheese samples are higher than that in daily diets of Turkish society and normal for RDA value.

Arsenic content

The differences between the As contents of milk and dairy products were significant (Table 7). Butter samples had the highest average As content (0.146 mg/kg). High contents in one yogurt sample (0.22 mg/kg) increased the average As contents of this group of samples. Whey powder samples had the lowest As content (0.010 mg/kg) among the other dairy products (Table 8). Only one milk sample contained As in detectable level and this sample may have been exposed to contamination. The As contents in cheese samples were generally low. The As contents of milk samples as well as the other dairy product samples were found to be significant within their own groups and between groups (P < 0.01).

The As contents of 75 milk samples taken from different locations of Turkey were reported to be between 0.0002 and 0.05 mg/kg (Şimşek et al. 2000). The As contents determined in this study were higher than those determined by Şimşek et al. (2000), because these studies were implemented in different regions of Turkey. The As concentraions in Mexico milk samples ranged from <0.900 to 27.4 ng/L. Cow milk biotransfer factor for As was up to 6×10^{-4} from forage, applying a pharmacokinetic approach. It was associated with the exposure not only to food but also to water As. The As contents in the water could affect human health through milk intake, since the allowable

limit for water used to feed cattle is 0.05 mg/L in Mexico. It is important to consider that more than 30% of the As measured in plants was adsorbed by leaves and probably only a very low proportion of this is accesible to cattle by ingestion (Rosas et al. 1999). In Turkey The mean As was found to be 0.0049 mg/L in cow milk (Aras et al. 1996).

The As, an environmental pollutant, is present in minute but invariable amounts in food, drinking water and ambient air. Now, if groundwater in Turkey contains As, and if water is not treated to remove As then the groundwater being used by food industries may contain As. The cows may eat As contaminated hay and drink contaminated water, yet their milk could be remain quite free from the element. However, some time it was found that As content was elevated in the affected villages cow milk and that As is due to contaminated tube-well water added by milkman to increase the volume of milk. This As contaminated milk also comes to dairy processing units (Rosas et al. 1999).

However, the As contents of milk and dairy products obtained in this study were below the limits of the Codex (0.1–1.0 mg/kg). The As content intake from daily diets in Turkey is 0.102 mg (Aras et al. 2001). It was determined that As contents in milk and dairy products except for butter, yogurt and ayran samples is lower than those of daily diets in Turkey.

Conclusion

Different contents of Al, Pb, Cd, Se and As were determined in milk and dairy products. Nevertheless, except for Pb content, the trace metal contents of all samples were below the maximum contents allowed by the TFC. Milk and dairy product consumption do not cause intolerable contents in the human body and do not pose severe problems for health. Pb contents of certain dairy products were above of the permissible contents in the TFC. Milk and dairy products may pose a risk with regard to elemental Pb.

Increased awareness and controlled manufacture of these products are necessary in order to decrease the contents of elements, in addition to Pb, which showed a wide range of contents. It is vital to inform both farmers and company managers about this issue. The using water for producing and cleaning in milk and dairy factory must be controlled side of trace metals. Metal migration from the milk containers is important. Therefore, used containers for milk must not contain those toxic metals, or those containers must be isolated with right matter. Dairy factories must using new technology and techniques. The milk and dairy products must not be allowed to sell without package and in open locations. Besides, the selling as without package and in open locations of dairy products were banned by TFC. However, the application of TFC don't enough in Turkey. In addition to information, an effective control mechanism (e.g. HACCP and ISO series) imposed by government would play an important role in the prevention of contamination of milk and dairy products with these metals.

References

- Anastasioa, A., Caggianob, R., Macchiatoc, M., Paolod, C., Ragostae, M., Painof, S., et al. (2006). Heavy metal concentrations in dairy products from sheep milk collected in two regions of southern Italy. *Acta Veterinaria Scandinavica*, 47, 69–74.
- Anonymous (1998). *Mineral matter analysis*. Matthews, NC: CEM.
- Anonymous (2003) Heavy Metal Handbook A Guide for Healthcare Practitioners. pp 1–148,
- Aras, N. K., Aklan, S., & Yılmaz, G. (1996). *Diet data*. Ankara: Middle East Technical University.
- Aras, N. K., Nazli, A., Zhang, W., & Chat, A. (2001). Dietary intake of zinc and selenium in Turkey. *Journal of Radioanalytical and Nuclear Chemistry*, 249, 33–37.
- Ayar, A., & Sert, D. (2005). The important of milk and dairy products in society nutrition. *Food and Food Technology*, 7, 1–5.
- Coni, E., Bocca, A., Coppolelli, P., Caroli, S., Cavallucci, C., Trabalza, S., et al. (1996). Minor and trace element content in sheep and goat milk and dairy products. *Food Chemistry*, 57, 253–260.
- Costat (1990). *Costat reference manual (version 2.1)*. Berkeley, CA: Copyright CoHort Software.
- DPT (2001). Milk and dairy products industries. The report of private specialization's commission, 8. The studies of five annual improvement plan (pp. 1–83). Ankara: Turkey. DPT.
- Ereifej, K. I., & Gharaibeh, S. H. (1993). The levels of cadmium, nickel, manganese lead, zinc, iron, tin, copper and arsenic in the brined canned Jordanian cheese. Z. Lebensmittel Unters Forsch 123–126.
- Fernandez-Lorenzo, J. R., Cocho, J. A., Rey-Goldar, M. L., Couce, M., & Fraga, J. M. (1999). Aluminum contents of human milk, cow's milk, and infant formulas. *Journal of Pediatric Gastroenterology and Nutrition*, 28, 270–275.
 FU (DE (1990). Bulleting Ma 50A

FIL/IDF (1980) Bulletin No 50A.

Gambelli, L., Belloni, P., Pizzoferrato, L., & Santaroni, G. P. (1999). Minerals and trace elements in some Italian dairy products. *Journal of Food Composition and Analysis*, 12, 27–35.

- Garcia, M. I. H., Puerto, P. P., Baquero, M. F., Rodriguez, E. R., Martin, J. D., & Romero, C. D. (2006). Mineral and trace element concentrations of dairy products from goats' milk produced in Tenerife (Canary Islands). *International Dairy Journal*, 16, 182–185.
- Gulbas, S. Y., & Saldamlı, I. (2005). The effect of selenium and zinc fortification on the quality of Turkish White cheese. *International Journal of Food Sciences and Nutrition*, 56, 141–146.
- Hejtmankova, A., Kucerova, J., Miholova, D., Kolihova, D., & Orsak, M. (2002). Levels of selected macro- and microelements in goat milk from farms in the Czech Republic. *Czech Journal of Animal Science*, 47, 253–260.
- Hura, C. (2002). Chemical contaminants in food and human body, 1990–2000. Cermi Press, Iasi, ISBN 973-8188-01-6
- Karkacıer, O. (2000). The importation analysis of milk and dairy products in Turkey. *Turkish Journal of Agriculture and Forestry*, 24, 421–427.
- Kiliçel, F., Tarakçi, Z., Sancak, H., & Durmaz, H. (2004). Mineral and heavy metal contents of Otlu Lor. *Journal of Agricultural Sciences*, 14, 41–45.
- Lante, A., Lomolino, G., Cagnin, M., & Spettoli, P. (2006). Content and characterisation of minerals in milk and in Crescenza and Squacquerone Italian fresh cheeses by ICP-OES. *Food Control*, 17, 229–233.
- Lawal, A. O., Mohammed, S. S., & Damisa, D. (2006). Assessment of levels of copper, cadmium and lead in secretion of mammary gland of cows grazed on open fields. *Science World Journal*, 1, 8–10.
- Li, Y., Mccrory, D. F., Powell, J. M., Saam, H., & Jackson-Smith, D. (2005). A survey of selected heavy metal concentrations in wisconsin dairy feeds. *Journal of Dairy Science*, 88, 2911–2922.
- Markert, B., & Friese, K. (2000). Trace elements—Their distribution and effects in the environment (1st Ed.). Oxford: Elsevier.
- Mendil, D. (2006). Mineral and trace metal levels in some cheese collected from Turkey. *Food Chemistry*, 96, 532–537.
- Merdivan, M., Yilmaz, E., Hamamci, C., & Aygun, R. S. (2004). Basic nutrients and element contents of white cheese of Diyarbakır in Turkey. *Food Chemistry*, 87, 163– 171.
- Paclovic, I., Sikiric, M., Havranek, J., Plavljanic, L. N., & Brajenovic, N. (2004). Lead and cadmium levels in raw cow's milk from an industrialised Croatian region determined by electrothermal atomic absorption spectrometry. *Czech Journal of Animal Science*, 49, 164–168.
- Pennington, J. A., & Schoen, S. A. (1995). Estimates of dietary exposure to aluminium. *Food Additives and Contaminants*, 12, 119–128.
- Rosas, I., Belmont, R., & Armienta-Baez, A. (1999). Arsenic concentrations in water, soil, milk and forage in Comarca Lagunera, Mexico. *Water, Air and Soil Pollution, 112*, 133–149.
- Şahin, G., Aydin, A., Isimer, A., Ozalp, I., & Duru, S. (1995). Aluminum content of infant formulas used in Turkey. *Biological Trace Element Research*, 50, 87–96.
- Şimşek, O., Gültekin, R., Öksüz, O., & Kurultay, S. (2000). The effect of environmental pollution on the heavy metal content of raw milk. *Nahrung*, 44, 360–363.

- TFC (2002). Türk food codex. Communication on determination of maximum levels of some contaminants in foods (pp. 1– 198). Ankara: T.C. Tarım ve Köy İşleri Bakanlığı.
- Tripathi, R. M., Raghunath, R., Sastry, V. N., & Krishnamoorthy, T. M. (1999). Daily intake of heavy metals by infants through milk and dairy products. *Science of the Total Environment*, 227, 229–235.
- Vidovic, M., Sadibasic, A., Cupic, S., & Lausevic, M. (2005). Cd and Zn in atmospheric deposit, soil, wheat, and milk. *Environmental Research*, 97, 26–31.
- WHO (1996). Guidelines for drinking-water quality, 2nd ed. Vol. 2. Health criteria and other supporting information. Geneva: World Health Organization.
- Yüzbasi, N., Sezgin, E., Yildirim, M., & Yildirim, Z. (2003). Survey of lead, cadmium, iron, copper and zinc in Kaşar cheese. *Food Additives and Contaminants*, 20, 464–469.
- Zurera-Cosano, G., Moreno-Rojas, R., & Amaro-Lopez, M. A. (1994). Effects of processing on the concentration of lead in Manchego-type cheese. *Food Additives and Contaminants*, 11, 91–96.