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Comparison of Heavy Metal Levels of Organic and Conventional Milk and Milk Products in Turkey

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ABSTRACT

This study aimed to determine and compare aluminum (Al), arsenic (As), cadmium (Cd), and lead (Pb) levels in conventional and organic milk, white cheese, and butter samples which are sold in the markets of Turkey. Within the scope of the study, totally 72 samples (36 for organic, and 36 for conventional) were collected, and analyzed between March 2010 and February 2011. After the samples were burned by microwave burning, element measurements were performed on atomic absorption spectrophotometer (AAS) device. As a result of the study, on the 49 samples (29 conventional, 20 organic) of the 72 collected product, element levels were determined above the limit of detection (LOD) (0.02 ppm). Pb and Al were the most common elements above the LOD. However, milk samples with a Pb level above the LOD still remained below the limit reported by the Turkish Food Codex Regulation for Contaminants. Since Turkish Food Codex Regulation does not have legal limits for Al, As, Cd and Pb for dairy products (cheese and butter), it was accepted as safe in terms of Al, As, Cd and Pb according to food limits in Turkish Food Codex and ADI values of FAO / WHO.

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Introduction

The United States (USA), Canada, Austria, Denmark, Germany, England, France, and Argentina are the leading countries in organic livestock production. In the USA, organic dairy products have a share of 2% in total milk production. EU countries Austria and Denmark take the first place in the production of organic milk with 300 tons/year production. In Turkey, almost all of the organic food production consists of herbal products. Apart from organic honey production, the production quantity of organic milk, dairy products, and other animal products is a little (Çiçek and Tandoğan, 2009).

The use of tools and equipment that are not in compliance with the standard in the production of dairy products and the closeness of their production facilities to the industrial establishments are significant in the exposure of milk and cheese samples to heavy metal contamination (Temurci and Güner, 2006). Heavy metals that have no vital importance such as aluminum (Al), arsenic (As), cadmium (Cd), lead (Pb), etc., even in very low concentrations, can affect the physiological structure and cause health problems (Gövercin, 2010). The International Agency for Research on Cancer (IARC) classified substances such as arsenic, cadmium, and inorganic lead compounds as carcinogens (IARC, 1993).

Organic farming avoids using synthetic chemicals, hormones, antibiotic agents, genetic engineering, and irradiation (Forman and Silverstein, 2012). However, sometimes organic products may contain some contaminants (Baydan et al., 2017). There has been little research on the safety of organic foods, especially organic animal products. There are some studies on the determination of pollutants such as heavy metal, pesticide and mycotoxin in organic products (Malmuret et al., 2002; Wang et al., 2003). Yet, there is only one research conducted to determine heavy metal levels in some organic products (wheat, lentils, flowers honey, and eggs) in Turkey (Arslanbaş and Baydan, 2013). Therefore, the aim of this research was to determine some heavy metal (Al,

As, Cd, and Pb) levels in conventional and organic dairy products offered for sale in Turkey and compare the results with national and international studies.

Materials and Methods

In this study, 36 organic and 36 conventional samples with different serial/batch numbers, consisting of milk, cheese and butter were sold in markets of Turkey were collected; 3 samples for each kind of product (9 for organic, and 9 for conventional) in every three months period between March 2010 and February 2011. Organic samples were belonging to a single company due to lack of other company's products are sold in markets in Turkey on the dates indicated. Conventional samples belonged to different companies. The collected samples were stored in the freezer (-20°C) until analyzed. Samples were analyzed for their Al, As, Cd and Pb content and level, if any.

Metal levels of the extracts obtained after burning 2 ml milk, 0.5 g white cheese, and 0.5 g butter samples in microwave oven (Berghof MWS-2, Germany) were detected according to parameters in Table 1 in the AAS-Graphite device (Perkin Elmer Analyst 700, Graphite Furnace, USA) (Çakır, 2009).

Frozen milk, white cheese, and butter samples were thoroughly dissolved in the analysis stage. Dissolved samples were weighed and put into teflon containers separately in the quantities of 2 ml for milk samples and 0.5 g for cheese and butter samples. The samples were mixed well by adding 3 ml of HNO_3 (65%) and 1 ml H_2O_2 (30%). After about 20 minutes, the lids of the Teflon containers were closed and placed in a microwave oven. At the end of the burning process, the extract was added deionized water and brought to the level that can be analyzed in AAS device with the element's parameters in Table 2. Al, Cd, and Pb levels of the samples were measured in a graphite furnace unit. The As level was measured as the analyte hydrides (arsenic hydride) after making hydrolysis with $NaBH_4$ (sodium borohydride) in acidic solution with sending it into the quartz tube heated by flame (or electricity) by means of inert gas.

Statistical analysis of the data obtained at the end of the study was done by the statistical package program (SPSS 15.0). In this context, the median, the minimum, and the maximum values were determined. Group comparisons were made with Mann-Whitney U test for the groups with sample quantity 3 or higher. The level of significance was set at $P<0.05$.

Results and Discussion

Al, As, Cd, and Pb levels (median, min-max) of the 72 conventional and organic milk, white cheese, and butter samples analyzed were given in Table 3. The LOD values in the AAS-Graphite device are for Al was 0.02 ppb, for as 0.001 ppb, for Cd 0.001 ppb, for Pb 0.02 ppb. Values below the LOD were accepted as zero and evaluated as missing observation in statistical analyzes. Al (10 ppb), As (2.5 ppb), Cd (3 ppb), and Pb (10 ppb) were used for recovery studies. Recovery percentages by products and by metal sequence were; 99.4, 99.9, 102.6, and 87.9 for milk (n: 1); 94.3, 100.7, 82.8, and 101.6 for white cheese (n: 1); 84, 97.6, 109.9, and 72.9 for butter (n: 1).

As a result of the analyzes, there was no sufficient sample number above the LOD value, so statistical evaluation in terms of products and seasons could not be made (Figures 1 and 2).

According to the results of the study, 49 of the 72 samples were identified elements (Al, As, Cd, Pb) with values above the LOD levels. The frequency of elements wıth values above the LOD was higher in the conventional (29 conventional samples > LOD) than the organics group (20 organic samples > LOD), and among the sample groups, in the white cheese group (n: 17) (Figure 1). It was followed by conventional milk, organic white cheese, organic milk, and organic butter. In terms of incidence of metals, Pb was the first in all samples and Al was the second (Figure 1). In terms of Pb values, the difference between conventional and organic milk and white cheese groups was not statistically significant ($P>0.05$). It was observed that the frequency of Pb was increased in the samples collected in winter (Figure 2).

In Turkey and the world, although there are a limited number of studies to determine levels of elements in organic milk and dairy products, especially there are many studies for determining the elemental level of conventional milk samples. But organic products should also be screened for safety (Baydan et al., 2017). In a study on comparing element levels of conventional and organic dairy products in Southern Poland, there was no significant difference between organic and traditional products. Moreover, the presence of lead was detected in one of the organic milks (5.24 mg/l), and it was stated to be within acceptable limits (Halagarda et al., 2018). The results of this study showed that element levels in organic and conventional dairy products (cheese and butter) were higher than milk samples but below ADI values (Figure 1). Banks (1981) has been described cheese production as a process of condensing milk components, especially fat and protein contents (Abd El-Gawad and Ahmed, 2011). As in this study, elemental levels of condensed products such as white cheese and butter can be expected to be higher than milk samples. Indeed, Eleboudy et al. (2017) found that Pb and Cd values in condensed milk, evaporated milk and infant formula were significantly higher than milk values in their study. This is probably because they are condensed and evaporated products. In addition, higher element frequency and level in conventional and organic dairy products than milk samples may be associated, in addition to the causes of contagion in milk, with the contamination in the processing/storage/maturation conditions (container, packaging) in these stages (İnci et al., 2017; Shahria et al., 2014; Ziarati et al., 2018). In the study conducted by AI-Ashmawy (2011), Al levels in processed cheese wrapped in Al foil were significantly higher than those found in samples packed in glass containers. In a study on determination of levels of heavy metals (arsenic, lead, cadmium and mercury) in tin milk produced in Ghana, results of research have been indicated milk samples contamination by some heavy metals residues (Hg, Pb, As and Cd) (Amponsah, 2014). The results of research on milk and dairy products show that the element values of the products such as butter, cheese or condensed and evaporated milk are higher than milk samples and therefore different limits should be applied to dairy products provided that they do not exceed the ADI value.

According to the Turkish Food Codex Regulation for Contaminants, the limit values of the elements likely to be present in foods are given as 15 mg/kg for Al, 0.1-1 mg/kg for As, 0.01-1 mg/kg for Cd, and 0.02 mg/kg for Pb in milk (Anon, 2011). On the 49 samples (29 conventional, 20 organic) of the 72, element levels were determined above the limit of detection (LOD) (0.02 ppm). Pb and Al were the most common and above the LOD level elements in the samples. However, milk samples that have Pb level above LOD were below the reported limit by the Turkish Food Codex Regulation for Contaminants. Since there are no legal limits for Al, As, Cd and Pb in dairy products, dairy products with elemental levels above LOD were considered safe for Al, As, Cd and Pb according to food limits in Turkish Food Codex Regulation. According to FAO/WHO, acceptable daily intake of Pb, Cd, and Al (ADI; µg/70kg person) were given as 500, 70, and 1200, respectively (Abd-El Aal et al., 2012). Considering that an adult can consume 200 ml of milk per day (Abd-El Aal et al., 2012), Al, As, Cd and Pb levels in milk samples are below ADI values. Since the ADI for cheese and butter was not stated, the evaluation could not be made regarding them. However, Turkey's Health Ministry Nutrition Guide 2015 (TÜBER) by approximately 40-60 grams a serving of cheese. Therefore, even if an adult consumes 3 servings a day, it was well below the limits given by FAO / WHO for Al, Cd and Pb (Abd-El Aal et al., 2012; Anon, 2016).

Table 1. Element reading parameters in AAS device.

Reading parameters in AAS device				
Parameters	Al	As	Cd	Pb
Wavelength (nm)	309.3	193.7	228.8	217
Slit clearance (nm)	0.7	0.7	0.7	0.7
Lamp Power	25 - 30 V	0 - 40 V	8 V	10 - 12 V
Linear Range (mg/lt)	100	100	2	20
Gas Type Used	Argon	Argon	Argon	Argon

Table 2. Al, Cd, and Pb parameters in AAS device.

Al, Cd, and Pb parameters in AAS device						
Step	T (°C) *	T (°C) **	Rise Time (s)	Retention Time (s)*	Retention Time (s)**	Argon Flow (ml/min)
Dehumidification	100	100	5	15	25	250
Drying	140	140	10	25	30	250
Incineration	850	350	150	35	25	250
Atomization	1650	1650	0	1	4	0
Cleaning	2600	2400	1	2	2	250

* For Al and Pb; ** For Cd, T:Temperature.

Table 3. Comparison of heavy metal levels of organic and conventional dairy products.

Heavy metal levels of organic and conventional dairy products				
Groups	Heavy metals			
	Al (ppm) Median (min - max)	As (ppm) Median (min - max)	Cd (ppm) Median (min - max)	Pb (ppm) Median (min - max)
Conventional Milk (n: 12)	0.233 n: 1 n: 11 < LOD	0.002 (0.001 – 0.003) n: 2 n: 10 < LOD	0.088 n: 1 n: 11 < LOD	0.0055* (0.001 – 0.01) n: 6 n: 6 < LOD
Organic Milk (n: 12)	0.726 n: 1 n: 11 < LOD	0.226 n: 1 n: 11 < LOD	0.003 n: 1 n: 11 < LOD	0.001* (0.001 – 0.009) n: 3 n: 9 < LOD
Conventional White Cheese (n: 12)	0.9865 (0.348 – 8.725) n: 4 n: 8 < LOD	0.57 (0.01 – 0.839) n: 3 n: 9 < LOD	0.449 (0.034 – 0.898) n: 4 n: 8 < LOD	0.032* (0.002 – 0.053) n: 6 n: 6 < LOD
Organic White Cheese (n: 12)	2.281 n: 1 n: 11 < LOD	LOD n: 12 < LOD	LOD n: 12 < LOD	0.008* (0.003 – 0.084) n: 7 n: 5 < LOD
Conventional Butter (n: 12)	1.287 n: 1 n: 11 < LOD	LOD n: 12 < LOD	0.037 n: 1 n: 11 < LOD	LOD n: 12 < LOD
Organic Butter (n: 12)	2.08 n: 1 n: 11 < LOD	0.03 n: 1 n: 11 < LOD	0.0185 (0.018 – 0.019) n: 2 n: 10 < LOD	0.0195 (0.003 – 0.036) n: 2 n: 10 < LOD

*****There is no difference between the same kind of products in terms of Pb values (P>0.05).

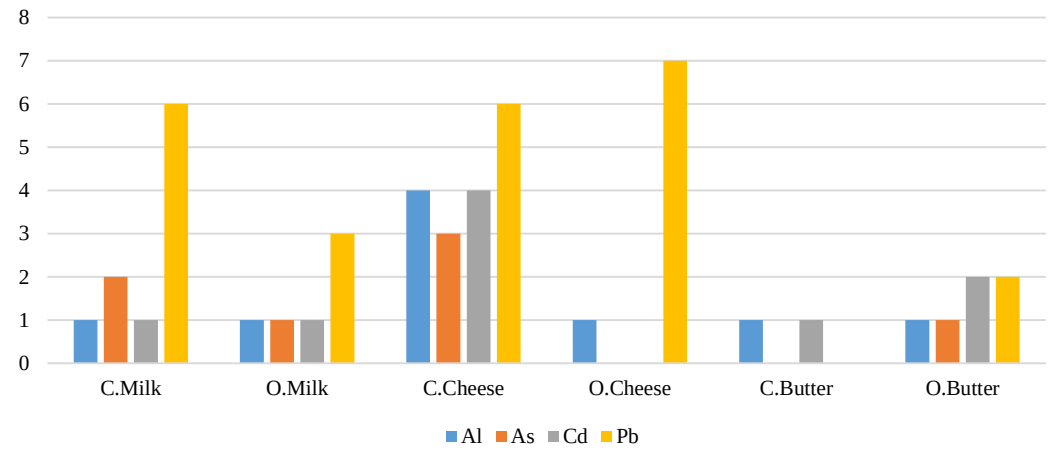

Figure 1. Heavy metal distribution of the dairy products (y↑, n: 12).

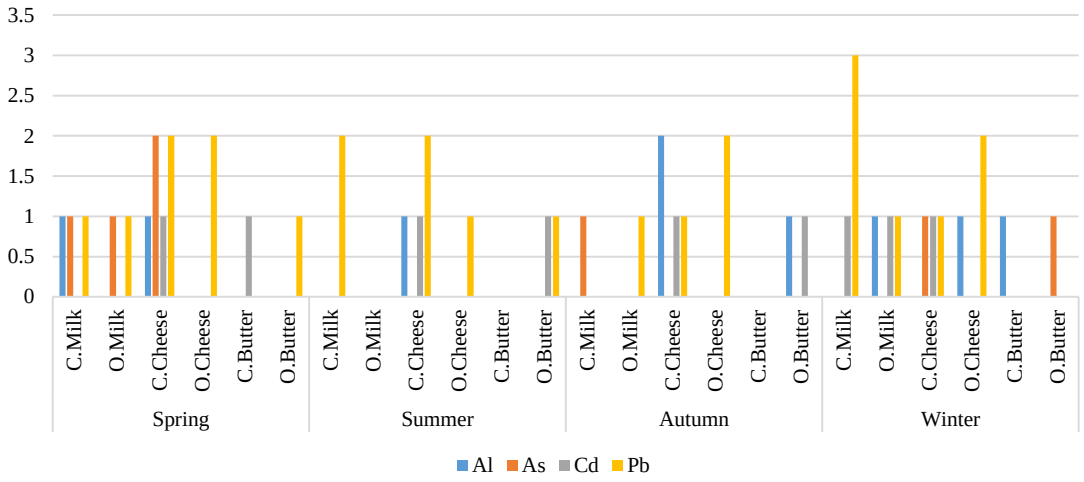

Figure 2. Heavy metal distribution of the dairy products per seasons (y↑, n: 12).

The maximum estimated daily intake (MEDI) value of aluminum (1 mg/kg b.w./d) according to JECFA is 4.282 mg/kg for processed cheese wrapped in Al foil (Anon, 2007; Anon, 2008). In this study, the values for cheese and butter were significantly lower than this limit and the value (5.718 mg / L or kg) -processed cheese wrapped in Al foil- found by AI-Ashmawy (2011). In a research conducted with 36 conventional milk and 40 conventional white cheese samples collected from Ankara, Turkey and neighboring districts, Al, Cd, Pb, and some metal levels were measured by ICP-AES device. In the study, there was no presence of Pb in the samples. The mean Al value of milk was 6 ± 0.57 ppm and the mean Cd value was 0.114 ± 0.03 ppm. Meanwhile, the mean Al value of white cheese was 23.276 ± 9.19 ppm and the mean Cd value was 0.073 ± 001 ppm (Temurci and Güner, 2006). Al and Cd values of milk and white cheese were higher than those found in this study. The fact that no Pb has been found can result from the difference in LOD values between methods. In another study was conducted on dairy products, heavy metal levels of total 96 samples which sold in Konya, Turkey were determined by ICP-AES. While the Al, As and Pb values of conventional and organic butter in this study were lower than those found by Ayar et al. (2007) (7.63 ± 0.96 ppm, 0.146 ± 0.59 ppm, 0.116 ± 0.21 ppm) Cd values were higher (0.015 ± 0.016 ppm) (Ayar et al., 2007). In terms of elements analysis of 400 raw milk samples collected from a total of 6 regions in Aydın Province (central district and 5 districts connected to the center), they could not find detectable levels of Cd and Pb (İnci et al., 2017). In an analysis of the 140 conventional milk samples from 9 regions in Turkey with AAS, Pb level was found as 8.52 ± 1.64 ppb and Cd level was found as 1.09 ± 0.33 ppb (Aktan et al., 1991), and they were higher than the Pb values found in this study for conventional milk (0.0055 ppm) and organic milk (0.001ppm). In a study on organic and conventional dairy and meat products in Northern Italy, Pb and Cd residues were very low and did not differ between organic and conventional products (Gihidini et al., 2005). In a study conducted on the market milk and dairy products in Bangladesh (30 samples in total), it was observed that most of the milk samples contained copper and lead, and also copper and lead limits (0.007 mg/kg-0.02 mg/kg) were similar to the results of this research (Shahria et al., 2014).

When the results of this study are examined in terms of seasonal distribution (Figure 2), the high Pb level of dairy products may be related to indirect contamination caused by fuels (Özrenk, 2002) used for heating purposes and exhaust gases, especially in winter. As a matter of fact, in the study carried out in order to determine the seasonal (summer and winter) and change of some

element levels of 400 milk samples according to their place of origin in Pakistan. Especially Pb levels (0.455 mg / kg in summer; 2.0 mg / kg in winter) at the point of sale and milk obtained in winter were higher than Pb values of samples taken from canal edge farms (0.227 mg / kg in summer; 1.25 mg / kg in winter) (Younus et al., 2016). Among a total of 260 conventional milk samples (130 in summer and 130 in winter) collected from Van province and its surroundings, Pb was found in 189 samples with the mean value of 0.002 ± 0.01 ppm (0.001 - 0.007). It is stated that the rate of metal pollution is high in milk obtained in winter (Malmuret et al., 2002). Erdoğan et al. (2004), in a study of industrial and rural regions in the winter sampling, found the mean values of milk in rural regions as 190 µg/L for Al, as 17.1 µg/L for As, and as 1.1 µg/L for Cd. In the industrial zone, they found to be 366.2 µg/L for Al, as 18.0 µg/L for As, and as 1.8 µg/L for Cd, in milk (Erdoğan et al., 2004).

As a result of this study, 72 samples were considered safe for Al, As, Cd and Pb according to the Turkish Food Codex Regulation and also ADI values reported by FAO/WHO.

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