Research Paper / Araştırma Makalesi

Changes in Non-essential Element Concentrations during Torba Yoghurt Production

Hasan Şanal, Zehra Güler

Department of Food Engineering, Faculty of Agriculture, Mustafa Kemal University, 31034 Antakya, Hatay, Türkiye E-mail: zguler@mku.edu.tr

ABSTRACT

In this study, the concentrations of non-essential elements during the manufacture of torba yoghurt were determined. Daily intakes of elements were also estimated. Quantitative determinations of these elements [aluminum (AI), antimony (Sb), arsenic (As), boron (B), beryllium (Be), cadmium (Cd), nickel (Ni), lead (Pb), silver (Ag), titanium (Ti), thallium (TI) and vanadium (V)] were performed by Varian Vista-MPX simultaneous inductively coupled plasma optical emission spectrometer (ICP-OES). For the daily intake evaluation, the weighted average for each element in milk, yoghurt and torba yoghurt was calculated, and then multiplied by the respective consumption rate. Boron was the most abundant element in all samples. Except for Be and V, the concentrations of the other elements were significantly varied during torba yoghurt-making. The total daily intakes of AI, As, Sb, Be, B, Cd, Pb, Ni, Ag, TI, Ti and V from milk and yoghurt were estimated as 0.84, 0.33, 0.28, 7.16x10⁻³, 3.39, 0.023, 0.44, 0.31, 0.054, 0.974, 0.032 and 0.155 mg, respectively.

Key Words: Cow milk, Concentrated yoghurt, Non-essential elements

Torba Yoğurdu Üretimi Sırasında Esansiyel Olmayan Elementlerin Konsantrasyonlarındaki Değişimler

ÖZET

Çalışmada, torba yoğurt üretimi sırasında esansiyel olmayan elementlerin konsantrasyonları belirlenmiş ve bu elementlerin günlük alımları hesaplanmıştır. Elementlerin [alüminyum (Al), antimum (Sb), arsenik (As), bor (B), berilyum (Be), kadmiyum (Cd), nikel (Ni), kurşun (Pb), gümüş (Ag), titanyum (Ti), talyum (TI) ve vanadyum (V)] belirlenmesi, Varian Vista-MPX indüktif eşleşmiş plazma optik (atomik) emisyon spektrometresi (ICP-OES) ile gerçekleştirilmiştir. Süt, yoğurt, torba yoğurt ve serumda en fazla belirlenen element Bor (B) olmuştur. Be ve V hariç diğer elementlerin miktarı torba yoğurt üretimi sırasında önemli düzeyde değişmiştir (P<0.05, P<0.01). Süt ve yoğurtlardan oniki elementin günlük alımı 0.84 mg (Al), 0.33 mg (As), 0.28 mg (Sb), 7.16x10⁻³ mg (Be), 3.39 mg (B), 0.023 mg (Cd), 0.44 mg (Pb), 0.31 mg (Ni), 0.054 mg (Ag), 0.974 mg (TI), 0.032 mg (Ti) ve 0.155 mg (V) olarak hesaplanmıştır.

Anahtar Kelimeler: İnek sütü, Torba yoğurt, Esansiyel olmayan elementler

INTRODUCTION

Milk and milk products contain non-essential as well as essential elements [1-7]. Actually, all elements, including essential ones, may be toxic if their intakes exceed safe levels. Elements such as arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg) in foods pose significant risks for human health [7]. Therefore, such non-essential elements need to be determined in milk and dairy products. Aluminum (Al), arsenic, cadmium and lead may accumulate especially in the lungs, liver, kidney, thyroid and brain [8]. An excess of Al intake can inhibit several important enzyme activities and contribute to impairment of mental development and bone mineralization [8]. Generally, cadmium intake via respiration is minimal, and exposure is almost exclusively through food consumption [9]. Lead can affect individuals of any age, but children are at higher risk, may be due to their behavioral patterns. Pb absorbed by newborns of all species ranges from 10% to 40%. [10]. Therefore, the determination of toxic elements in food samples require the use of sensitive and selective techniques such as inductively coupled plasma optical emission spectrometer (ICP-OES) or atomic absorption spectrometry (AAS). The growing importance of food safety has greatly encouraged the improvement of the quality of analytical methods to guarantee quality to the end users. Therefore, the measurement of non-essential element concentrations in milk and milk products during processing is essential, with regard to product quality or potential health risks.

In order to extend the shelf life of yoghurt, removal of water by straining, cooking or sun drying of yoghurt is applied in Turkey and other countries. Therefore, the final product has several advantages such as long shelf life, reduced volume, less packaging requirement, reduction in storage and transportation costs and no need of refrigerated conditions for storage.

In Turkey, concentrated yoghurt products are known as Kurut, torba yoghurt, Tulum, Peskütan or Tuzlu (salted) yoghurt [4, 11]. Among these, torba yoghurt is the most common and consumed. In general, torba yoghurt produced by using a traditional method is more preferred by consumers due to its sensorial properties. In this method, yoghurt is strained through a special cloth bag (torba). Modern methods like ultrafiltration and centrifugation have recently been employed to produce strained voghurt [11]. On the other hand, torba voghurt has superior properties to those of regular yoghurt in terms of protein and lactose contents. Higher protein and very low lactose contents of torba yoghurt makes this product even more suitable for lactose-intorelant individuals than regular yoghurt. In addition, the fat content of torba yoghurt can be varied according to consumer demand [18]. In Turkey, the annual per capita consumption of liquid milk and fermented milks including regular yoghurt and torba yoghurt is about 21 and 31 kg. respectively [12]. Few references are available on gross chemical composition and concentrations of some essential minerals in yoghurt, torba yoghurt and labneh [13-18], but no scientific literature has been cited on the non-essential elements of yoghurt and related products like torba voghurt. Therefore, the objective of this study was to determine the changes in the concentrations of non-essential element in cow milk, yoghurt, torba yoghurt and whey. Daily intakes of each element from milk and yoghurts were also estimated.

MATERIALS and METHODS

Material

Cow (Holstein) milk was obtained from Güzelburç village in Hatay province. Cows were milked by hand twice, in a day, morning and evening, and then milks were mixed for yoghurt production. Direct-to-vat system (DVS) yoghurt culture (CH-1; *Streptecoccus thermophilus* and *Lactobacillus. delbreuckii* ssp. *bulgaricus*) was used in yoghurt-making (Chr.Hansen-Peyma, Istanbul, Turkey).

Production of Torba Yoghurt

Raw cow milk was strained using a cloth filter, and yoghurt was manufactured according to the protocol proposed by Tamime and Robinson [11]. Torba yoghurt was prepared from this yoghurt as described previously

[18]. The preparation of torba yoghurt was carried out in duplicates, and samples of milk, yoghurt, torba yoghurt and whey were taken for analyses.

Mineral Analyses

A Mars 5 model microwave labstation (CEM, Matthews, NC, USA) was used to digest samples. All measurements made with a Varian Vista-MPX simultaneous ICP-OES (Australia). The methods for determinations and the quality control of the measurements were similar to those described in a previous paper [4]. Similarly, the accuracy for method was checked with recovery assays. Recovery varied from 89.84% to 126.45% depending on element. For precision of method, variation coefficient of six assays was determined. In addition, precision was considered acceptable, with relative standard deviations always between 0.04% and 9.39%. Moreover, correction factor was calculated for each element using a mixed standard. Correction was considered necessary because of the differences in ICP-OES response and digestion yields of the individual element. Correction factors were: 1.020 for Ag; 0.088 (check figure) for Al; 0.965 for B; 1.024 for Ba; 0.989 for Ni; 0.940 for Sb; 0.938 for Ti; 0.900 for TI and 0.858 for V.

Statistical Analysis

The data were subjected to one-way analysis of variance (ANOVA) using SPSS computer program (version 9.05) (to test the differences among the three yoghurts and its products and to determine the effects of manufacturing procedure) omit. Duncan's multiple range test was used to compare the means when a significant variation was established by ANOVA at the significance level 0.05 (P<0.05).

RESULTS and DISCUSSION

In the present study, total 12 non-essential elements; namely Aluminum (Al), Antimony (Sb), Arsenic (As), Boron (B), Beryllium (Be), Cadmium (Cd), Nickel (Ni), Lead (Pb), Silver (Ag), Thallium (TI), Titanium (Ti) and Vanadium (V) were determined in cows' milk and in various products (Table 1). Most of the elements (Al, Ba, Be, Cd, Ni, Pb, Sb Ti, TI and V) found in milk and products were previously detected in infant formula samples [19]. Elements Ag, Al, Ba, B, Cd, Ni and Pb were also found in goats' milk and related products such as strained yoghurt and Tuzlu yoghurt [4]. The concentrations of some elements (Al, Ni, Pb, Ba and Cd) in milk were in consistent with those reported in literature for various animal species [2, 4, 7, 20-21]. However, considerable differences were reported previously among the levels of elements in cow milk samples collected during different periods of the same year [20]. Thus, animal feeding, year period of sample collection, environmental conditions and manufacturing processes all may play a key role in the distribution of non-essential elements during the manufacture of dairy products. On the other hand, the bioavailability, absorption, mobility, accumulation and extraction of given element are not the same for different animal species [2, 22]. Sometimes, within the same animal species, element metabolism can also be affected by the genetic make-up of the single animal [23]. No data have been cited on the partition of non-essential minerals between torba yoghurt and whey. We have evaluated the daily intake of elements from milk and yoghurt plus torba yoghurt since no report on

consumption rate for the each fermented milk is available, and torba yoghurt is produced from regular yoghurt. For the daily intake evaluation, the weighted average for each element in milk and yoghurt plus torba yoghurt was calculated, and then multiplied by the respective consumption rate.

Table 1. Changes in non-essential element concentrations during torba yoghurt making from cow milk

Milk***	Yoghurt	Torba yoghurt	Whey	Ρ
5.31±1.14 ^b	6.17±1.87 ^b	6.73±1.79 ^b	3.68±0.47 ^a	*
1.27±0.45 ^ª	1.76±0.43 ^b	2.32±0.67 ^b	1.35 ±0.53ª	*
1.91±0.57 ^a	2.11±0.93 ^ª	3.29±1.72 ^b	2.01±0.99 ^a	*
0.04±0.01	0.04±0.01	0.07±0.05	0.03±0.01	-
24.01±1.30 ^b	23.70±1.88 ^b	23.27±2.31 ^b	12.81±1.17 ^a	**
0.21±0.09 ^b	0.22±0.04 ^b	0.18±0.03 ^b	0.06±0.01 ^ª	*
2.47±0.39 ^b	1.94±0.26 ^b	2.72±0.49 ^b	1.51±0.23 ^ª	*
3.05±0.87 ^b	3.22±0.64 ^b	3.22±0.74 ^b	1.68±0.37 ^a	*
0.27±0.45 ^b	0.28±0.06 ^b	0.32±0.24 ^b	0.13±0.05 ^ª	*
0.31±0.23 ^b	0.42±0.37 ^b	0.47±0.24 ^b	0.08±0.01 ^ª	*
7.01±0.80 ^b	7.34±0.22 ^b	7.18±1.09 ^b	4.15±0.87 ^a	*
0.72±0.41	0.97±0.04	1.30±0.35	0.62±0.62	-
	$\begin{array}{c} 5.31 {\pm} 1.14^{b} \\ 1.27 {\pm} 0.45^{a} \\ 1.91 {\pm} 0.57^{a} \\ 0.04 {\pm} 0.01 \\ 24.01 {\pm} 1.30^{b} \\ 0.21 {\pm} 0.09^{b} \\ 2.47 {\pm} 0.39^{b} \\ 3.05 {\pm} 0.87^{b} \\ 0.27 {\pm} 0.45^{b} \\ 0.31 {\pm} 0.23^{b} \\ 7.01 {\pm} 0.80^{b} \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

*P<0.05, **P<0.01, ***Different superscripts within a row indicate significant differences

As can be seen in Table 1, the level of Al significantly increased during torba yoghurt making (P<0.05). Concentration of aluminum in cows' milk and its products was lower than maximum level (10.9 ppm) reported by Sahin et al. [24] for infant formula samples but was similar to maximum level (5.94 ppm) obtained by Coni et al. [20] for cows' milk samples. Aluminum exceeded the 0.2 ppm stipulated by the Turkish Food Codex Directive for drinking water. The daily intake of aluminum from milk and yoghurts including torba yogurt was estimated as 0.31 mg and 0.53 mg, which are approximately 0.43% and 0.76%, respectively, of tolerable value of 7 mg/day for a 70 kg adult [25]. These results were lower than values reported in literature, 1.9-12 mg/day [26-27]. This finding is of great importance since there is concern because of the possibility of increased AI amounts being deposited in the brain and the resulting risk of brain dysfunction [28]. Aluminum was reported to be implicated as interfering with a variety of cellular and metabolic processes [29]. Also, Al may cause bone disorders but the critical level of aluminum loading that results in bone disorders is not known [30].

Antimony was found to be the element of the lowest concentration in milk with value of 1.266 ppm, and its content increased significantly during torba yoghurt-making (P<0.05). This may be due to the increase in fat content of torba yoghurt since the amount of Sb in milk is depended on fat content of milk [31]. The concentration of Sb in milk was higher than that reported by Cava-Montesinos et al. [31]; namely 10 ng/g for partly skim milk and 13.6 ng/g for goat milk. The maximum tolerated levels of Sb are 0.05 mg/kg and 1 mg/kg in Czech Republic and Malaysia, respectively [32]. The daily intake of antimony was estimated as 0.1 mg from milk and 0.18 mg from yoghurts. Clinically, toxicities of antimony causes headache, dizziness, and

depression but larger doses cause violent and frequent vomiting, and would lead to death in a few days [31]. However some authors proposed essential biological function for Sb [33].

Arsenic is widely spread in the environment, usually associated with sulfur. Data reported in the literature about As concentration in cow milk varies from 0.2 to 4.93 ng/ml [34-35]. The As content of milk in Turkey has not been reported yet. Arsenic present in milk could have a natural origin, because it has been demonstrated that it is secreted in breast milk, or provided in part from external contamination such as mother's nutrition, environment and manufacture process [36]. The degree of arsenic toxicity is basically dependent on the form (e.g. inorganic or organic) and the oxidation state of the arsenical compounds. It is generally considered that inorganic forms are more toxic than organic ones [37]. It was observed that a protein-rich milk diet delayed the increase in the As concentration in the blood, liver and kidneys of mice [38]. Thus, the consumption of torba yoghurt in diet may cause less arsenic toxicity when compared with milk or yoghurt. The contributions of milk and voghurt to intake from arsenic were calculated as 0.14 mg/day and 0.19 mg/day, respectively. The total value was much lower than data (3.5 mg/day for a 70 kg adult) estimated by the WHO [25]. The values for milk and yoghurt fall in the range of data (10 to 200 μ g/day) reported in literature various countries [39-40].

The Be contents of milk and yoghurts were within the range of 0.040-0.065 ppm. A typical dietary intake was estimated as 2.16 μ g/day for milk and 5 μ g/day for yoghurt, which corresponds to 2.16 % and 5.00% of 100 μ g/day [41]. No studies are available on the health effects of ingested Be. However, as gastrointestinal absorption of Be is poor, toxicity is expected to be low via this route. On the other hand, as the continued exposure to this toxic element, it is thought to be

carcinogenic through its binding to specific regulatory proteins in cells and subsequent accumulation in mammalian cells [42].

Boron (B) was the most abundant element found in milk and related products. The amount of B in milk in the present study was higher than value of 0.28 ppm reported by Hunt et al. [43]. This may be due to differences in the level of B intake of cow. The daily intake of boron was calculated to be 1.38 mg from cows' milk and 2.01 mg for yoghurt and torba yoghurt. The total daily intake is estimated to be between 1.5 and 2 mg [44]. The contribution of B intake from cows' milk and yoghurt was 69% and 100%, respectively. However, the function of boron remains undefined since boron is becoming recognized as an element of potential nutritional importance (because of the findings) omit from human and animal studies [44].

The amount of Cd in the diet is of great importance as Cd accumulates mostly in the liver and kidney and has a long biological half-life of 17-30 years in humans [45]. It has been claimed that about one-third of the Cd accumulated in adults was absorbed during the first few vears of life [46]. If the amount of absorbed Cd (lethal dose 1.0 g) exceeds the body's ability to complexation of metallothionein, the metal is stored in the liver and kidney, leading to an increase in the likelihood of kidney diseases [47]. The level of cadmium levels in milk was higher than that previously reported by Santos et al. [7]. The content of cadmium as aluminum and arsenic in milk has not been published in Turkey yet. The daily intake of cadmium from milk and voghurt was calculated as 0.0086 mg and 0.0150 mg, respectively, that represents approximately 12.28% and 21% of 0.075 mg/day for a 70-kg adult [25].

Lead contents of all examined samples were considerably less than the value reported by Tajkarimi et al. [48] for cattle milk obtained from different regions of Iran (7.91 ppm). The daily intake of Pb was calculated as 0.17 mg for milk and 0.27 mg for yoghurt, the total amount of which was found on 2 times higher than the value of 0.25 mg/day for a 70-kg adult estimated by the WHO [25]. The mean Pb level of milk was found on 8.5 times higher than the maximum limit (0.02 ppm) stated in the Turkish Food Codex [49]. However, according to Renner [38] a high calcium and phosphate content in diet inhibits lead absorption and retention, but lactose promotes Pb retention. Therefore, lead in yoghurt and especially torba yoghurt may be of less risk for human beings due to the high calcium and phosphate, and low lactose contents of torba yoghurt [18].

The concentrations of nickel in various milks and related products were also investigated because the concentration control (level of toxicity) in samples of nutritional milk and dairy products is important. The participation of that element in human metabolism, as well as its quantity, are still unknown, but the lack of this mineral may cause disturbances in the growth and problems of hematopoieses [50]. The nickel concentration of milk was similar to those in yoghurt and torba yoghurts whereas it was significantly lower in whey (P<0.05). The concentration of nickel was 2.47 ppm for milk and 1.94 ppm for yoghurt. These results were higher than those reported by Santos et al. [7] and Soares et al. [21] for milk. The contributions of milk and yoghurt to the daily intake from Ni were estimated as 0.12 mg and 0.19 mg, respectively, which corresponds to 8.6% and 13.57% of 1.4 mg/day for a 70-kg adult [25].

Although there were no significant differences in silver (Ag) contents among milk, yoghurt and torba yoghurt, its amount was significantly low in whey (P<0.05). To our knowledge, no data has been available on silver content of milk and dairy products in literature. However, the values found for milk and yoghurts were very higher than the maximum level (100 µg/kg) in the various foods [51]. The daily intake of silver from milk and yoghurt was estimated as 0.015 mg and 0.039 mg, respectively. These values are lower than the maximum value (80 µg/day) reported by WHO [44]. This finding is of a great importance since silver is stored mainly in liver and skin and in smaller amounts in other organs [52]. The biological half-life in humans (liver) ranges from several to 50 days [53]. Silver and compounds containing silver (like colloidal silver) can be absorbed into the circulatory system and become deposited in various body tissues leading to a condition called argyria which results in a blue-gravish pigmentation of the skin, eyes, and mucous membranes [51].

In this study, the concentration of thallium in cows' milk was similar to those in yoghurt and torba yoghurt. The concentration of thallium was 7.01 ppm for milk and 7.26 ppm for yoghurts. The daily intake for this element from milk and yoghurt was estimated as 0.375 mg and 0.599 mg, respectively. After bor, thallium is one of the most found elements in milk and related to products. Thallium directly concentration depends thallium on concentrations in the soil, which can be transferred from soils to plants readily and accrues in food chain [54]. Thallium is one of the most toxic metals for human health. It affects several tissues and systems, such as the epidermal, gastrointestinal, cardiovascular, and renal systems. The major manifestations of toxicity consist of a rapidly progressive, ascending, extremely painful sensory neuropathy and alopecia [55]. More than 90% of water-soluble thallium salts are absorbed from the human gastrointestinal tract. Early symptoms of thallium poisoning include gastroenteritis, fever, tachycardia and, in serious cases, delirium and coma [56]. However, the toxic effect of thallium on human may depend on its chemical forms and the chemical composition of food since some thallium is rapidly excreted mainly into the feces but other components have half-life times in the order of about 2 weeks [57].

The titanium concentration was significantly low in whey, than milk, yoghurt and torba yoghurt (P<0.05). The daily intake of Ti was estimated as 0.01 mg for milk and 0.022 mg for yoghurt. Titanium is non-toxic even in large doses and does not play any natural role inside the human body [58]. An estimated 0.8 mg of titanium is ingested by humans each day but most passes through

without being absorbed [58]. It does, however, have a tendency to bio-accumulate in tissues that contain silica.

The distribution of vanadium in yoghurts and torba yoghurts was similar to milk. The vanadium found in cows' milk was much higher than value ($0.35 \mu g/L$) reported in literature [59]. The daily intake of vanadium from milk and yoghurt was calculated as 0.05 mg and 0.105 mg, respectively. The total intake of 0.155 mg/day was higher than the maximum value (100 $\mu g/day$) reported in literature [41] but the most of vanadium is excreted without being absorbed. The urine is the principal means of eliminating absorbed vanadium compounds [59].

The concentrations and distribution of elements between yoghurt samples showed a tendency similar to those in milk and whey. In spite of increases in total solids of yoghurts with removing of whey, there were no significant differences in element concentrations between regular and torba yoghurts since a substantial amount of elements transformed from yoghurt to whey. The losses of the elements were the highest in torba yoghurt made from cows' milk which followed by goat and ewe torba yoghurt samples, respectively (unpublished study). This could be attributed to the considerable decrease in pH value (from pH 4.6 to 4.1) during cow torba yoghurt-making [18] since pH values of other torba yoghurt samples unchanged the significantly, in comparison with yoghurt. Another reason may be that the total solids content was the lowest in yoghurt from cow milk. The much longer straining time for cow voghurt rather than other voghurts can cause large losses of element. The concentrations of elements were significantly lower in whey samples than those in milk, yoghurt and torba yoghurt (P<0.05). In present study, cow milk, yoghurt and torba yoghurt appear to be a source of boron, lead, thallium and vanadium when compared with whey. However, yoghurt and torba yoghurt have some advantages, in comparison to milk. The pH values (4.6-4.1) of yoghurt and torba voghurt and gastric pH (2-3) of adults are lower than those in different kinds of milk and gastric of newborn [18]. These differences in pH value affect the absorption of toxic elements since the availability of toxic elements are increased at high pH values [45]. The toxic effects of elements are partly due to direct inhibition of enzymatic system and to the indirect alteration of the essential metal ion-equilibrium. Consequently, their biological availability is inhibited and damage to the cell membrane can occur by the disruption of ion transport across it [60.]

CONCLUSIONS

This work provides important information on safety and quality standards of cows' milk and related products. Boron, thallium and aluminum were the most abundant elements in all samples analyzed. Our results showed that milk, yoghurt and torba yoghurt are important sources for lead and vanadium since the daily intake of these elements via milk and yoghurt may exceed the provisional tolerable daily intake. However, lead in yoghurt and especially torba yoghurt may be a less risk factor for human beings due to the high calcium and phosphate, and low lactose contents of torba yoghurt. On the other hand, the most of vanadium is excreted without being absorbed. The contribution to daily intake of toxic elements from milk and yoghurt was ranged between 2.16 % (Be) and 116 % (Pb). There is thus a clear need for continued monitoring of certain toxic elements in food and the environment coupled with research on the effect on man of long-term exposure to low levels of such elements.

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