# Selected Essential and Non-Essential Elements Content of Turkish Hazelnuts

Emine Elmaslar Ozbas<sup>1</sup>, H. Eser Okten<sup>2</sup>, H. Kurtulus Ozcan<sup>1</sup> & Goksel Demir<sup>2</sup>

<sup>1</sup>Department of Environmental Engineering, Engineering Faculty, Istanbul University, Istanbul, Turkey

<sup>2</sup> Department of Environmental Engineering, Faculty of Engineering, Bahcesehir University, Istanbul, Turkey

Correspondence: Emine Elmaslar Ozbas, Department of Environmental Engineering, Engineering Faculty, Istanbul University, Avcilar 34320, Istanbul, Turkey Tel: 90-212-473-7070 ext.17724. E-mail: elmaslar@istanbul.edu.tr

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## Abstract

Besides being the largest hazelnut producer in the world, Turkey was also the foremost hazelnut exporting country. In this study, content of essential metals (Na, Mg, Ca, K, Fe) and toxic metals (Cu, Pb, Cd) in hazelnut samples from eastern and western parts of Black Sea Region in Turkey were analyzed, and the relationship among these metals were investigated. In addition, the estimated daily intake (EDI) of heavy metals was calculated. It was shown that the calculated EDI values for daily average consumption (20 g) were lower than the recommended values for Cu. Moreover, Cd and Pb were not detected in any of the samples. Potassium was observed to have the highest concentration with an average of 2348.37 mg·kg<sup>-1</sup> among the investigated elements. In addition, Ca and Mg contents in hazelnut samples were also found to be rather high.

Keywords: hazelnut, heavy metals, elemental composition, Turkey

### 1. Introduction

The main production areas of hazelnut (*Corylus avellana*) in Turkey were categorized in two parts: the first part was at the eastern Black Sea region, including Ordu, Giresun, Rize, Trabzon and Artvin provinces. The second part included Sakarya, Samsun, Sinop, Kastamonu, Bolu, Duzce, Zonguldak, and Kocaeli provinces, which corresponded to middle and western parts of Black Sea region. Currently there were 180 crushing facilities and 40 processing facilities with annual capacities of 1.8 million tons and 350,000 tons, respectively (FTG, 2011).

In 2010, total hazelnut export of Turkey was reported to be 252,305 tons, which provided 1.5 billion US dollars in export revenue (BSEA, 2011). Hazelnut production in Turkey was on average 500,000 tons on a yearly basis, comprising about 70% of the world's hazelnut production. About 200,000 tons were exported to European countries such as Italy, Germany, France, Belgium, Netherlands, while around 24,000 tons were exported to other European countries such as Switzerland, Russia, Ukraine, Norway, and Serbia. Overseas countries such as USA, Australia, Brazil, South Africa Republic, and Japan got a smaller share from produced hazelnut of approximately 14,000 tons, half of which were exported to countries including Egypt, Israel, Tunisia, S. Arabia, and Syria (Cevik et al., 2009; THE, 2007).

Nuts and seeds were rich sources of several essential elements (e.g. B, Se, Cu, Zn, Fe, and Mn) in human nutrition, especially for vegetarian diets (Cabrera et al., 2002, Bond et al., 2005, Rodushkin et al., 2008). They had a growing popularity for various commercialized healthy diets (including Mediterranean) that relied on frequent use of nuts and seeds. On the other hand, reported accumulation of toxic elements (Pb, Cd, and Tl) in the matrices of nuts and seeds might hinder their wider inclusion in human nutrition (Rodushkin et al., 2008, Vallilo et al., 1999, Madejon et al., 2003). Among nut species, hazelnut played a major role in human nutrition and health due to its special composition of fat (mainly oleic acid), protein, carbohydrate, dietary fiber, vitamins (vitamin E), minerals, phytosterols (mainly â-sitosterol), and antioxidant phenolics (Cevik et al., 2007). Besides frequent inclusion in healthy diets, hazelnuts were also used in the confectionary, and food oil market. Their great potential for use in the renewable energy market should also be noted as a study conducted by Xu et al. (2007) demonstrated that 1000 kg of oil could be produced from one hectare of hazelnut shrubs whereas soybean

yield was only 500 kg·ha<sup>-1</sup>.

In this study, the concentration levels of 8 elements including 3 heavy metals (Cu, Pb, and Cd) in hazelnut samples obtained from western and eastern Black Sea regions were determined and the relation among them was investigated. The aim of this study was to investigate the toxic metal pollution through analyzing hazelnut samples for significantly high heavy metal concentrations.

### 2. Method

Hazelnut samples were obtained from a hazelnut processing factory in Giresun-Turkey, which received hazelnuts from four major producer provinces, namely Bolu, Ordu, Giresun, and Trabzon. Hazelnuts, which were produced at these different regions of Turkey, were processed separately in the factory. A map indicating the origins of hazelnuts could be seen in Figure 1. Collected hazelnut samples were labeled in accordance with their origins as (F1), (F2), (F3), (F4), (F5), (F6), (F7), and (F8) representing Bolu, Akcakoca, Ordu-Ulubey, Ordu-Unye, Ordu, Giresun-Bulancak, Giresun, and Trabzon-Akcaabat, respectively.

Hazelnut samples were retrieved following the shelling and separation processes. Collected hazelnut samples were stored in polyethylene bags until analysis. Drying was conducted at 50 °C during 24 hours, which was followed by fine grinding. Approximately 1 g of raw sample was weighed into a Teflon digestion vessel, followed by addition of 10 ml ultra pure nitric acid and 50  $\mu$ l hydrofluoric acid. Teflon containers were capped and then placed in a microwave oven (Berghof MWS-2 microwave-system). The digestion cycle was comprised of a 20-min ramp-time from room temperature to 170 °C (measured by infrared sensors), followed by a 30-min hold time at this temperature. After cooling the vessels to below 40 °C, sample digests were transferred to acid-washed 50 ml polystyrene test tubes. Samples were transferred to HDPE volumetric flasks and then flasks were filled with ultra pure water until 50 ml. Metal analyses of the prepared samples were conducted by using an ICP-OES (Perkin Elmer Optima 7000 DV) that was coupled with an autosampler (Perkin Elmer S10 Autosampler).



Figure 1. Location of hazelnut producing provinces of Turkey

## 2.1 Estimated Daily Intake (EDI) of Heavy Metals

The estimated daily intake (EDI) of heavy metals (Cu and Pb) depended on both the metal concentration level and the amount of consumption of hazelnuts. The EDI of metals for adults was determined using the following equation (Zhuang et al., 2009).

$$EDI = (C_{metal} \ x \ W) \ / \ B_w \tag{1}$$

where  $C_{metal}$  was the concentration of heavy metals in hazelnut; *W* represented the daily average consumption of hazelnut;  $B_w$  was the body weight. Calculations were made assuming body weight of 70 kg for adults and a 20 g average daily consumption (Cevik et al., 2009).

#### 3. Results

Concentrations of Na, Mg, Ca, K, Fe, and heavy metals Cu, Pb, and Cd in hazelnut samples were analyzed in this study. Cd and Pb were not detected in any of the samples. In other words, Cd and Pb concentrations were below the detection limits of the ICP-OES. Main sources of Pb were listed as the combustion of leaded fuel, waste incineration and industrial sources. Therefore lead pollution was also correlated with urbanization and density of population (Cevik et al., 2009). The reason for not detecting Pb in hazelnut samples could be the low urbanization rate and related low traffic density in the regions, where the samples were collected. A summary of the mean concentration of the elements in this study and the reported values in the literature for comparative purposes are shown in Table 1.

Elements	This study	Alasalvar et al. (2003)	Alasalvar et al. (2009)	Rodushkin et al. (2008)	
	mean, (mg kg <sup>-1</sup> )	mean, (mg kg <sup>-1</sup> )	mean, (mg kg <sup>-1</sup> )	Mean	
Na	14.1	31.3	17.7	2.6 (mg kg <sup>-1</sup> )	
Mg	585.1	1765	1038.6	0.2 (%)	
Ca	629.2	1934	2082	0.14 (%)	
Κ	2348.4	7610	6782	0.90 (%)	
Fe	27.8	49.7	39.5	$42 (mg kg^{-1})$	
Cu	2.4	16	13.8	18 (mg kg <sup>-1</sup> )	

Table 1. Element concentrations in hazelnut samples

The highest Na concentration (24.7 mg·kg<sup>-1</sup>) was detected in F8 samples, and the lowest Na concentration (6.44 mg·kg<sup>-1</sup>) was found in F5 samples (Figure 2). In the study of Rodushkin et al. (2008), the mean concentration of Na in hazelnut was reported to be 2.6 mg·kg<sup>-1</sup>. Sodium (Na) levels detected in the present study were quite higher than the findings of Rodushkin et al. (2008), while they were lower than the values (31.3 mg·kg<sup>-1</sup>) reported by Alasalvar et al. (2003) (Table 1). However a more recent study by Alasalvar et al. (2009) reported similar results for Na. The highest Fe concentration (71.68 mg·kg<sup>-1</sup>) was detected in F4 sample, and the lowest concentration (8.46) was detected in F7 sample (Figure 2). The mean Fe concentration (27.76 mg·kg<sup>-1</sup>) determined in the present study was lower than the values measured by Rodushkin et al. (2008) and Alasalvar et al. (2003; 2009) (Table 1).



Figure 2. Na and Fe concentration distribution of hazelnut samples

The highest Mg concentration (1052.4 mg·kg<sup>-1</sup>) was detected in F1 samples, while the lowest Mg concentration value (141.72 mg·kg<sup>-1</sup>) was found in F5 samples (Figure 3). The Mg concentrations determined in the present study were lower (approximately by 0.20%) than the findings of Rodushkin et al. (2008). Alasalvar et al. (2003; 2009) measured the mean Mg concentration as 1765 mg·kg<sup>-1</sup> and 1038.6 mg·kg<sup>-1</sup> in 2003 and 2009 studies respectively (Table 1). The latter value for Mg was significantly lower than the former one, however it was still quite higher than the mean results retrieved in this study. The highest Ca concentration (1142.8 mg·kg<sup>-1</sup>) was detected in F1 samples, while the lowest Ca concentration (140.96 mg·kg<sup>-1</sup>) was detected in F5 samples (Figure 3). Measured Ca concentrations were lower (approximately by 0.14%) than the findings of Rodushkin et al. (2008) and Alasalvar et al. (2003; 2009) (Table 1).



Figure 3. Mg and Ca concentration distributions for hazelnut samples

Potassium (K) was detected to be the most abundant element in hazelnut samples with an average concentration of 2348 mg·kg<sup>-1</sup>, and with a maximum of 4248 mg·kg<sup>-1</sup> for Bolu (F1) sample. The highest K concentration (4248 mg·kg<sup>-1</sup>) was measured in F1 samples, while the lowest K concentration (722.8 mg·kg<sup>-1</sup>) was found in F5 samples (Figure 4a). The mean K content in hazelnut samples was measured as 0.90% by Rodushkin et al. (2008). K concentrations in the present study were lower than the findings of Rodushkin et al. (2008) and Alasalvar et al. (2003; 2009) (Table 1). On the opposite side of the spectrum copper (Cu) was measured with the lowest average concentration of 2.38 mg·kg<sup>-1</sup>. The highest Cu concentration (11.4 mg·kg<sup>-1</sup>) was detected in F5 samples, and the lowest Cu concentration (below the detection limit) was measured in F2 samples (Figure 4b). Cu values measured in the present study were lower than the values reported by other studies given in Table 1.

Correlation analyses were carried out for the measured concentrations (Table 2). In general, positive correlation was determined between the elements investigated in the present study, except for Cu, which was negatively correlated with Fe and K.



Figure 4. Concentration distributions for hazelnut samples: a) Potassium concentrations, b) Copper concentrations

	Na	Mg	Ca	K	Fe	Cu
Na	1	0.0260	0.0648	0.0253	0.0022	0.3202
Mg	0.0268	1	0.958	0.9866	0.5288	0.5288
Ca	0.0648	0.9580	1	0.9492	0.0031	0.5194
Κ	0.0253	0.9866	0.9492	1	0.0277	-0.4702
Fe	0.0022	0.5288	0.0031	0.0277	1	-0.0045
Cu	0.3202	0.5288	0.5194	-0.4702	-0.0045	1

Table 2. Correlation coefficients matrix

Reported estimated daily intakes (EDI) of heavy metals were 0.5  $mg \cdot kg^{-1}$  PMTDI (Provisional Maximum Tolerable Daily Intake) for Cu, 0.025  $mg \cdot kg^{-1}$  PTWI (Provisional Tolerable Weekly Intake) for Pb and 0.007  $mg \cdot kg^{-1}$  PTWI for Cd (WHO, 1982; 2000; 2006). According to Equation1, calculated EDI value for Cu was 6.8 x  $10^{-4} mg \cdot kg^{-1}$ . It was shown that the calculated EDI values for daily average consumption (20 g) were lower than the recommended values for Cu. On the other hand, Cd and Pb were not detected in any of the samples. For this reason there was no need to calculate EDI values for these heavy metals.

### 4. Discussion

According to the findings of the present study, heavy metal concentrations in the hazelnut samples collected from three different production regions were in accordance with a healthy diet from the perspective of public health. Also, anthropogenic pollution could be claimed to be minimal at these regions due to the absence of industrial facilities and low transportation rate.

In Table 1 there were some discrepancies between the results reported in this study and in the literature. That may be due to changing mineral composition of the hazelnuts, which were affected by factors such as geographic location, harvest time, climate, soil structure and fertilizers (Bonvehi & Coll, 1993; Ackurt et al., 1999). The hazelnut samples investigated in the study were found to be rich in K, Ca and Mg. In addition, hazelnut samples were observed as a good source of iron with an average of 27.76 mg·kg<sup>-1</sup>.

Low concentrations of heavy metals in hazelnut samples investigated in the study (Pb and Cd were below the detection limits) could be attributed to the low industrialization and traffic density at the regions, where the samples were collected.

The most important result of this research was that examined Turkish hazelnuts were safe from the human health risk point of view. Also their contents of Cu, Pb, and Cd were low enough to guarantee that human daily intake remained below tolerable levels of PMTDI and PTWI.

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