ASSESSMENT OF MINERAL ELEMENTS AND HEAVY METAL CONTENTS OF WALNUT SAMPLES (JUGLANS REGIA L.)

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ASSESSMENT OF MINERAL ELEMENTS AND HEAVY METAL CONTENTS OF WALNUT SAMPLES (*JUGLANS REGIA* L.)

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ABSTRACT

The aim of the present study was to evaluate the levels of essential and non-essential elements of different walnut samples *(Juglans regia* L.*)* collected near and away from highway area in Gumushane, Turkey. The mean amounts of Al Cd, Cr, Cu, Fe, Ni, Mn, Zn, Ba, Na, and Sr in the walnut samples collected near highway area were 10.39, 0.055, 0.503, 15.82, 32.54, 1.16, 19.96, 21.48, 3.90, 116.12 and 3.22 μg g^{-1}, respectively, and the mean amounts of Ca, K, and Mg were 0.72, 3.40, and 1.15 mg g^{-1}, respectively. When comparing these results with the mean data obtained for the control samples, it was observed that the levels of Al, Cd, Cr, Cu, Ca, K, Na, and Sr are higher in walnut samples collected near highway area. To verify the accuracy of the procedure, the certified reference materials were analyzed.

KEYWORDS: Determination; mineral elements; heavy metals; walnut; inductively coupled plasma atomic emission spectrometry

1. INTRODUCTION

The mineral elements and heavy metals are released into the environment unrestrainedly as a result of several industrial applications including milling, textile, metal plating, stabilizers, battery manufacturing, metallurgical alloying, and mining operations [1]. These elements may have beneficial or harmful effects on living organisms depending on their concentrations. Chromium, copper, iron, cobalt, and zinc, as essential elements, are taken by the humans for the support of biological and physiological functions at a certain concentration levels; however, the intake of excess amounts of these elements can cause serious health problems [2]. On the other hand, some of the elements, such as lead, cadmium and mercury, are classified as exactly toxic, even at very low concentrations, and enter the body through the consumption of food and water. Concordantly, the determination of mineral elements and heavy metal contents of highly consumed food and water samples is important for quality control and nutritional aspects [3].

Although several instrumental methods have been performed to determine the trace and major elements in different samples, the inductively coupled plasma atomic emission spectrometry (ICP-AES) technique has become very attractive in recent years due to its sensitivity and easy usage. Moreover, it gives opportunity to simultaneous determinations of various metals at several spectral lines at low detection limits [3]. Walnut *(Juglans regia* L.*)* is a part of the nut tree family, and it has a lot of benefits for the human metabolism; it decreases cholesterol, aortic endothelin-1, tumor necrosis factor alpha, and platelet aggregation rate, but it increases γ-tocopherol and omega-3 fatty acids in red blood cells. Walnut has a wide variety of antioxidant and anti-inflammatory nutrients, and thus it has anti-cancer benefits [4-6]. Walnut is the most widely distributed tree species in Gumushane/ Turkey, hence, the people living in this region consume large amounts of walnuts for different purposes, especially for healthy life. They also commercialize a huge amount of walnuts to different countries. No investigation has been performed to evaluate the mineral elements and heavy metal contents of walnut samples from Gumushane; therefore, in the present study, we aimed to determine the element levels (Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Co, V, Zn, Al, As, Ba, Cd, Hg, Pb, and Sr) by ICP-AES technique in walnut samples collected near and away from highway area in Gumushane, after digestung the samples by dry-ashing method.

2. MATERIALS AND METHODS

2.1 Sampling

A total of 48 walnut samples from 16 different walnut trees near highway area were collected in 6 regions of Gumushane: Mescitli, Hacıemin, Akçakale, Tekke, Çamlıköy and city center, in September 2012. The traffic density is extremely high in this region, and for many years, exhaust fumes have been released in this area without taking any precautions. Similarly, a total of 48 walnut samples from 16 different walnut trees away from highway area were collected. The samples were cleaned without washing, their shell was broken, and then, the crushed walnut samples were dried in an oven at 105 °C for 48 h. The dried samples were ground, homogenized and stored in polyethylene bottles until analysis.

2.2 Instruments and reagents

All chemicals used in this work were of analytical reagent grade. HNO_3, H_2O_2 and HCl, used for the digestion of the samples, were of supra-pure quality and purchased from Merck (Darmstadt, Germany). All glassware and sample bottles were cleaned by soaking overnight in 10% (w/v) HNO_3 solution, and then, rinsing with deionized water several times. Distilled/deionized water obtained from a Sartorius Milli-Q system (arium® 611UV) was used throughout the experiments. The certified reference materials, IMCT-MPH-2 mixed polish herbs and BCR-679 white cabbage, used for checking the accuracy, were obtained from the Institute of Nuclear Chemistry and Technology (Warsan-Poland) and Institute for Reference Materials and Measurements (Geel, Belgium), respectively. The element standard solutions used for the calibration were prepared by step dilution of stock solutions of 1000 mg L^{-1} of each element (Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Co, V, Zn, Al, As, Ba, Cd, Hg, Pb, and Sr) purchased from Sigma-Aldrich (St. Louis, MO USA). The dilution of the stock solutions was done with 0.2% HNO_3 solution.

An inductively coupled plasma atomic emission spectrometer (ICP-AES, Varian Vista RL) was used for determination of the elements (analytical wavelengths (nm) for Al: 396.152, As: 188.980, Ba: 455.403, Cd: 228.802, Co: 238.892, Cr: 276.653, Cu: 324.754, Fe: 238.204, Hg: 253.652, Mn: 257.610, Ni: 231.604, Pb: 283.305, Sr: 407.771, and Zn: 213.857).

2.3 Digestion of the walnut samples

The digestion of the walnut samples was carried out according to dry ashing procedure [7]. For that purpose, 1.000 g of the dried walnut samples were placed in a porcelain crucible. The crucibles were put into the furnace observantly and the temperature was slowly increased to 450 °C from room temperature. The samples were kept at this temperature about 16 h until a white ash residue occurred. Thereafter, the ashed samples were treated with 5 ml of HNO_3 (25%, v/v) solution, and to provide the exact dissolution of the residues, the mixtures were additionally heated for about 1 h. The solutions were filtered through Whatman filter paper, and the final volume of the samples was diluted to 10 ml in a volumetric flask. Blanks were prepared in the same way, but omitting the sample. Then, the levels of the elements in the walnut samples were determined by ICP-AES. The digestion procedure was performed in three replicates for each sample.

3. RESULTS AND DISCUSSION

Before determination of the essential (Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Co, V, and Zn) and non-essential (Al, As, Ba, Cd, Hg, Pb, and Sr) elements [8] in the walnut samples, the accuracy of the method was checked by analyses of two certified reference materials (IMCT-MPH-2 mixed polish herbs and BCR-679 white cabbage). The results are given in Table 1 to compare the found and certified element levels. It is evident that the determined metal amounts are compatible with the certified values, indicating the accuracy and also suitability of the developed procedure.

The limits of detection (LOD), defined as the concentration that gives a signal equivalent to three times of the standard deviation of 10 replicate measurements of the blank samples, were found to be 2.1, 19.7, 0.13, 3.7, 5.7, 3.0, 1.8, 3.4, 10.3, 0.60, 16.0, 90.0, 3.7, 0.20, 1.9 µg L^{-1} for Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, Sr, and Zn, respectively. The relative standard deviations (RSD) were in the range of 1-10% for all the studied elements. The concentrations of Co, V, As, Hg, and Pb in all walnut samples were below LOD values.

The statistical analyses were carried out by using SPSS software package. Independent sample *t*-tests were used to check the differences in metal concentrations between the walnut samples collected near and away from highway area. The level of $p < 0.01$ was evaluated to be statistically significant.

TABLE 1 - Assessment of the accuracy of the method by the certified reference materials (mean ± standard deviation, n = 3).

	BCR-679 white cabbage		IMCT-MPH-2 mixed polish herbs	
Elements	Certified value (mg kg^{-1})	Found value (mg kg^{-1})	Certified value (mg kg^{-1})	Found value (mg kg^{-1})
Cd	1.66 ± 0.07	1.51 ± 0.05	199 ± 15**	ND
Cu	2.89 ± 0.12	2.76 ± 0.08	7.77 ± 0.53	7.71 ± 0.25
Fe	55.0 ± 2.5	56.3 ± 3.4	460*	471 ± 32
Mn	13.3 ± 0.5	12.8 ± 0.4	191 ± 12	176 ± 3
Ni	27.0 ± 0.8	25.3 ± 2.2	1.57 ± 0.16	1.53 ± 0.15
Sr	11.8 ± 0.4	10.9 ± 0.1	37.6 ± 2.7	34.8 ± 0.4
Zn	79.7 ± 2.7	79.1 ± 3.3	33.5 ± 2.1	31.2 ± 1.4
Ba	10.3 ± 0.6*	9.7 ± 0.3	32.5 ± 2.5	29.8 ± 0.5
Ca	7768 ± 655*	7451 ± 372	-	-
Cr	0.6 ± 0.1*	0.48 ± 0.03	1.69 ± 0.13	1.61 ± 0.09
Mg	1362 ± 127*	1312 ± 66	-	-
Al	-		670 ± 111	658 ± 69
Co	-		210 ± 25**	ND

* Information values; **ng g^{-1}

TABLE 2 - Levels of the elements in the walnut samples collected near highway area (weighted sample amounts: 1.000 g, concentrations in µg g^{-1}, mean ± standard deviation, n = 3).

Sample No	Al	Cd	Cr	Cu	Fe	Ni	Mn	Zn
1	2.7 ± 0.2	ND*	0.46 ± 0.01	19.5 ± 0.8	34.4 ± 0.7	1.76 ± 0.11	23.7 ± 1.2	27.0 ± 1.6
2	4.2 ± 0.3	ND	0.36 ± 0.01	14.8 ± 2.1	30.8 ± 0.4	1.44 ± 0.03	32.7 ± 0.9	26.5 ± 1.1
3	6.4 ± 0.5	ND	0.25 ± 0.02	12.7 ± 0.9	30.0 ± 1.0	0.67 ± 0.20	25.1 ± 0.7	23.4 ± 0.9
4	14.4 ± 1.2	ND	0.38 ± 0.02	14.2 ± 0.6	22.6 ± 0.5	0.50 ± 0.09	19.7 ± 1.2	13.6 ± 0.8
5	19.7 ± 1.7	0.13 ± 0.01	0.53 ± 0.01	12.1 ± 2.4	42.6 ± 1.2	1.69 ± 0.06	21.5 ± 1.0	15.7 ± 1.4
6	17.2 ± 1.3	0.12 ± 0.01	0.31 ± 0.03	16.1 ± 0.3	25.5 ± 0.9	0.89 ± 0.06	16.7 ± 0.9	21.4 ± 0.8
7	8.4 ± 0.2	ND	0.45 ± 0.01	14.3 ± 2.8	29.2 ± 0.6	1.54 ± 0.07	16.7 ± 0.7	20.1 ± 1.4
8	11.2 ± 0.9	0.12 ± 0.00	0.24 ± 0.01	14.8 ± 1.0	43.5 ± 0.6	1.68 ± 0.06	21.6 ± 1.3	27.0 ± 2.2
9	9.7 ± 0.7	ND	0.41 ± 0.04	15.6 ± 1.2	33.4 ± 1.4	1.16 ± 0.04	19.7 ± 0.6	18.7 ± 1.5
10	7.1 ± 0.4	0.15 ± 0.01	0.33 ± 0.00	13.1 ± 0.7	28.8 ± 0.8	0.54 ± 0.05	19.8 ± 1.4	18.0 ± 0.6
11	11.8 ± 0.9	0.15 ± 0.01	0.35 ± 0.04	15.7 ± 0.8	29.0 ± 0.4	0.82 ± 0.08	10.3 ± 0.5	14.5± 0.9
12	16.7 ± 1.1	0.20 ± 0.02	0.37 ± 0.02	16.4 ± 1.2	28.4 ± 0.9	0.89 ± 0.04	13.9 ± 0.7	18.0 ± 0.9
13	2.8 ± 0.1	ND	0.33 ± 0.03	25.1 ± 1.7	34.2 ± 0.4	1.06 ± 0.05	16.9 ± 1.1	23.6 ± 3.2
14	16.1 ± 1.4	ND	2.07 ± 0.15	17.6 ± 0.6	36.7 ± 0.9	1.18 ± 0.06	27.9 ± 0.9	15.4 ± 0.9
15	8.0 ± 0.3	ND	0.24 ± 0.04	12.3 ± 1.1	26.6 ± 0.5	1.17 ± 0.04	16.8 ± 0.7	16.8 ± 1.1
16	9.8 ± 0.8	ND	0.96 ± 0.03	18.9 ± 1.0	44.8 ± 2.8	1.60 ± 0.06	16.4 ± 1.0	43.9 ± 0.7

TABLE 2 - Continued

Sample No	Ba	Ca**	K**	Mg**	Na	Sr
1	0.63 ± 0.01	0.89 ± 0.02	3.90 ± 0.09	1.22 ± 0.02	139.5 ± 6.4	4.82 ± 0.10
2	0.80 ± 0.03	0.91 ± 0.03	3.17 ± 0.05	1.21 ± 0.01	98.7 ± 1.6	7.15 ± 0.09
3	4.36 ± 0.05	0.92 ± 0.01	2.71 ± 0.06	1.06 ± 0.01	199.5 ± 15.6	4.06 ± 0.12
4	0.95 ± 0.01	0.76 ± 0.01	3.49 ± 0.02	0.96 ± 0.02	87.5 ± 0.9	3.05 ± 0.09
5	3.32 ± 0.01	0.76 ± 0.04	2.95 ± 0.03	0.87 ± 0.01	85.5 ± 5.5	2.56 ± 0.21
6	2.33 ± 0.03	0.73 ± 0.02	3.03 ± 0.04	1.14 ± 0.00	175.9 ± 9.0	4.40 ± 0.09
7	5.47 ± 0.01	0.70 ± 0.01	2.84 ± 0.03	1.18 ± 0.02	197.1 ± 5.4	2.86 ± 0.08
8	8.71 ± 0.03	0.74 ± 0.02	2.76 ± 0.05	1.30 ± 0.06	190.3 ± 2.4	2.51 ± 0.17
9	6.07 ± 0.08	0.61 ± 0.02	3.49 ± 0.03	1.24 ± 0.01	226.9 ± 9.8	2.41 ± 0.09
10	3.84 ± 0.11	0.60 ± 0.01	3.17 ± 0.05	1.16 ± 0.04	106.8 ± 2.4	2.37 ± 0.10
11	0.70 ± 0.05	0.48 ± 0.01	3.20 ± 0.02	1.10 ± 0.02	33.1 ± 0.8	2.32 ± 0.07
12	0.95 ± 0.03	0.65 ± 0.00	4.45 ± 0.01	1.27 ± 0.03	77.1 ± 5.4	2.34 ± 0.09
13	5.58 ± 0.04	0.97 ± 0.02	5.05 ± 0.05	1.21 ± 0.05	114.4 ± 7.5	3.38 ± 0.09
14	8.63 ± 0.12	0.74 ± 0.03	2.95 ± 0.03	0.92 ± 0.04	30.9 ± 7.8	3.07 ± 0.05
15	6.40 ± 0.09	0.48 ± 0.01	3.62 ± 0.05	1.19 ± 0.01	46.9 ± 3.7	2.14 ± 0.13
16	3.60 ± 0.06	0.58 ± 0.01	3.60 ± 0.08	1.45 ± 0.03	47.7 ± 1.6	2.12 ± 0.01

* not detected; **concentrations in mg g^{-1}

TABLE 3 - Average levels of the elements in walnut samples collected near highway area and control samples (mean ± standard deviation, n = 48 for each group, concentrations in µg g^{-1}).

Elements	Mean levels of the elements in the samples	Mean levels of the elements in the control samples	*p*
Al	10.39 ± 5.27	2.90 ± 0.60	<0.01*
Cd	0.055 ± 0.074	0.000 ± 0.000	<0.01*
Cr	0.503 ± 0.440	0.357 ± 0.036	<0.05**
Cu	15.82 ± 3.42	5.44 ± 0.99	<0.01*
Fe	32.54 ± 6.47	37.77 ± 2.88	<0.01*
Ni	1.16 ± 0.42	1.96 ± 0.16	<0.01*
Mn	19.96 ± 5.45	27.42 ± 2.81	<0.01*
Zn	21.48 ± 7.39	21.74 ± 1.66	>0.05***
Ba	3.90 ± 2.68	5.64 ± 0.42	<0.01*
Ca[a]	0.72 ± 0.15	0.45 ± 0.04	<0.01*
K[a]	3.40 ± 0.62	3.37 ± 0.25	>0.05***
Mg[a]	1.15 ± 0.15	1.29 ± 0.10	<0.01*
Na	116.12 ± 63.50	33.47 ± 6.65	<0.01*
Sr	3.22 ± 1.31	1.69 ± 0.018	<0.01*

[a] concentrations in mg g^{-1}; The differences between the mean levels of the elements in the walnut samples collected near highway area and the mean levels of the elements in the control samples are very important ($p < 0.01$)*, important ($p < 0.05$)**, not important ($p > 0.05$)***.

The mean concentrations of the elements in the walnut samples collected near 16 different highway areas are given in Table 2. The mean levels of each investigated element in 48 walnut samples collected near and away from highway area (control) are given in Table 3.

Among the determined non-essential and toxic elements (Al, As, Ba, Cd, Hg, Pb, and Sr), Al level was high. Al is found in almost all food, air, soil and water samples. The ingestion of high levels of Al may cause serious health problems such as osteomalacia and neurodegenerative disorders including encephalopathy, dementia and Alzheimer's disease [9]. The tolerable weekly intake of Al was determined to be 7.0 mg/kg body weight [10]. In the present study, Al concentrations ranged from 2.7 to 19.7 μg g^{-1} (average 10.39 μg g^{-1}) in the 48 walnut samples collected near highway area. Furthermore, the average Al level in the control samples was 2.90 μg g^{-1} which is lower than those obtained from the near highway area (p <0.01). Cabrera *et al*. [11] reported that Al contents in nuts obtained from Spain were in the range of 1.2-20.1 μg g^{-1}, and Momen *et al*. [12] detected a 2.9 μg g^{-1} Al level in walnut samples obtained from Greece.

Cadmium is one of the most common toxic elements, and generally present at low concentrations in nature. The accumulation of Cd in human body affects kidney, bones, and causes acute and chronic metabolic disorders, such as itai-itai disease, renal dysfunction, lung damage, emphysema, hepatic injury, hypertension and testicular atrophy [13]. In most of the walnut samples and also the control samples, Cd was not detected. The detectable Cd levels were in the range of 0.12-0.20 μg g^{-1}, with an average value of 0.055 μg g^{-1}. The detectable Cd levels in the analyzed samples were higher than those of the maximum permissible limits determined by both Turkish Food Codex and European communities (0.05 μg g^{-1}) [14]. Cd levels in the literature have been reported in the range of 0.12-0.54 μg g^{-1} in dried fruit samples [7], and it was found to be at an average value of 0.006 μg g^{-1} in walnut samples [11]. It is also important to notice that there is a significant difference in the Cd levels between the walnut samples collected near highway area and the control samples ($p < 0.01$).

Barium and strontium, as alkaline earth metals, naturally occur in food and groundwater. Both of them are the most toxic radionuclides and released into the environment by natural processes, or as a result of human activities including milling, processing, coal burning and phosphate fertilizer. The exposure of the excess Ba may cause muscle weakness and tremors, difficulty in breathing, anxiety, and cardiac irregularities [15], while Sr causes several bone and cartilage abnormalities, including impaired calcification and reduced mineral content [16]. The amounts of Ba and Sr in the walnut samples varied between 0.63 and 8.71 μg g^{-1} (average of 3.90 μg g^{-1}) and between 2.12 and 7.15 μg g^{-1} (average of 3.22 μg g^{-1}), respectively. In the control samples, the mean levels of Ba and Sr were determined to be 5.64 μg g^{-1} ($p < 0.01$) and 1.69 μg g^{-1} ($p < 0.01$), respectively. As can be seen, the control samples contain higher amounts of Ba but lower ones of Sr, with a significant difference to the walnut samples collected near the highway area. Ba contents of Brazil nuts have been reported in the range of 888-1868 mg kg^{-1} [17], which is higher than that obtained herein.

Chromium exists in two stable and common forms, namely Cr(III) and Cr(VI). Cr(III), generally found in some foods, vegetables and fruits, has many functions in the human body by taking part in fat and carbohydrate catabolism. However, Cr(VI) is an extremely toxic element and has many harmful effects on the human body. The intake of Cr(VI) above a certain level may cause epigastric pain, nausea, vomiting, severe diarrhea, hemorrhage, and cancer in the digestive tract and lungs [18]. The maximum permissible limit for daily intake of total Cr was determined as 0.20 mg [19]. In the present investigation, the Cr concentrations in the walnut samples were found to be in the range of 0.24-2.07 μg g^{-1}, with an average of 0.503 μg g^{-1} while in the control samples, the mean value was 0.357 μg g^{-1} ($p < 0.01$). The obtained values are compatible with those previously reported for nut samples [11, 12].

Nickel is an essential element for living organisms at a certain level, with its roles in the maintenance and production of body cells [20]. However, to be exposed to high amount of Ni causes some disorders on human body including skin rash, nausea, dizziness, diarrhea, headache, vomiting, and chest pain [21]. The recommended daily intake of Ni is determined as 0.1-0.3 mg by World Health Organization [10]. The mean value of Ni in walnut samples was 1.16 μg g^{-1} (lowest value: 0.50 μg g^{-1}, highest value: 1.76 μg g^{-1}). When comparing the obtained with reported data, it can be noticed that the Ni amount is slightly higher in the investigated walnut samples [11].

Copper is an essential micronutrient, and up to 40 ng ml^{-1}, it has important functions in carbohydrate and lipid metabolism. The higher levels of Cu damage mainly the blood and kidneys [22]. The tolerable daily intake of Cu is given as 2.0 mg [19]. The levels of Cu in walnut samples from UK [23] and Chile [24] were reported to be 14.6 and 17.7 μg g^{-1}, respectively; in the present study, we have determined Cu levels in the range of 12.2-25.1 μg g^{-1}, with an average value of 15.82 μg g^{-1}, supporting the above data obtained by previous researchers. It is also important to notice that the mean Cu levels are considerably lower in the control samples (5.44 μg g^{-1}), with a significant difference ($p < 0.01$), with regard to the walnut samples collected near the highway area.

Iron, manganese and zinc are also vital elements for almost all living organisms depending on their concentration range. Fe, a cofactor in many enzymes, has important roles in metabolic processes, including oxygen and electron transports, and DNA synthesis [25] while Zn is important in production of insulin in the human body [26]. Mn is present in various pharmaceutical, biological and environmental samples [27]. The excess intake of Fe causes endocrine problems, arthritis, diabetes, and liver disease;

Mn causes memory impairment, disorientation, hallucinations, speech disturbance, compulsive behavior and acute anxiety; and Zn causes failure in energy metabolism [28]. The recommended daily intakes of Fe, Mn, and Zn are limited as 18.0, 5.0 and 15.0 mg [19]. The levels of Fe, Mn, and Zn in the analyzed walnut samples were in the ranges of 22.6-44.8 µg g^{-1} (with an average value of 32.54 µg g^{-1}), 10.3-32.7 µg g^{-1} (with an average value of 19.96 µg g^{-1}), and 13.6-43.9 µg g^{-1} (with an average value of 21.48 µg g^{-1}), respectively while in control samples the mean levels of Fe, Mn, and Zn were 37.77 µg g^{-1} ($p < 0.01$), 27.42 µg g^{-1} ($p < 0.01$), and 21.74 µg g^{-1} ($p > 0.05$), respectively. There is a significant difference between the walnut samples near highway area and the control samples for Fe and Mn levels. However, there is not any significant difference for Zn. Plessi *et al*. [29] have reported Fe and Zn levels in the walnut samples from Italy to be 20.0 and 40.0 µg g^{-1} while they did not detect Mn in these samples. Fe, Mn, and Zn levels in the walnut samples from France were found to be in the ranges of 18-24 µg g^{-1}, 24-43 µg g^{-1} and 18-19 µg g^{-1}, respectively [30]. These previously reported data for Fe, Mn, and Zn levels in walnut samples are also close to our results.

Na, K, Ca and Mg are quite common essential elements and found in various foods, such as nuts, fish, meat, seafood, fruits vegetables, and soy milk. Due to their important biological functions in the living organisms, the tolerable limits of them are given at high levels by Food and Drug Administration [31]. The levels of Na, K, Ca and Mg found in walnut samples varied between 30.9 and 226.9 µg g^{-1} (with an average value of 116.12 µg g^{-1}), between 2.71 and 5.05 mg g^{-1} (with an average value of 3.40 mg g^{-1}), between 0.48 and 0.97 mg g^{-1} (with an average value of 0.72 mg g^{-1}), and between 0.87 and 1.45 mg g^{-1} (with an average value of 1.15 mg g^{-1}), respectively. Significant differences were also noticed between the amounts of Na, Ca and Mg in walnut samples near highway area and control samples ($p < 0.01$). The mean percentage amounts of Na, K, Ca and Mg in the walnut samples were calculated as 0.012%, 0.34%, 0.072% and 0.12%, respectively. Rodushkin *et al*. [32] have reported K, Ca, and Mg percentages in walnut samples to be 0.51%, 0.12%, and 0.21%, respectively.

4. CONCLUSIONS

By the use of an easy, rapid, and reliable technique, ICP-AES, a total of 14 elements (Al, Ba, Cd, Sr, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, and Zn) have been detected in walnut samples collected near a highway area (48 samples in 16 different regions), and away from the highway area as control samples (48 samples in 16 different regions) in Gumushane/Turkey. The study is important with respect to evaluation of the levels of different elements in highly consumed types of nut and to compare the results with their maximum tolerable limits. The levels of essential elements in the walnut samples were higher than those of toxic elements. The obtained results are in good agreement with previously reported literature data. It is also important to notice that the levels of Al, Cd, and Sr, as the non-essential and toxic metal ions, are higher in walnut samples collected near highway area than in control samples, indicating pollution of the samples by different sources including several directionless industrial applications and high-density traffics. These results will give an idea to the authorities in order to take the necessary precautions.

The authors have declared no conflict of interest.

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