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Dates: Received: 06 July, 2017; Accepted: 31 July, 2017; Published: 01 August, 2017

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Keywords: Heavy metals; Samsun; Vegetables; FAAS; Voltammetry; *Phaseolus vulgaris* L.

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Research Article

Determination of Fe, Mn, Cu, Zn and Cd after Heat Treatment in some vegetables and Green Bean (*Phaseolus vulgaris* L.) grown in the Middle Black Sea Region

Abstract

Background: In this study, Fe, Mn, Cu, Zn and Cd were determined after heat treatment of spinach (*Spinacia oleracea* L.), leek (*Allium porrum* L.), green bean (*Phaseolus vulgaris* L.), lamb's-quarters (*Chenopodium album* L.) and mad parsley (*Oenanthe pimpinelloides* L.) grown in Samsun the city, in the Middle Black Sea region. In this way, it has been aimed to contribute to the subject whether boiled liquors are consumable or should be thrown away.

Methods: In our study, before heat treatment, vegetables and green bean (*Phaseolus vulgaris* L.) analyzed as raws material and after heat treatment separately as pomace and pot liquor. Chopped vegetables are washed, dried and then HNO₃ and HClO₄ are added and them wet ashing method was using. By taking five samples from each vegetable and fruit, the concentration of Fe, Mn, Cu, Zn were determined with Flame AAS, but Cd was determined with voltammetry. This process was also applied to vegetable and green bean pomaces. The content of the heavy metals in pot liquor was determined by standard addition method.

Results: The highest metal ion was iron in spinach (135.1, 181.6 mg kg⁻¹) on the other hand the lowest metal content was cadmium in leek (0.007, 0.001 mg kg⁻¹) in raw samples and pomace respectively. In pot liquor the highest metal concentration belonged to iron with a concentration of 22.9 mg kg⁻¹ in spinach (*Spinacia oleracea* L.) and the lowest metal concentration belonged to cadmium with a concentration of 0.001 mg kg⁻¹ in mad parsley (*Oenanthe pimpinelloides* L.).

Conclusion: As a result of our experiments, although the industrial areas emit some heavy metals to the environment, the heavy metal content of studied vegetables and green bean (*Phaseolus vulgaris* L.) were not exceeded the literature and WHO values. Especially pot liquors of mad parsley (*Chenopodium album* L.), green bean (*Phaseolus vulgaris* L.) and lamb's-quarters (*Chenopodium album* L.) must be thrown away. On the other hand, boiled pot liquor of spinach (*Spinacia oleracea* L.) and leek (*Allium porrum* L.) can be consumed.

Introduction

A human body needs minerals, vitamins and proteins in order to live in a healthy way. One of the routes of entry of metals into the living organisms is through plants. Vegetables and fruits naturally contain the necessary vitamins and minerals but at the same time they may contain toxic substances which can be carried in various ways from such as soil, air and water, those contaminated during industrial processing [1,2]. Plants contain minerals such as calcium, iron, manganese and other micronutrients. From these micronutrients copper

(Cu), iron (Fe), manganese (Mn) and zinc (Zn) are not only constitutive elements with specific functions in plant growth, photosynthesis and respiration [3]. Also these elements are essential for living organisms at low concentrations. However, the high concentrations of even the essential metals are toxic and cause various metabolic abnormalities [1]. Today, heavy metals form a large part of the environmental pollution that threatens our health and have a toxic and carcinogenic effects. Thus, vegetables can contain some toxic elements in addition to essential substances [4]. High concentrations of heavy metals (Cu, Cd and Pb) in fruits and vegetables were correlated

to high prevalence of upper gastrointestinal cancer cases [2]. The affected levels of vegetables due to heavy metallic pollution depend on factors such as traffic congestion, the wind, the distance to the road and the rain.

Spinach (*Spinacia oleracea* L.), leek (*Allium porrum* L.), green bean (*Phaseolus vulgaris* L.), lamb's-quarters (*Chenopodium album* L.) and mad parsley (*Oenanthe pimpinelloides* L.) grown in Samsun, in the Middle Black Sea region have both low calories and health benefits.

Samsun has an important place in the residential and manufacturing areas and industries in the Black Sea province shows continuous improvement. This is also why our city pollution and industrialization threatens human health and thus food resources are also polluted.

Heavy metals are determined by various methods in the air, water, cigarette filter, cigarette smoke, soil and food. Many methods have been used for the determination of very low concentrations heavy metals, especially flame AAS, Graphite Furnace AAS, ICP, ICP-MS or voltammetry [5-9]. The most used of these are graphite furnace and flame atomic absorption spectrometry (GFAAS and FAAS) for the determination of trace heavy metal ions (Zn, Fe, Mn, Cu, etc.) due to low cost, easy usage, high sensitivity and short analyzing time [10-11]. Very low concentrations trace metals are also determined with voltammetry within various samples due to simplicity and low cost.

In the previous studies metals were determined in raw vegetables and fruits [12-14]. It is known that certain parts of the food stuff interwine to the pot liquor at high-temperatures. However, the portion of metal content transferred to the pot liquor is unknown. In this study, it has been aimed to contribute to the subject of whether the boiled liquors of the plants are to be or not which is a confusing subject for people.

In this study, the determination of Fe, Mn, Cu, Zn and Cd contents after heat treatment of spinach (*Spinacia oleracea* L.), leek (*Allium porrum* L.), green bean (*Phaseolus vulgaris* L.), lamb's-quarters (*Chenopodium album* L.) and mad parsley (*Oenanthe pimpinelloides* L.) grown in Samsun, in the Middle Black Sea region was aimed. FAAS was used to determine Fe, Mn, Cu and Zn. We preferred voltammetry for Cd quantification because of its low concentration.

Materials and Methods

Materials

The fruit green bean (*Phaseolus vulgaris* L.) and vegetables spinach (*Spinacia oleracea* L.), lamb's-quarters (*Chenopodium album* L.) and mad parsley (*Oenanthe pimpinelloides* L.) were collected from Tekkekoy Yag Basan, Carsamba Irmaksirti and Calti villages of Samsun. Leek (*Allium porrum* L.) was collected from Bafra Kuscular village at the west of Samsun during the vegetation session of 2011.

Preparation of the sample

Vegetables and green bean were studied as: raw samples,

heat treated samples as pomace. Also the pot liquor of samples were analysed.

All samples obtained from different villages were washed with tap water, than deionized water to clean their damaged, dried leaves and dust, dirt, possible parasites and their eggs on them. Afterwards, samples were divided into small pieces with a plastic knife and dried in the oven at 90 °C for 24 h [15]. This process was also applied to heat treated vegetables and green bean. The concentrations of Cu, Mn, Fe, Zn in raw vegetable and green bean samples were determined by flame atomic absorption spectrometer (FAAS) after digestion by wet-ashing method. An aliquot of 1 g sample was digested in Kjeldahl flask. The wet-ashing method was applied as: a 50 mL mixture of acids HNO₃: HClO₄ in the ratio of 8:2 (v/v) was added onto the raw vegetable sample and the flask was covered with a watch glass and stored at room temperature for an overnight. The samples were digested with an increasing temperature programme: 100 °C for one h, two h at 200 °C then at 300 °C for one h lasty at 400 °C for two h. Then, 4 mL HNO₃ were added and filtered from glass wool to remove solids. The filtrate was diluted to 10 mL volume with deionized water. Each vegetable and green bean were studied five times. The concentration of Fe, Mn, Cu, Zn using determined with Flame AAS, Cd was analysed by voltammeter.

For the heat treated samples, an aliquot of 0.500 kg vegetables and green bean of each species were used for the analysis. Samples were cooked for 30 min with 1 L of tap water has been boiled in teflon pot. Then boiled green bean and vegetables were filtered through plastic strainer into pot. The filtrate was washed with deionized water and pot liquor was evaporated until it decreased to 15 mL volume. An aliquot of 1 g dried filtrate was digested as raw samples.

The content of the heavy metals in pot liquor was determined by standard addition method. Filtrates were divided into five volumetric flasks as each one was 4 mL in volume. The standard addition method was employed to avoid the matrix effect. For this purpose, only deionized water was added to the first volumetric flask containing filtrate and then 0.5; 1; 3 and 5 mg L⁻¹ standard solutions were added to other four volumetric flasks successively. All flasks were completed to 10 mL volume.

Reagents

All reagents are in high purity and the metal salts used in the preparation of stock solution (1000 mg L⁻¹) were supplied from Merck.

Standard solutions

The standard solutions were prepared by the diluting of stock solutions of metal salts (1000 mg L⁻¹).

Apparatus and analysis conditions

In this study, UNICAM 929 Flame Atomic Absorption Spectrometry was used for defining the concentration of metals. UNICAM hollow cathode lamps were used for copper, manganese, iron and zinc. Except for the pot liquor analyses,

quantification of analytes was done by external calibration where a series of standard solutions was prepared by dilution of the stock solution.

Gamry Reference 600 voltammeter was used to analyze the Cd content of the vegetable and lady's finger samples. The anodic stripping voltammetric experimental conditions were selected as: initial potential -1.0V , final potential 0.0V , pulse size 25mV , frequency 25Hz , accumulation time 60s while using a hanging mercury drop electrode as working electrode. The supporting electrolyte was 0.5M acetate solution at pH 4.5 . Cadmium gave a single peak at -0.64V versus Ag/AgCl . Quantification of Cd was performed by using standard addition method. Limit of detection and limit of quantification for Cd were calculated from the calibration curve.

For defining the limit of detection for the digestion process and analytical measurement with FAAS sample-free (blank) solutions were analyzed. The mean and the standard deviation of absorbance for 10 blank data were calculated. Three times of the standard deviation of blank was summed with the average of blank absorbance.

Ten times more of the standard deviation obtained in the determination of the detection limit was added to the average of blank absorbance, and Mn, Zn, Cu, Fe concentration corresponding to this value was calculated as the limit of determination.

Statistical analysis

For statistical analysis, one-way analysis of variance (ANOVA) test was applied to metal concentrations in raw vegetables and green bean, pomace and pot liquor with confidence at level 95% . Levene test was used to determine the homogeneity of data. The differences between groups were determined with the Duncan test. These analyses were performed using the program SPSS 15.0. The experiments were repeated 5 times in each plant with five different plants and the total number of experiments was 25.

Results and Discussion

Plant samples used in the study were prepared by analytical pretreatment with wet ashing and their heavy metal contents were determined using flame atomic absorption spectrophotometer.

The accuracy of the method was determined by recovery studies. Two different vegetable samples were spiked with the standard solutions including Mn, Zn, Cu, Fe metals. Lamb's-quarters and leek vegetable samples were used for recovery studies. Lamb's-quarters except iron are in the range of $90-112\%$, because of this reason the method can be accepted as an accurate method. The iron recovery percentage was found to be 136 . However, in the blank analysis, the limit of determination of iron was found to be 5.37mg kg^{-1} . In this case the percent recovery is calculated as 123% . The recovery of metals values in the leek are in $86-119\%$. Spiked vegetable samples were determined with good recoveries. The limit of detection (LOD) and quantification (LOQ) and recovery values for the analyzed metals are given in table 1,2.

The heavy metal concentrations before and after heat treatment of spinach (*Spinacia oleracea* L.) Leek (*Allium porrum* L.) green bean *Phaseolus vulgaris* L.) Lamb's-quarters (*Chenopodium album* L.) and mad parsley (*Oenanthe pimpinelloides* L.) grown in Samsun, in the Middle Black Sea region are presented in table 3–8.

In our study, in raw samples the highest and the lowest metal concentrations were found in spinach the highest metal concentration belonged to iron (135.1mg kg^{-1}) and the lowest metal concentration belonged to cadmium (0.006mg kg^{-1}). Similarly, after heat treatment, the highest and lowest concentrations of metal belonged to iron and cadmium in spinach 181.6mg kg^{-1} , 0.007mg kg^{-1} , respectively (Table 3). In

Table 1: LOD and LOQ for Fe, Mn, Cu, Zn, Cd metals.

Metals	LOD (mg kg^{-1})	LOQ (mg kg^{-1})
Fe	1.629	5.374
Mn	0.111	0.356
Cu	0.451	1.495
Zn	0.220	0.681
Cd	0.0009	0.0026

Table 2: The recoveries of metals in spiked vegetable samples (n=3).

Metals	Added concentration mg kg^{-1} (Lamb's-quarters)	Recovery % \pm RSD (Lamb's-quarters)	Added concentration mg kg^{-1} (Leek)	Recovery% \pm RSD (Leek)
Fe	45	123 ± 3	28	95 ± 4
Mn	40	93 ± 1	21	119 ± 3
Cu	3	112 ± 6	21	119 ± 5
Zn	40	90 ± 7	21	86 ± 6

RSD: Relative Standard Deviation

n: The number of samples.

Table 3: Metal concentrations (mg kg^{-1} dry weight) in the spinach *Spinacia oleracea* L.), 95 % CL, in 2011 (n=5).

Metals	Raw spinach	Spinach pomace	Spinach pot liquor
Fe	135.1 ± 1.5	181.6 ± 17.2	19.9 ± 1.0
Mn	9.3 ± 0.2	7.8 ± 0.2	1.6 ± 0.5
Cu	5.2 ± 0.2	7.3 ± 0.2	1.4 ± 0.2
Zn	37.1 ± 0.1	43.2 ± 0.1	12.3 ± 0.2

CL: Confidence Limit ($\bar{X} \pm ts/\sqrt{n}$)

n: The number of samples.

Table 4: Metal concentrations (mg kg^{-1} dry weight) in the leek (*Allium porrum* L.), 95 % CL, in 2011 (n=5).

Metals	Raw leek	Leek pomace	Leek pot liquor
Fe	21.4 ± 5.6	10.8 ± 2.3	4.2 ± 0.4
Mn	4.3 ± 3.3	4.3 ± 1.1	$1.4 \pm 0.01^*$
Cu	2.9 ± 1.8	4.9 ± 1.3	0.7 ± 0.1
Zn	6.5 ± 2.5	4.8 ± 1.1	13.6 ± 0.1

CL: Confidence Limit ($\bar{X} \pm ts/\sqrt{n}$)

n: The number of samples

* The mean difference is significant at the 0.05 level.

pot liquors the highest metal concentration belonged to iron with a concentration of 22.9 mg kg⁻¹ in spinach and the lowest metal concentration belonged to cadmium with a concentration of 0.001 mg kg⁻¹ in mad parsley (Table 7).

Iron is an important element for living things. It is used as crude content in steel industry and iron oxides are used in paint industry as pigments [16]. In this study, iron levels in green bean and vegetables were found between 21.4 mg kg⁻¹ and 135.1 mg kg⁻¹. These results are in compatible with literature values. The iron concentrations in our study were found (except for spinach) lower than the value reported by Al-Taif (Saudi Arabia) by Mohamed *et al.* (2003) [17] as 118.2 mg kg⁻¹ in a study conducted and the concentration reported as 8 mg kg⁻¹ in a study carried out in Turkey by Kaya *et al.* (2004)[18]. However, it was found to be generally higher than the vegetables other than vine leaves (0.01– 41.98 mg kg⁻¹) in the study carried out in Manisa (Turkey) by Bagdatlioglu *et al.* (2010)[19]. Iron levels in heated vegetables and green bean are between 10.8 mg kg⁻¹ and 181.6 mg kg⁻¹. The lowest iron level was in the *Allium porrum* L and the highest iron level was in the *Spinacia oleracea* L. The second highest concentration level in *Chenopodium album* L, which is 68 mg kg⁻¹ and in its pot liquor, which is approximately 71 mg kg⁻¹. The iron concentration in spinach

Table 5: Metal concentrations (mg kg⁻¹ dry weight) in the green bean (*Phaseolus vulgaris* L.), 95 % CL, in 2011 (n=5).

Metals	Raw green bean	Green bean pomace	Green bean pot liquor
Fe	35.0 ± 1.1	42.3 ± 0.9	4.9 ± 0.7
Mn	4.7 ± 0.1	5.8 ± 0.1	2.1 ± 0.9
Cu	3.9 ± 0.2	3.5 ± 0.1	4.8 ± 0.8*
Zn	12.0 ± 0.02	10.1 ± 0.1	17.6 ± 1.1

CL: Confidence Limit ($\bar{X} \pm ts/\sqrt{n}$)

n: The number of samples

* The mean difference is significant at the 0.05 level.

Table 6: Metal concentrations (mg kg⁻¹ dry weight) in the lamb's-quarters (*Chenopodium album* L.), 95 % CL, in 2011 (n=5).

Metals	Raw lamb's-quarters	Lamb's-quarters pomace	Lamb's-quarters pot liquor
Fe	67.9 ± 0.3	70.7 ± 0.4	22.9 ± 7.2*
Mn	31.3 ± 0.1	36.6 ± 0.1	15.2 ± 1.1
Cu	5.2 ± 0.1	5.8 ± 0.2	1.4 ± 0.5
Zn	16.4 ± 0.5	16.3 ± 0.1	12.1 ± 4.3*

CL: Confidence Limit ($\bar{X} \pm ts/\sqrt{n}$)

n: The number of samples

* The mean difference is significant at the 0.05 level.

Table 7: Metal concentrations (mg kg⁻¹ dry weight) in the mad parsley (*Oenanthe pimpinelloides* L.), 95 % confidence limit, in 2011 (n=5).

Metals	Raw mad parsley	Mad parsley pomace	Mad parsley pot liquor
Fe	44.4 ± 3.2	60.5 ± 1.2	3.4 ± 1.5
Mn	35.3 ± 0.2	41.6 ± 0.5	9.7 ± 2.4
Cu	3.5 ± 0.1	4.1 ± 0.1	0.7 ± 0.2
Zn	20.2 ± 0.1	25.1 ± 0.1	5.9 ± 0.5

CL: Confidence Limit ($\bar{X} \pm ts/\sqrt{n}$); n: The number of samples.

Table 8: Cd concentrations (mg kg⁻¹ × 10² dry weight) with voltammetric method, 95 % CL, in 2011 (n=5).

Samples	Raw samples	Pomace	Pot liquor
Spinach	3.8 ± 2	1.3 ± 2	2.8 ± 0.2
Leek	0.6 ± 0.1	0.7 ± 0.2	0.1 ± 0.2
Green bean	0.8 ± 0.3	1.1 ± 4	0.2 ± 0.2
Mad Parsley	4.5 ± 3	2.4 ± 1.0*	4.5 ± 0.2
Lamb's-quarters	1.7 ± 2	1.7 ± 2	1.4 ± 0.1

CL: Confidence Limit ($\bar{X} \pm ts/\sqrt{n}$)

n: The number of samples

*The mean difference is significant at the 0.05 level.

was observed considerably higher than expected because in the neighborhood of the field a steel factory is located. According to the World Health Organization (WHO), the maximum iron concentration should be 425 mg kg⁻¹ [20]. Our results are lower than standard value of WHO. There is a statistically significant difference in the levels of iron ($P \leq 0.05$) in all raw vegetables and green bean, in pomaces and in pot liquors except lambs quarters. There is no statistically significant difference between raw lamb's - quarters and lamb's - quarters pomace. Therefore difference between raw lamb's - quarters and lamb's - quarters pot liquor is statistically significant. Similarly difference between lamb's - quarters pomace and lamb's - quarters pot liquor is statistically significant.

Manganese is a mineral which serves as an enzyme activator in the human body and the daily manganese need of the human structure is about 4.50 mg [21]. In this study, manganese concentrations were found between 4.3 mg kg⁻¹ and 35.3 mg kg⁻¹. The lowest manganese level was found in *Allium porrum* L. and the highest manganese level was found in *Oenanthe pimpinelloides* L. In the literature, the study carried out by Santos *et al.* in Rio de Janerio, Mn content was reported lower than our data for all green-leaved vegetables (1.7 – 18 mg kg⁻¹) [22]. In heated vegetables the lowest manganese concentration is in *Allium porrum* L. (4.3 mg kg⁻¹) and the highest manganese concentration is 36.6 mg kg⁻¹ in *Chenopodium album* L. In pot liquor manganese is the lowest in *Allium porrum* L. (1.4 mg kg⁻¹) and the highest in *Chenopodium album* L. (15.2 mg kg⁻¹). The Mn concentrations in vegetables and fruit were found to be lower than WHO maximum limit that WHO defined the maximum permissible Mn concentration in vegetables as 500 mg kg⁻¹ [23]. There is a statistically significant difference in the levels of manganese ($P \leq 0.05$) in all raw vegetables and green bean, in pomaces and in pot liquors except leek. Leek pot liquor is statistically difference from the others.

Copper is one of the essential elements for feeding and health of people. But if taken in abundance, copper can cause some health problems [24]. It is used widely in electricity, electronic industry and mining enrichment. Copper is left to the environment by means of drain water [16]. In the study, in raw vegetables, copper levels changed from 2.9 mg kg⁻¹ to 5.2 mg kg⁻¹. It was observed that the lowest copper level was in *Allium porrum* L. and the highest copper level was in *Chenopodium album* L. We have been thinking that the reason why the concentration level of copper was high in *Spinacia oleracea* L.

and *Chenopodium album* L. probably resulted from the fact that the fields on which these plants grew were near the factories. The copper concentrations were found to be lower in our study in comparison to a study conducted in Kayseri (Turkey) [25] reported as 22.19 – 76.5 mg kg⁻¹ for urban and rural areas. Also Yusuf et al reported 25.08 – 56.84 mg kg⁻¹ copper in plants in a study carried out in Nigeria which had higher values than our study [15]. On the other hand, our data except for vine leaves (0.01 – 5.67 mg kg⁻¹) was found to be compatible with the study carried out in Manisa (Turkey) by Bagdatlioglu et al. [19]. In heated vegetables the copper levels were between 3.5 mg kg⁻¹ and 7.3 mg kg⁻¹. The lowest copper concentration was in *Phaseolus vulgaris* L. and the highest copper concentration was in *Spinacia oleracea* L. In pot liquor copper was determined between 0.7 mg kg⁻¹ and 4.8 mg kg⁻¹. In this process the lowest copper concentration was in *Oenanthe pimpinelloides* L. and in *Allium porrum* L. whereas the highest copper concentration was in *Phaseolus vulgaris* L. WHO defined the maximum permissible Cu concentration in vegetables as 4.0 mg/100g [26], which is 40 mg kg⁻¹. In this case, our results for Cu concentrations are within the safe. There is a statistically significant difference in the levels of copper ($P \leq 0.05$) in all raw vegetables and green bean, in pomaces and in pot liquors except green bean. There is no statistically significant difference between raw green bean and green bean pomace.

When the necessity of zinc and its low toxic influence on people – if people don't expose to zinc in their work place too much – are taken into consideration, the lack of zinc compared with the exposure of zinc causing from environmental reasons is believed to have higher risks. In regions polluted with zinc, plants especially green-leafy vegetables store a great deal of zinc [5]. In our study, zinc levels ranged from 6.5 mg kg⁻¹ to 37.1 mg kg⁻¹. It has been observed that the lowest zinc level was in *Allium porrum* L. and the highest zinc level was in *Spinacia oleracea* L. The reason for this might be that the soil in which spinach grows on was richer than soils in which other vegetables grew or it can result from the leaves' storing zinc more. The Zn concentrations in this study were found to be similar to the Zn concentrations of 12 different vegetable samples grown in the area of Al-Taif (Saudi Arabia) which was reported within the range of 4.50–105.2 mg kg⁻¹ [17], and the concentration reported as 3.99 mg kg⁻¹ in leek the study carried out in Ioannia (Greece) by Stalikas et al. (1997) [27] and 14 different vegetable samples from Manisa (Turkey) reported within the range of 2.41–10.81 mg kg⁻¹ [19]. However, Zn level reported as 136 mg kg⁻¹ in the spinach carried out by Smolen and Sady (2012) [28] in Krakov (Poland) was found to be higher than the our values. In heat-processed vegetables the zinc level changes from 4.8 mg kg⁻¹ to 43.2 mg kg⁻¹ and the lowest zinc concentration was in *Allium porrum* L. and the highest zinc concentration is in *Spinacia oleracea* L. In pot liquor zinc concentration was in the change of 5.9 mg kg⁻¹ to 17.6 mg kg⁻¹. After the boiling process the lowest concentration was in *Oenanthe pimpinelloides* L. and the highest concentration is in *Phaseolus vulgaris* L. According to the World Health Organization (WHO), the maximum Zn concentration should be 60 mg kg⁻¹ [16]. In all the vegetables and the level of Zn was found to be lower than upper limits. There is a statistically significant difference in the levels of zinc

($P \leq 0.05$) in all raw vegetables and green bean, in pomaces and in pot liquors except lamb's – quarters. There is no statistically significant difference between raw lamb's – quarters and lamb's – quarters pomace.

For cadmium quantification anodic stripping voltammetric method was preferred due to the low Cd contents of samples, which was below than the LOD of Flame AAS (Table 1). In raw vegetables, cadmium levels were in the range of 0.006 mg kg⁻¹ to 0.038 mg kg⁻¹. The lowest cadmium concentration was seen to be in *Allium porrum* L. and the highest cadmium concentration in *Chenopodium album* L. The high levels of Cd in *Chenopodium album* L. may arise from the presence of industrial area in the vicinity of fields. In heat-processed vegetables and fruit, the cadmium levels were between 0.007 mg kg⁻¹ and 0.024 mg kg⁻¹ and the lowest cadmium concentration was in *Allium porrum* L. In boiled vegetable broths, cadmium was detected between 0.001 mg kg⁻¹ and 0.045 mg kg⁻¹. In this study while the lowest cadmium concentration belonged to *Allium porrum* L., the highest concentration belonged to *Chenopodium album* L. The mean levels of cadmium in *Allium porrum* L. (leek) was lower than the reported values as 0.80, 1.90 mg kg⁻¹ by Mohammed et al. (2003), in Saudi Arabia and Smolen and Sady (2012) in Poland respectively [17,28]. Furthermore, Bagdatlioglu et al. (2010), Mor and Ceylan (2008) and Erdogru et al. (2005), found as 0.05, mg kg⁻¹ cadmium contents of plants grown in Turkey, which was higher than the values of this study and the concentration reported as 0.28 mg kg⁻¹ in spinach the study carried out in Bursa (Turkey) by Mor and Ceylan (2008) [4,19,25]. According to the WHO, the maximum Cd concentration should be 0.3 mg kg⁻¹ [12]. In all the vegetables and fruit, the level of Cd was found to be lower than the permissible limits. There is a statistically significant difference in the levels of cadmium ($P \leq 0.05$) in all samples except raw green bean and green bean pot liquor. Also mad parsley pomace and lamb's quarter pot liquor are a statistically significant difference from the others.

Heavy metals which are toxic and some of which are known to have carcinogenic effects are determined high in vegetables except *Allium porrum* L. in Samsun and around Samsun. The reason for this is that the places from which these plants are purchased are industrially developed and that those vegetables can probably accumulate metals. First of all, especially *Spinacia oleracea* L. (spinach) and *Chenopodium album* L. (lamb's-quarters) are plants that contain heavy metallic contents and they should not be grown in those regions or the filter systems of factories and waste water treatment plants should be examined again. As regards the issue whether pot liquor should be thrown away or not, it depends on the kind of vegetable. Whether spinach pot liquor should be removed or not unimportant due to the heavy metallic contents of it except cadmium. The content of cadmium is also below the limit of WHO (According to the World Health Organization (WHO), the maximum Cd concentration should be 0.3 mg kg⁻¹). For this reason, spinach can be eaten in both ways. It's thought that it's better for people to remove the pot liquor of spinach in order to prevent the accumulation of cadmium in bodies. But we have the opinion that not only the pot liquor of *Phaseolus*

vulgaris L. (green bean) should be thrown away but also the juice of green beans should not be eaten at all. However, if green bean is consumed higher than 250 g in a day, the limit of WHO exceed. WHO defined the maximum permissible Cu and Zn concentrations in vegetables as 40 mg kg⁻¹ and 60 mg kg⁻¹, respectively. As for leeks, it can be suggested to be eaten raw because metals determined are below the limit value of WHO and with the boiling process the amount of metals are found less. But the amount necessary for the human body can be taken better by eating raw leek. As for *Oenanthe pimpinelloides* L., metal concentration increases by boiling. We're of the opinion that this plant, too, should be eaten raw without being cooked as salad like some people do. With regard to *Chenopodium album* L., it is suitable to be eaten by throwing away the boiled juice.

In Black Sea Region, frequently, vegetables are consumed as fried after boiling and separating from the pot liquor. In this study, heavy metal contents of vegetables as raw and boiled were determined. Besides the heavy metals were also investigated in pot liquors. To our knowledge, there is no publishes data concerning the ratio of metals passing to the pot liquor from boiling vegetables. In our study its planned to enlighten whether pot liquor should be removed or not, which causes confusion in public.

Conclusion

In conclusion, heavy metals in vegetables analysed in our study are determined to be lower than limit values of WHO. When compared with other vegetables grown in the world, our results are in the range of literature values. When compared with the studies made in Turkey, usually the data of this study have been found higher. For this reason, our municipalities have to inspect factories in places where the iron concentration is high and check the water purification and also the waste water treatment plants. Besides it is a must that the natural gas systems. And it is suggested that our people should throw away the boiled vegetable juice then consume as fried.

Acknowledgement

This work was supported by the Ondokuz Mayıs University Research Foundation (BAP) Project (PYO.Fen.1904.12.001).

This work was presented in part at the 6th Black Sea Basin Conference on Analytical Chemistry, Karadeniz Technical University, 10-14 September 2013, Trabzon, Turkey.

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Citation: Aygun SF, Ince AY, Erdogan BY (2017) Determination of Fe, Mn, Cu, Zn and Cd after Heat Treatment in some vegetables and Green Bean (*Phaseolus vulgaris* L.) grown in the Middle Black Sea Region. *Int J Agric Sc Food Technol* 3(3): 042-048. DOI: <http://doi.org/10.17352/2455-815X.000021>